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Phase formation and transformation in the R-Fe-T systems: (R=Nd, Gd, Tb, Dy, Er, Ho, Tm and Lu, T=Si, Ti and Zr)

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Phase Formation and Transformation in the R-Fe-T Systems
(R=Nd, Gd, Tb, Dy, Er, Ho, Tm and Lu, T=Si, Ti and Zr)

A Thesis in
Materials Engineering
by
Jianmin Xu

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Ph. D of Engineering

December, 1996
Dedicated to My Wife and Parents.
DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment is made in the text.
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I am sincerely grateful to the many people who gave me advice, assistance and encouragement during the course of this work.

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ABSTRACT

A systematic study of the R-Fe-T (R = Nd, Gd, Tb, Dy, Ho, Er, Tm and Lu, T = Si, Ti, Zr) systems has shown that besides the well-known rhombohedral 2:17 (2:17-R), hexagonal 2:17 (2:17-H) and tetragonal 1:12 (1:12-T) phases, several novel ternary Fe-rich rare-earth (R) transition metal (T) compounds, namely R$_3$(Fe$_{1-x}$Si$_x$)$_{22}$ (3:22), R$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ (3:29), R(Fe$_{1-x}$Ti$_x$)$_{10}$ (1:10), P$_{1:12}$, orthorhombic 1:12 (1:12-O), R(Fe$_{1-x}$Ti$_x$)$_{11}$ (1:11) and (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ (1:3), also crystallize in these systems. Like the 2:17 and 1:12 phases, all the new phases have close structural relationships with the hexagonal CaCu$_5$-type structure (1:5). The 3:22, 3:29 and 1:10 phases are intermediate phases between the 1:5 and 1:12 phases and their structures can be directly derived from the CaCu$_5$ structure by replacing a proportion of the large R (Ca) atoms with pairs of small transition metal atoms (dumb-bell) along the c-axis of the CaCu$_5$ structure. This procedure can be facilitated by a simple equation

\[ R_{1-x}T_5 + (T-T)_x \Rightarrow RT_y \]

with the phase being given by 3:22 \((x = \frac{1}{4})\), 2:17 \((x = \frac{1}{3})\), 3:29 \((x = \frac{2}{5})\), 1:10 \((x = \frac{5}{12})\) and 1:12 \((x = \frac{1}{2})\).

The structures of the P$_{1:12}$ and orthorhombic 1:12 phases are closely related to the tetragonal 1:12 structure which, as shown above, is derived from the 1:5 structure by replacing \(\frac{1}{2}\) of the R atoms with dumb-bells. The structure of the orthorhombic 1:12 phase is a result of an extreme preferential site occupation by the Ti atoms in the 1:12-T structure.
The novel pseudo-ternary (Nd\textsubscript{1/3}Zr\textsubscript{2/3})Fe\textsubscript{3} phase has a PuNi\textsubscript{3}-type (1:3) structure. Although the 1:3 phase forms in many binary R-T systems, it does not crystallize in the binary Nd-Fe system. By introducing the third element, Zr, into the Nd-Fe system the 1:3 phase is stabilized with a well defined stoichiometric composition (Nd\textsubscript{1/3}Zr\textsubscript{2/3})Fe\textsubscript{3} which suggests that all the crystallographic 6c and 3a R sites are exclusively occupied by Zr and R atoms, respectively, while all 18h sites are occupied by Fe atoms. The extremely preferential occupation of the transition metal Zr atoms at rare-earth Nd sites instead of transition metal (T) sites is consistent with a fact that Zr has an atomic size (1.45Å) closer to that of Nd (1.64Å) than that of Fe (1.17Å). This suggests that the atomic size plays a very important role in stabilizing the pseudo-ternary (Nd\textsubscript{1/3}Zr\textsubscript{2/3})Fe\textsubscript{3} phase.

It has long been noticed that the structural similarities of the intermetallic compounds formed between transition metals can be resolved by seeing the structures in the form of the coordination polyhedra of large atoms. Only limited types of coordination polyhedra that satisfy the closely-packed arrangement are abundantly transition metals, it was noted that the rare-earth (R) atoms in all the structures studied in observed in the real structures. In the study of the structures formed between the rare earths and the present work have 20 coordination neighbors and actually all these structures can be viewed as simple stackings of the 20-vertex coordination polyhedra formed by the 20 coordination neighbors around the R atoms, which we refer to as the CPR (CPR stands for coordination polyhedron of R atom). To understand the structures and structural relationships of the novel phases identified in the present work, as well as the 1:5, 2:17 and 1:12 compounds, we extended this by assuming that the R atoms in our new structures would reserve 20 coordination neighbors. From the CPR point of
view, all the structures of the 1:5, 2:17, and 1:12 phases, as well as the novel 3:22, 3:29, 1:10 and (Nd\textsubscript{1/3}Zr\textsubscript{2/3})Fe\textsubscript{3} phases can be viewed as simple stackings of the 20-vertex CPRs along one direction. Although the direct relationships between the CaCu\textsubscript{5} and BaCd\textsubscript{11} structures and the CaCu\textsubscript{5} and Nd\textsubscript{2}Fe\textsubscript{14}B structures are not obvious in the dumb-bell replacement model, their relationships are apparent from the CPR point of view. Both the BaCd\textsubscript{11} and Nd\textsubscript{2}Fe\textsubscript{14}B structures are also simple stackings of the 20-vertex CPRs along one direction. From the CPR point of view, the only differences between these structures are the CPR structure as well as the CPR stacking sequences.

Considering our CPR model, we propose possible structures for our novel R\textsubscript{3}(Fe\textsubscript{1-x}Si\textsubscript{x})\textsubscript{22} (3:22), R\textsubscript{3}(Fe\textsubscript{1-x}Ti\textsubscript{x})\textsubscript{29} (3:29) and R(Fe\textsubscript{1-x}T\textsubscript{x})\textsubscript{10} phases. R\textsubscript{3}(Fe\textsubscript{1-x}Si\textsubscript{x})\textsubscript{22} is an intermediate phase between 2:17 and 1:12 and undergoes a structural change correlated with that undergone by the 2:17 phase as R changes from Gd and Tb to Dy. R\textsubscript{3}(Fe\textsubscript{1-x}Si\textsubscript{x})\textsubscript{22} with R=Dy, Er, Ho, Tm and Lu has an intermediate structure between the hexagonal 2:17 and tetragonal 1:12 structures, which is an orthorhombic with a possible space group Pmm\textsubscript{2} (No. 25). R\textsubscript{3}(Fe\textsubscript{1-x}Ti\textsubscript{x})\textsubscript{29} is an intermediate phase between the rhombohedral 2:17 and tetragonal 1:12 phases and has a monoclinic structure with a possible space group A\textsubscript{2}/m. R(Fe\textsubscript{1-x}T\textsubscript{x})\textsubscript{10} is an intermediate phase between the hexagonal 2:17 and tetragonal 1:12 phases and has an orthorhombic structure with a possible space group Pmm\textsubscript{2} (No. 47).

Like the 1:12 phase, all the novel phases identified in the present work do not exist in binary R-Fe systems and a third element T (Si, Ti and Zr) is essential to stabilize them. The key to the role of the third element atoms in stabilizing these structures is a size effect that can be well explained by our CPR model.
Chapter One:

INTRODUCTION

1-1. THE HISTORY OF PERMANENT MAGNET MATERIALS

1-1-1. AN OVERVIEW OF THE HISTORY OF PERMANENT MAGNETS

Permanent magnetic materials are essential components of a wide variety of electromechanical and electronic devices. The applications of permanent magnets range from acoustic devices, electric motors and generators, toys to magnetomechanics, actuators in data technology, NMR topography systems, beam control systems, water filters and electric watches, etc..

Lodestone was the first permanent magnet reported and used in history. It is principally composed of the ore magnetite (Fe₃O₄) and was used more than 2000 years ago in China in navigational compasses. Substantial developments of permanent magnets, however, only started at the beginning of this century. Since then, many revolutionary developments have happened and all of them have been invariably connected with the discovery of new classes of materials characterized by even better properties. This evolution can be monitored generally by the two most important magnetic properties for a permanent magnet, the maximum energy product \( (BH)_{max} \) and the intrinsic coercivity \( (M H_C) \). \( (BH)_{max} \) expresses the quality of a permanent magnet and provides a measure of the magnetic field that can be produced outside a unit volume of magnet material. The so-called theoretical maximum energy product, the largest realizable value in principle, is an intrinsic quantity defined by
\[ (BH)_{\text{max}} = \frac{1}{4} \mu_0 M_s^2 \]

where \( M_s \) is the saturation magnetization. This can be achieved only if the magnet retains \( M_s \) in a reverse field at least as large as \( \frac{1}{2} \mu_0 M_s \). This introduces another very important permanent magnet property — intrinsic coercivity, \( M_HC \). \( M_HC \) is the reverse magnetic field that decreases \( M \) to zero, which is a measure of the magnet’s resistance to demagnetization and describes the ability of a permanent magnet to withstand the influence of a counteracting magnetic field.

Figure 1-1: The history of the development of permanent magnet materials showing the highest (a) \( (BH)_{\text{max}} \) values and (b) intrinsic coercivities versus time during the past century. 

(b)
As an illustration of the development of permanent magnet properties this century, the maximum energy product \((BH)_{\text{max}}\) and the intrinsic coercive force \(M_H C\) are plotted as a function of time in Figure 1-1. Since the end of the last century, both \((BH)_{\text{max}}\) and \(M_H C\) values have increased by a factor of more than 100. This great achievement was not realized by improving a single material, but rather by the discoveries of new classes of materials. Each new material was followed by a period of intense technological improvement, which in turn was followed by the discovery of another new class of permanent magnet materials.

The first artificial permanent magnets were carbon steels, tungsten steels and cobalt steels used around the end of the last century and at the beginning of this century. These materials are based on iron and its solutions. Thus, they essentially take advantage of the magnetic properties of elemental iron and are characterized by very high magnetization \(M_s\), for which \(4\pi M_s = 21.5\ \text{kG} \approx 1.7\ \text{MA/m}\) implies an enormous \((BH)_{\text{max}}\) of 115 MGOe \((\approx 915\ \text{kJ/m}^3)\). However, there is no way to realize this potential \((BH)_{\text{max}}\), because the anisotropy field \(H_a\) for iron is only about 500 Oe \((\approx 40\ \text{kA/m})\) and the actual coercivities that can be achieved by defect pinning for these materials are less than a few hundred Oe. The additives in these steels simply serve to create defects that act as the energy barriers to translate the meager anisotropy field of iron into a useful coercivity.

Since a larger magnetic anisotropy is also essential to achieve a larger energy product, high intrinsic coercivities became another main consideration in searching for new permanent magnet materials. A major advance was made in 1932. Starting with the thermally treated Al-Ni-Fe alloys featuring coercivities more than twice those of the best cobalt steels, the alnico magnets were developed. Because of their resistance to
stray magnetic fields, mechanical shock, and elevated temperatures, the alnico magnets were seen as the first magnets to be aptly designated permanent. The magnetic properties of these materials are strongly dependent on their microstructure which are characterized by finely dispersed, oriented, elongated single-domain particles precipitated by appropriate thermal treatment in a magnetic field. Based on the Fe-Co alloys, this kind of material is also characterized by very high remanence. However, since their coercivities are contributed merely by the shape anisotropy of the precipitated particles, the intrinsic coercivity for this magnet family is still very low, 2–3 kOe (0.16–0.24 kA/m). With such low coercivity, only a very small fraction of its potential $(BH)_{\text{max}}$ can be realized. The highest energy product reported for this kind of material is about 103.5 kJ/m³ (13 MGOe)⁸. Alnicos magnets are still widely used today. Its main advantages are its high $T_c$, low negative temperature coefficients of flux and coercivity and very good machinability.

Although the theoretical $(BH)_{\text{max}}$ is determined solely by the saturation magnetization, it can only be realized with enough coercivity. The highest possible coercivity for a particular material is confined by its anisotropy field. Comparing with shape anisotropy, magnetocrystalline anisotropy is much higher and is potentially a better way to obtain high coercivity. The hexagonal ferrites were the first group of the materials using magnetocrystalline anisotropy to generate their coercivity.

The hard ferrites are based on the hexagonal oxides $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$ and their solid solutions. The coercivity of ferrite magnets derives from the uniaxial magnetocrystalline anisotropy of single-domain particles, rather than the shape anisotropy, and so is substantially larger (5–10 kOe (0.4–0.8 kA/m)) than that of the alnico magnets (2–3 kOe (0.15–0.25 kA/m)). However, this kind of material is
characterized by very low remnant flux density (B,) and so the (BH)_{max} is severely limited by its low B_r instead of low coercivity. The maximum energy product for this kind of material is no larger than 5 MGOe (~40 kJ/m^3). Despite its relatively low (BH)_{max}, the hard ferrites remain the most popular permanent magnetic materials. The popularity of hard ferrite is largely due to its low cost. Since the hexagonal ferrite magnets (BaFe_{12}O_{19} and SrFe_{12}O_{19}) do not contain any rare and expensive elements such as nickel or cobalt and it is relatively easy to manufacture; ferroxdure is one of the cheapest magnet materials with suitable magnetic properties. The fundamental properties of the ferrites, and the technological issues have been reviewed by many authors^{9-11}

Since 1966, a new family of permanent magnet materials has been evolving which is generically known as the “rare earth permanent magnets” (abbreviated as REPM hereafter). The discoveries that the 3d-transition metals cobalt and iron form many ferromagnetic intermetallic compounds with the lanthanide (or rare-earth, R) elements, and that certain R are capable of imposing a high uniaxial crystal anisotropy on these compounds, led to the successive development of the three new families of magnetic materials typified by SmCo_5, Sm_2(Co, Fe, Cu, Zr)_{17} and Nd$_2$Fe$_{14}$B. The magnetic properties of this new permanent magnet family totally surpassed those of all earlier magnets. As illustrated in Figure 1-1, Nd-Fe-B magnets have energy densities up to five times higher and intrinsic coercivities about ten times higher than the best magnets available in the 60’s and either of these key properties are about 100 times greater than those known before 1930. With such outstanding properties, the REPM have brought a series of revolutionary developments in the field of hard magnetic materials, which resulted in the large scale commercialization of the “rare-earth permanent magnets".
The REPM have not only been displacing more conventional magnet types in many cases but also rapidly broadening the field of applications for permanent magnets in general.\textsuperscript{12-13}

In addition to their high performance, the REPM also have other properties that are unique and technologically important, such as a very square demagnetization curve.

\section*{1-1-2. RARE-EARTH PERMANENT MAGNETS (REPM)}

In terms of basic magnetic properties, a ferro- or ferrimagnetic substance is a potential candidate for permanent magnet applications when it fulfills the following three conditions:

\begin{itemize}
\item It has a high spontaneous magnetization, $M_s$, in the temperature range of practical interest, generally at and above room temperature. The saturation intrinsic induction, $B_s = 4\pi M_s$ sets the upper limits for the remanent flux density, $B_r = B_s$, and thus the maximum energy product, $4\pi (\frac{1}{2} M_s)^2$ (in MGOe) that can be achieved with the magnet.
\item The main phase has a reasonably high magnetic ordering temperature, $T_c$. For ferromagnetic materials, $M_s$ is monotonically decreased to a value of zero at the Curie point with increasing temperature\textsuperscript{14}. The Curie point should be substantially higher than the magnet's operating temperature since as the temperature is increased the magnetic flux decrease becomes increasingly rapid.
\item Finally, the main phase should have a large uniaxial anisotropy field that permits the attainment of the high intrinsic coercivity, $H_{ci}$. $H_{ci}$ is a measure
of the magnet's resistance to demagnetization. High intrinsic coercivity is essential to obtain a large energy product and is needed especially for magnets intended for use in environments and designs in which they are subject to large internally generated or externally imposed demagnetizing fields.

Iron, cobalt, and especially Fe-Co alloys have the best combinations of $B_{is}$ (at room temperature) and $T_c$. Based on fully dense Fe-Co alloy with $B_{is} \approx 24.5$ kG, the highest conceivable room-temperature energy product could be about 1.2 MJ/m$^3$ (150 MGOe). However, no way has been found to obtain a sufficiently high coercivity in this material, i.e. $955\sim 1035$ kA/m (12\sim 13 kOe), to achieve such a high $(BH)_{max}$. Fe-Co is the main component of the alnico magnets and of the elongated-single-domain particle (ESD) magnets, but because the coercivity of these magnets are developed merely from the shape anisotropy of precipitated particles, the best coercivity that could be derived from single-domain behavior, using shape anisotropy as the energy barrier, was only about 160 kA/m (~2 kOe), or about 30% of the value needed to realize the predicted energy products of 1.2 MJ/m$^3$ (150 MGOe)$^{15}$.

Magnetocrystalline anisotropy offers a better way than particle shape anisotropy to generate sufficiently high coercivity. Ferromagnetic crystals having a single strongly preferred axis of magnetization, when in the form of micron-sized "single-domain particles", will require fields about equal to their anisotropy field, $H_a = 2K/M_s$ ($K$ is anisotropic constant), for magnetization reversal$^{16\sim 18}$. This led to a systematic search for the materials having a strong uniaxial crystal anisotropy in the 1950s and 1960s as the candidate for new magnet materials. As mentioned above, the hexagonal ferrites were
the first group of such materials, the rare-earth intermetallic RCo$_5$ compounds were next, leading to the broader family of rare earth magnets.

Based on the discussion above, the class of compounds formed between rare-earth and 3d transition metals is obviously of particular interest. The 4f electron shell of the R and the 3d electron shell of T are only partly full. The unpaired electrons in these shells give rise to the observed magnetism. Combining these two elements together, one might simultaneously benefit from the intrinsic properties of both components, that is, from the high magnetic moment per atom and the strong single-ion magnetocrystalline anisotropy of the rare-earth partner and from the high magnetic coupling strength of the moments of the 3d transition-metal partner. Indeed, the majority of investigations of rare-earth-transition metal intermetallics reported in the literature deal with the magnetic properties of these compounds.

However, because high-purity rare earths in metallic form were almost unavailable before the 1960's, there were only few studies on rare earth-transition metal alloy systems reported before the 1960s and they were mainly concentrated on the existence of intermetallic compounds and their crystal structures. As the result of such studies, CeCo$_5$ and Ce$_2$Co$_{17}$ were discovered. In the 1960's, a technique for the separation and reduction of the rare-earth elements was developed which made the R metals commercially available and brought on a surge of scientific research in the R-T alloys and their properties.

Several early investigations of the magnetic ordering phenomena in R-T compounds yielded preliminary information for the later development of rare-earth permanent magnets. Succeeding these early works, the systematic study of the magnetism and crystal structure of R-T intermetallics revealed that the binary RCo$_5$
compounds with "light" R (Ce, Pr, Nd, Sm) combine sufficiently high Curie
temperature and saturation values with a uniaxial crystal anisotropy, and so they might
be used as the starting materials for new permanent magnets. Further studies on the
magnetocrystalline anisotropy revealed that most RCo5 compounds have an
extremely large crystal anisotropy with a single easy axis of magnetization. This
confirmed that these materials were indeed candidates for outstanding new permanent
magnets. However, it took several years to realize practicable SmCo5 magnets. The
discovery of the liquid-phase sintering technique made the development of fully
dense and stable SmCo5 magnets with high coercive forces possible. Energy products in
the 127–223 kJ/m³ (16–28 MGOe) range have been obtained from sintered SmCo5
magnets.

Because a large portion of the moment observed in the LRCo5 and LR2Co17 (LR =
"light" rare-earth) compounds is contributed by the cobalt atoms, in view of the richer
cobalt content and, hence, higher magnetization and larger (BH)max values, the R2Co17
compounds were also heavily investigated at the same time as the SmCo5 magnets. The
results of these studies showed that some binary R2Co17 compounds, such as Sm2Co17
and Er2Co17, do have strong anisotropy with an easy axis. The anisotropy field of
Sm2Co17 is about 5.6 MA/m (70 kOe), definitely large enough to theoretically provide
sufficiently large \( M_{CH} \) values. However, the realization of the 2:17 magnets proved even
more difficult than 1:5 magnets. All the methods suitable to produce SmCo5 magnets
yield only very low coercivity, when they were used on 2:17 magnets. The
development of the R2T17 permanent magnets progressed largely by developing
microstructures that promote domain wall pinning within the grain interiors to use their
potential high coercivity. The commercial Sm2(Co, Fe, Co, Zr)17 magnets came about
ten years later after the SmCo$_5$ magnets. The best Sm$_2$(Co, Fe, Cu, Zr)$_{17}$ magnet reported has an energy product of 263 kJ/m$^3$ (~33 MGOe), combined with a coercivity $H_c = 1.0$ MA/m (~13 kOe)\textsuperscript{45}.

The dramatic progress in magnet materials brought by the Sm-Co rare earth permanent magnets also opened up possibilities for equally revolutionary developments in permanent magnet devices and machines. The excellent magnetic properties of REPM made it possible to miniaturize devices and improve energy efficiency by replacing the older magnet types. In addition to this, REPMs also broadened the permanent magnets’ applications in the areas where no permanent magnets had been used before. By the late 1970’s the rare-earth permanent magnets had found a firm niche in the spectrum of commercial magnet materials, and the use of Sm-Co magnets was rapidly growing.

However, widespread use of the SmCo$_5$ and Sm$_2$(Co, Fe, Co, Zr)$_{17}$ magnets was hindered by their economical constraints. The main components in both types of the Sm-Co magnets are the expensive Sm and Co elements. Samarium is the least abundant, and hence most expensive, of the “light” rare earth elements (i.e., La, Ce, Pr, Nd, Sm). The price and availability of cobalt are also subject to gross, unpredictable excursions. As a result, the Sm-Co magnet is one of the most expensive magnets in permanent magnet material families.

This obstacle spurred new research into the possibilities of making iron-based rare-earth alloys with good magnetic properties\textsuperscript{46}. However, no suitable compounds were known before 1978. R-Fe compounds with the CaCu$_5$-type structure do not exist, and the R$_2$Fe$_{17}$ compounds in which R is a “light” rare earth have unacceptably low Curie temperatures. Despite this, there were two lines of research in the preparation of
iron-based rare-earth permanent magnets. One approach based on the rapid solidification of rare-earth-iron-metalloid alloys\textsuperscript{47-68}, and the other involved the traditional powder-metallurgy (sintering) techniques\textsuperscript{69-70}. As a result of these studies the Nd\textsubscript{2}Fe\textsubscript{14}B magnets were announced in 1983.

Since the supply of cheap iron is essentially unrestricted, and Nd is about ten times more abundant than Sm in the common ores and thus much cheaper than Sm, the Nd\textsubscript{2}Fe\textsubscript{14}B magnet immediately attracted great attention in both academic and industrial circles. Considerable technological interest was centred on Nd\textsubscript{2}Fe\textsubscript{14}B. Although the largest theoretical maximum energy product for Nd\textsubscript{2}Fe\textsubscript{14}B magnet, (BH)\textsubscript{max}\ approximately 509 kJ/m\textsuperscript{3} (~64 MGOe), is much lower than that of alnico, practical Nd\textsubscript{2}Fe\textsubscript{14}B magnets with energy products in the 240~320 kJ/m\textsuperscript{3} (30~50 MGOe) range, which are significantly larger than any previously attained, have been prepared from melt-spun\textsuperscript{71-72} and sintered\textsuperscript{73} alloys, helped by its high magnetic anisotropic field, H\textsubscript{a}~73 kOe. Because of its excellent intrinsic properties and economical advantages, the spectrum of applications for Nd\textsubscript{2}Fe\textsubscript{14}B magnets expanded rapidly. Nd\textsubscript{2}Fe\textsubscript{14}B and its derivatives have become the second most important magnet material family after the hexaferrites and it has been predicted that by the year 2000, Nd\textsubscript{2}Fe\textsubscript{14}B magnet will exceed the hexaferrites and become the number one permanent magnet.

However, Nd\textsubscript{2}Fe\textsubscript{14}B magnets have some definite shortcomings compared with the Sm-Co based magnets: their low Curie temperature, high negative temperature coefficients of flux and coercivity, and a low resistance to corrosion mean that for certain more demanding applications requiring high operating temperatures, or good thermal, or chemical stability, the more expensive Co-based REPMs still have to be used.
The shortcomings of the present magnets naturally stimulated further search for new compounds that could possibly be used as starting materials for a newer generation of magnets. Although no dramatic advance has been obtained, several compounds are being intensively studied because of their potential to be developed as new permanent magnets; the most attractive among them are $R_2Fe_{14}C^{74-78}$ and $R_2Fe_{17}N_8^{79-81}$.

1-1-3. RARE-EARTH TRANSITION METAL COMPOUNDS—THEIR CRYSTAL STRUCTURES AND STRUCTURAL RELATIONSHIPS

As mentioned above, the compounds formed between rare earths and transition metals are of particularly interest in permanent magnet applications. The atomic diameters of the rare-earth (R) atoms are substantially larger than those of the transition metal (T) atoms. According to the Hume-Rothery rules, this precludes any significant substitutional solid solubility between the R and T groups. Because of this large size discrepancy, a very large number of intermetallic compounds are formed in the R-T systems. Many of these compounds have non-cubic structures with unique crystallographic axes.

A survey of the structures formed between the rare-earths and 3d-transition metals are listed in Table 1-1. Concerning the practical permanent magnet applications, most compounds listed in this table are of little interest because of their poor intrinsic magnetic properties. Besides $RT_5$, $R_2T_{17}$ and $R_2Fe_{14}B$, from which three families of REPM were developed, however, some of the compounds listed in Table-1-1 do attract great attention. Amongst these, the most interesting compounds are $R_2Fe_{17}M_6$, $R(Fe_{1-x}T_x)_{12}$, $R(Fe_{1-x}T_x)_{12}M_8$ and $R_2Fe_{14}C$ ($M = N, C$). The good intrinsic magnetic properties of these compounds make them the potential candidates as starting materials for new permanent magnet series.
Table 1: A survey of the intermetallic compounds formed between rare-earth and 3-d transition metals and their crystal structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Symmetry</th>
<th>Structure Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R}_3\text{T}^{84-85}$</td>
<td>Orthorhombic</td>
<td>Al$_2$Ni</td>
</tr>
<tr>
<td>$\text{R}_7\text{T}_3^{86}$</td>
<td>Hexagonal</td>
<td>Th$_7$Fe$_3$</td>
</tr>
<tr>
<td>$\text{R}_4\text{T}_3^{87-88}$</td>
<td>Hexagonal</td>
<td>Ho$_4$Co$_3$</td>
</tr>
<tr>
<td>$\text{RT}^{89}$</td>
<td>Orthorhombic</td>
<td>FeB</td>
</tr>
<tr>
<td>$\text{RT}_2^{90,91}$</td>
<td>Cubic</td>
<td>MgCu$_2$, MgNi$_2$</td>
</tr>
<tr>
<td>$\text{RT}_3^{92,93}$</td>
<td>Hexagonal</td>
<td>CeNi$_3$, PuNi$_3$</td>
</tr>
<tr>
<td>$\text{R}_2\text{T}_7^{94,95}$</td>
<td>Hexagonal</td>
<td>Ce$_2$Ni$_7$, Gd$_2$Co$_7$</td>
</tr>
<tr>
<td>$\text{R}<em>6\text{T}</em>{23}^{95,96}$</td>
<td>Cubic</td>
<td>Th$<em>6$Mn$</em>{23}$</td>
</tr>
<tr>
<td>$\text{RT}_5^{90,97}$</td>
<td>Hexagonal</td>
<td>CaCu$_2$</td>
</tr>
<tr>
<td>$\text{R}<em>2\text{T}</em>{17}^{98,99}$</td>
<td>Hexagonal</td>
<td>Th$<em>2$Ni$</em>{17}$, Th$<em>2$Zn$</em>{17}$</td>
</tr>
<tr>
<td>$\text{R}<em>2\text{T}</em>{17}\text{M}_8^{100,101,102}$</td>
<td>Hexagonal</td>
<td>Th$<em>2$Ni$</em>{17}$, Th$<em>2$Zn$</em>{17}$</td>
</tr>
<tr>
<td>$\text{RT}_{12}^{103,104}$</td>
<td>Tetragonal</td>
<td>ThMn$_{12}$</td>
</tr>
<tr>
<td>$\text{RT}_{11}^{105,106}$</td>
<td>Tetragonal</td>
<td>BaCd$_{11}$</td>
</tr>
<tr>
<td>$\text{R}<em>2\text{T}</em>{14}\text{B}^{107,108}$</td>
<td>Tetragonal</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
</tr>
<tr>
<td>$\text{R}<em>2\text{T}</em>{14}\text{C}^{109}$</td>
<td>Tetragonal</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
</tr>
<tr>
<td>$\text{R}<em>5\text{Fe}</em>{62}\text{B}_{14}^{109}$</td>
<td>Cubic</td>
<td></td>
</tr>
<tr>
<td>$\text{RCO}_{12}\text{B}_6^{110,111}$</td>
<td>Rhombohedral</td>
<td>SrNi$_{12}$B$_6$</td>
</tr>
<tr>
<td>$\text{RT}_6\text{Sn}_6^{112}$</td>
<td>Hexagonal</td>
<td>HfFe$_6$Sn$_6$</td>
</tr>
<tr>
<td>$\text{R}<em>6\text{T}</em>{11}\text{M}_5^{113}$</td>
<td>Tetragonal</td>
<td>La$<em>6$Co$</em>{11}$Ga$_3$</td>
</tr>
<tr>
<td>$\text{R}<em>{1\cdot\varepsilon}\text{T}</em>{4}\text{B}_4^{114}$</td>
<td>Tetragonal</td>
<td>RT$_4$B$_4$</td>
</tr>
</tbody>
</table>
Although the magnetic properties of the compounds formed between rare-earths and transition metals differ dramatically, the structures of the majority of these compounds are closely related to and most originate directly from the hexagonal lattice of the CaCu$_5$-type structure. The representative examples are the structural relationships between the main phases of the three famous REPM families, SmCo$_5$, Sm$_2$(Fe, Co, Cu, Zr)$_{17}$, and Nd$_2$Fe$_{14}$B.

The RT$_5$ compounds that characterize the first generation of rare earth permanent magnets SmCo$_5$ crystallize in the CaCu$_5$-type structure. It belongs to the space group P6/mmm. The R atoms are located in the crystallographic sites 1a: (0,0,0) and the T atoms are located in two crystallographic sites, 2c: ±(1/3, 1/3, 0), and 3g: (1/2, 1/2, 1/2), (0, 1/2, 1/2) and (1/2, 0, 1/2). The unit cell of the SmCo$_5$ structure is shown in Figure 1-2. It has two types of layers: in the basal layer both R and T atoms are found whereas in the middle layer only T atoms are accommodated.

![Figure 1-2: The structure of hexagonal RT$_5$ (CaCu$_5$)](image)

The R$_2$T$_{17}$ compounds have two structural modifications depending on the R atom. The rhombohedral R$_2$T$_{17}$ phase with Th$_2$Zn$_{17}$-type structure (space group...
R$^3$m) forms with R = Pr, Nd, Sm, Gd, Tb and Dy, based on which the second generation of REPM—Sm$_2$(Fe, Co, Zr, Cu)$_{17}$ was developed. With R = Dy, Ho, Er, Tm and Lu, R$_2$T$_{17}$ crystallizes in the hexagonal Th$_2$Ni$_{17}$-type structure (space group P6$_3$/mmc). It is well known that both the Th$_2$Zn$_{17}$-type and Th$_2$Ni$_{17}$-type structures are directly derived from the CaCu$_5$ structure via appropriate replacement of one third of all

![Diagram of R atom arrangement on the 001 plane](image)

(a) R atom arrangement on the 001 plane

![Diagram of Th$_2$Ni$_{17}$ and Th$_2$Zn$_{17}$ structures and their relationship to the CaCu$_5$ structure](image)

(b) Th$_2$Ni$_{17}$ and (c) Th$_2$Zn$_{17}$ structures and their relationship to the CaCu$_5$ structure. Both the Th$_2$Ni$_{17}$ and Th$_2$Zn$_{17}$ structures can be derived from the CaCu$_5$ structure by simple dumb-bell replacement.
R atoms by pairs of T atoms (dumb-bells) along the hexagonal axis of the CaCu₅ structure. The edge of the unit cell in the basal plane is given now by $a_{2:17} = \sqrt{3}a_{1:5}$ for both the Th₂Zn₁₇-type and Th₂Ni₁₇-type structures. Figure 1-3 illustrates the structural relationships of Th₂Zn₁₇ and Th₂Ni₁₇ to CaCu₅. If, in the basal plane, the dumb-bell replacement occurs at site B, it will occur at site C in the next layer containing R atoms. In the following layer containing R atoms it may occur either at site E, leading to a rhombohedral Th₂Zn₁₇ structure with $c_{2:17} = 3c_{1:5}$ or again at site B, leading to a hexagonal Th₂Ni₁₇ structure with $c_{2:17} = 2c_{1:5}$.

Figure 1-4: The unit cell of Nd₂Fe₁₄B structure. The $c/a$ ratio in the figure is exaggerated to emphasize the puckering of the iron nets.
The lattice symmetry of Nd$_2$Fe$_{14}$B is tetragonal (space group P4$_2$/mmn), and each unit cell contains 68 atoms (see Figure 1-4). Although the Nd$_2$Fe$_{14}$B structure cannot be derived from the CaCu$_5$ structure directly, many structural parallels exist between them. Both structures can be seen as stacks of triangular and hexagonal layers. The hexagonal arrays of Fe(k$_1$), Fe(k$_2$), Fe(j$_1$), and Fe(e) atoms in R$_2$Fe$_{14}$B are the cognates of the T(g) arrays in RT$_5$; both form hexagonal prisms enclosing the R atoms. Furthermore, the B and Fe(j$_2$) sites of R$_2$Fe$_{14}$B correspond to the T(c) and R sites, respectively, in RT$_5$.

Given the similarities between RT$_5$ and Nd$_2$Fe$_{14}$B on the one hand and of RT$_5$ and R$_2$T$_{17}$ on the other, it is not surprising that many structural parallels exist between Nd$_2$Fe$_{14}$B and R$_2$T$_{17}$. Both structures have a layered arrangement and the presence of hexagonal T nets surrounding the R atoms (see Figure 1-3 and 1-4). Despite the different symmetries, the lattice parameters of Nd$_2$Fe$_{14}$B ($a=8.80\text{Å}, c=12.20\text{Å}$) are very similar to those of its nearest corresponding R$_2$T$_{17}$, Nd$_2$Fe$_{17}$ ($a=8.57\text{Å}, c=12.44\text{Å}$). Perhaps the most significant correlation is the fact that the Fe(j$_2$) atoms in Nd$_2$Fe$_{14}$B and the Fe(c) atoms in Nd$_2$Fe$_{17}$ are similar both magnetically as well as crystallographically. A very interesting further perspective on the analogy observed between the j$_2$ sites in Nd$_2$Fe$_{14}$B and the c sites in Nd$_2$Fe$_{17}$ is that the j$_2$ and c sites are the only T sites in their respective structures which have a major ligand line i.e., a line connecting the sixfold faces of the Wigner-Seitz polyhedral constructed about the lattice sites. It has been suggested that the occurrence of such lines generally encourages large magnetic moments. The orientation of the major ligand lines has also been related to the magnetocrystalline anisotropy in a number of R-T materials.
Besides the structural relationships between the main phases in the three main rare-earth magnet families, most of the other structures formed in the R-T systems can also be derived from the hexagonal CaCu$_2$ structure by the judicious replacement of R and T atoms$^{142-143}$. They arise through either dumb-bell replacement or some simple substitutions accompanied by some minor atomic rearrangements and layer shifts. Examples are the RT$_{12}$$^{144-147}$ (tetragonal ThMn$_{12}$-type) structure, RT$_2$ (cubic Laves phase, MgCu$_2$-type) structure$^{148}$, the RT$_3$ (rhombohedral; PuNi$_2$-type) structure, the R$_2$T$_7$ (hexagonal Ce$_2$Ni$_7$-type and rhombohedral Gd$_2$Co$_7$) structures.

Because of its potential as a starting material for new permanent magnets the R(Fe$_{1-x}$T$_x$)$_{12}$ phase has been extensively studied$^{149-154}$. It was discovered recently that the absorption of nitrogen or carbon by the R$_2$Fe$_{17}$ and R(Fe$_{1-x}$T$_x$)$_{12}$ compounds dramatically improves the intrinsic magnetic properties of such intermetallics$^{155-157}$. The high Curie temperatures coupled with strong uniaxial anisotropy makes the nitride and carbides of the R$_2$Fe$_{17}$ and R(Fe$_{1-x}$T$_x$)$_{12}$ compounds, such as Sm$_2$Fe$_{17}$M$_6$ and NdFe$_{11}$TiM$_6$ (M = N, C)
very promising for possible technological application as high performance permanent magnets. Sm$_2$Fe$_{17}$M$_6$ crystallizes in the rhombohedral Th$_2$Zn$_{17}$-type (2:17-R) structure, which, as mentioned above, is derived from CaCu$_5$ by replacing 1/3 of the R(Ca) atoms with T-T pairs (dumb-bells) along the c-axis of CaCu$_5$. R(Fe$_{1-x}$T$_x$)$_{12}$ and NdFe$_{11}$TiM$_6$ crystallize in the tetragonal ThMn$_{12}$ structure which, like the 2:17 structures, is also derived from CaCu$_5$ directly by replacing 1/2 of the R(Ca) atoms in the CaCu$_5$ structure with dumb-bells along the c-axis of the CaCu$_5$ structure. The 1:12 structure and its relationship with the 1:5 structure is illustrated in Figure 1-5.

Because the magnetization observed in the LR-T (LR = “light” rare-earth, T = Fe or Co) compounds is largely contributed to by the 3d transition metal atoms, due to the richer T contents, resulting in higher M and larger $(BH)_{max}$ values, only high T-containing R-T compounds are interesting for permanent magnet applications. Most such compounds, as mentioned above, are derived from RT$_5$ by replacing R atoms with T-T pairs. Although the higher R-containing R-T compounds are not viable for permanent magnet materials, because of their poor magnetic properties, it is worth noting that the structures of most of these compounds are also derived from RT$_5$. In order to obtain the structures of these compounds such as R$_2$T$_7$, RT$_3$ and RT$_2$, however, one has to replace T atoms by R atoms in RT$_5$. This is illustrated by the MgCu$_2$ and PuNi$_3$ structures in Figure 1-5. Replacing one of the two T atoms in every top and basal plane of the RT$_5$ unit cell by an R atom followed by a layer shift and minor rearrangement of the atoms results in the 1:2 structure. If one of the two T atoms is replaced by an R atom in the top or basal plane of every second RT$_5$ unit cell followed by a layer shift and minor atomic rearrangements, the PuNi$_3$ structure will be formed. In
a similar way one can obtain the $R_2T_7$ structures. Their stacking arrangements are shown in Figure 1-7.

![Diagram of $R_2T_7$ structures](image)

**Figure 1-6: The (b) 1:2 and (c) 1:3 structures and their relationships to the (a) 1:5 structure**

All the structural derivations mentioned above represent ordered substitutions. In addition to these ordered substitutions, random dumb-bell substitutions have also been observed in the 1:5 and 2:17 phases. Reasonably broad homogeneity ranges at high temperatures for the $RCo_5$ and the $R_2Co_{17}$ compounds (where $R = \text{Sm}$ and Gd) have been observed\textsuperscript{161-162}. The homogeneity range of SmCo$_5$ at 1200-1300$^\circ$C has been reported to be between about 14.5 and 17 at.% Sm\textsuperscript{163}. Because of the difficulty in Sm atoms occupying Co atom sites owing to the large size difference between the two...
atoms, there is only a minimal solubility of excess Sm in SmCo$_5$. Benz and Martin$^{164}$ have postulated that the limited excess Sm solubility in SmCo$_5$ is made possible by the creation of Co vacancies. In contrast to Sm, Co has a larger solubility in SmCo$_5$. In fact, the equilibrium RCo$_5$ compound with R = Er$^{165}$ and some other “heavy” rare earths (Gd)$^{166,167}$ only stabilizes with $T/R \approx 6$ instead of 5. The much larger homogeneity seen on the Co-rich side of SmCo$_5$ stoichiometry was believed to result from the random substitution of Sm atoms with Co atom pairs (“dumb-bells”) aligned along the c axis of the SmCo$_5$ crystal$^{168}$. When this dumb-bell substitution is ordered, the $R_2$Co$_{17}$ structure results$^{169}$. The broad homogeneity range, observed on the R-rich side of the $R_2$Co$_{17}$ stoichiometry for the Sm and Gd compounds at high temperatures, is also associated with such substitution and indicates that the $R_2$Co$_{17}$ compound can stabilize with fewer dumb-bells than expected. Consequently, $R_2T_{17}$ magnets covering a range of $T/R$ ratios have been made possible in which the alloys are essentially single phase at high temperatures. A near-zero solubility of Co is seen in excess of the $Sm_2Co_{17}$ stoichiometry$^{170}$. Correlation between structures not belonging to the CaCu$_5$ family can be found in the book by Schubert$^{171}$.

1-2. THE AIM OF THE PRESENT WORK

Although the number of possible compounds formed between rare-earths and transition metals is enormous, so far only a limited number of them have been identified and most are binaries. Regarding the ternary and higher-component-containing compositions of interest, only a limited amount of information is available. The fact that many more intermetallic compounds than are known so far are likely to exist between 3-d transition metals and the rare-earths naturally bring about the expectation that some of these unknown compounds may be useful for totally new permanent magnet materials.
that will be better, cheaper or more appropriate for specific uses than those currently in use. Although no such alloys can be theoretically predicted, this possibility cannot be denied.

In the search for novel compounds, the early development of permanent magnet materials proceeded entirely by trial and error. Although some theories predicting the stability of possible intermetallic phases, such as Miedema’s macroscopic atom model\textsuperscript{172}, Pettifor’s structure maps\textsuperscript{173} and the structural stability diagrams of Villars\textsuperscript{174,175} were developed and may provide helpful guidelines, trial-and-error remains the most effective method of searching for new intermetallic compounds.

Given the relationships amongst most of the structures formed between rare earths and transition metals, especially the structures of the most interesting compounds such as 1:5, 2:17, 2:14:1 and 1:12, it is natural to wonder whether there exist other unknown R-T compounds whose structures can also be derived from the CaCu\textsubscript{5} structure by the replacement of large R atoms with pairs of small T atoms.

As mentioned above, replacing $\frac{1}{3}$ and $\frac{1}{2}$ of the R atoms in the 1:5 structure leads to the 2:17 and 1:12 structures, respectively. Besides those phases, if $\frac{1}{4}$, $\frac{2}{5}$ and $\frac{5}{12}$ of the R atoms in the 1:5 structure are replaced by T-T dumb-bells, 3:22, 3:29 and 1:10 phases might be formed. These phases, if they exist, will be intermediate between the 1:5 and 1:12-T phases. It is worth mentioning that the maximum dumb-bell replacement fraction allowed in the CaCu\textsubscript{5} structure is $\frac{1}{2}$ and above this limit there would be dumb-bells located at adjacent positions along the c-axis of the CaCu\textsubscript{5} structure, resulting in too short interatomic distances.
In the present work reported in this thesis, systematic studies on several R-Fe-T systems (R = Nd, Gd, Tb, Dy, Ho, Er, Tm and Lu, T = Si, Ti and Zr) were carried out in an attempt to identify the possible new phases existing between the 1:5 and 1:12 phases and the structural relationship characteristics between these possible phases as well as the 1:5 and 1:12 structures. Adding the third element T is based on the consideration that the 1:12 phase does not exist in any binary R-T systems and the third element is essential to stabilize the structure.
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Chapter Two:

EXPERIMENTAL METHODS

All the samples used in this study were prepared by arc-melting pure elements (>99.9 wt.%) in a copper crucible cooled with running water under an argon atmosphere. In order to get homogeneous samples, each sample was re-melted at least 5 times and was turned over after each melting. Since the loss of rare earth elements during arc-melting is much greater than the other components in the samples, extra rare earth component was added to compensate for such losses. In this study, all the samples were prepared with the same weight of about 5 grams before arc-melting in order to make total losses of rare-earth element relatively controllable. The EDAX results on the as-cast ingots show that the loss of the rare earth elements during the arc-melting varies over a wide range with different samples. Generally, 7-10 wt.% extra rare earth elements should be added for a 5 gram ingot with the 5 times re-melting process in our experiment.

Because of the complex phase diagrams of the systems investigated, most of the as-cast samples were multi-phases, even the samples with compositions corresponding to the stoichiometric compositions of the specific phases. In order to study the phase formation at the chosen composition, the samples were annealed for long periods (3-25 days) to reach thermal equilibrium at the specified temperatures, then quenched to the room temperature, so the phases in the samples can reflect the equilibrium phase formation at the designed composition. The annealing conditions for the specific samples will be given in the following chapters.
Another purpose of the annealing is to investigate the phase formation at different temperatures. If a phase only stabilizes in a narrow temperature range, it would be unlikely to form in the as-cast sample. Thus, the annealing at certain temperatures would be essential to constitute such a phase.

To prevent oxidization during annealing, the samples were sealed in quartz tubes under a partial pressure of argon. The annealing was terminated by rapidly cooling to room temperature.

The characterization of all the samples was carried out with (i) a JEOL JSM-840 scanning electron microscope (SEM) equipped with Link System AN 10000 energy dispersive X-ray analyser (EDAX); (ii) powder x-ray diffraction (XRD) with Cu Kα (λ=1.5409 Å) or Co Kα (λ=1.79021 Å) radiation; (iii) a modified thermo-gravimetric analyser (TGA) for the Curie-temperature measurement and (iv) $^{57}$Fe Mössbauer spectroscopy at room temperature in a standard transmission geometry using a $^{57}$CoRh source.

The samples for SEM were carefully polished to get nearly mirror surfaces in order to get best SEM image and reduce the error in the EDAX analysis. It is known that the phases with large different mean atomic number can be distinguished by the contrast in the back-scattered SEM image or even secondary-electron image. Since the compositions of the phases in some of the samples investigated in this study are very similar, the contrast created by the different mean atomic number alone is insufficient. Thus, the samples were etched with a 2% solution of nitric acid in alcohol (Nital) for about 10-40 seconds to create topological difference for better contrast.
The compositions of the phases reported in this work are the non-standardized EDAX results. Because of the overlap of the K series lines of Fe and the L series lines of the R elements, the errors in the EDAX analysis reported in this work could be quite large, even though the program used in the EDAX has some correction on such overlapping. By comparing our results with those reported in the literature, it seems that the average errors for both the Fe and rare earth contents in the matrix phases in this work should be within ±0.5~1.5at.%. However, the actual error for each individual analysis is unpredictable. In order to make the results consistent with each other in this work, the EDAX analysis on each phase was repeated 4 times and the results presented in this work are the averages over these analyses. The largest difference between a single analysis result and the average values is simply used as the compositional error in this work. It should be further mentioned that a larger EDAX error exists in the composition reported for the intergranular impurity phases with high R content. This is because of the fact that good EDAX analysis requires a flat surface with a large enough area. Since the samples were etched using Nital solution, the intergranular impurity phases with high R content were etched off to small holes on the surface of the samples, resulting in a larger error for EDAX analysis.

In our x-ray diffraction experiments, we used both Cu and Co Kα radiation. Since the dominant component in our samples is Fe, considering the selected x-ray absorption by the sample (Fe), the best choice for our samples is Co target with an Fe filter. However, in the early stages of the experimental work, no Co target was available on the x-ray Diffractometer we used (Siemens Diffractometer D5000 in the School of Materials Sciences and Engineering, the University of New south Wales), so the Cu target with a Ni filter was used instead of Co. Because of the strong absorption of Cu
Ka x-ray. by the Fe in the samples, the diffraction results have a quite strong background and weak reflection peaks. Since the weak superlattice reflections are extremely important in this work for us to identify the possible new structures, we had to run every sample at the slowest scanning speed that the machine allows to get the better diffraction results, so the weak peaks are strong enough to be detectable. It generally took about 20 hours per sample. At the later stage of the study, the x-ray diffraction was carried on the x-ray diffractometer in the Department of Materials Engineering, the University of Wollongong, which has a Co target available, so the much better results were obtained. The lattice parameters of the phases reported in this work were calculated by refining the powder x-ray diffraction results using the Pirum program written by Werner1 2. In analyzing the x-ray diffraction results, the LAZY-PULVERIX program3 was also used to calculate the theoretical powder x-ray diffraction patterns for the phase identification and structural analysis.

The Curie temperature (Tc) measurement is another useful tool to determine the phase content in the samples with some phases in a very small quantity or phases with similar compositions and structures, since the SEM and XRD results alone sometimes are not enough to do so. We modified a thermo-gravimetric analyzer (TGA/DTA) for the Curie-temperatures measurement, which is illustrated in Figure 3-1. The operating principle of the TGA is to detect the weight change of the sample as a function of the temperature using an accurate balance. To modify the TGA/DTA for the Tc measurement, we placed a pair of magnets around the sample chamber to create a magnetic field inside the sample chamber. The principle here is simple. At room temperature, the magnetic sample interacts with the magnetic field and such interaction reduces the monitored weight of the sample. If we adjust the zero point of the TGA at
this stage, as the sample is heated up from room temperature, the measured weight of the sample will increase because of the reduction of the magnetic interaction between the sample and magnetic field resulting from the reducing magnetic flux of the sample. At the $T_c$ point, the phase becomes non-magnetic so a clear weight change can be observed. To get more sensitive and so more accurate measurement, the stronger the magnetic field acting on the sample, the better. To achieve this, the magnets have to be put as close as possible to the sample, but this will result in the magnets being too close to the heating element. To prevent the magnets being heated at the same time, insulating material was used between the magnets and the heater.

![Schematic illustration of the modified TGA used to measure the magnetic ordering temperature ($T_c$)](image)

*Figure 2-1: Schematic illustration of the modified TGA used to measure the magnetic ordering temperature ($T_c$)*

The error of our $T_c$ measurement mainly comes from the unstable condition of the TGA machine we used and its data recording system. The TGA machine used in this work is a very old model. Although we recalibrated the thermal-couple in order to
minimize the temperature measurement error, the measured results sometimes are not quite repeatable because of the machine's unstable condition. Another major error came from the data recording system. The data recording system for our TGA/DTA is an old x-y recorder whose accuracy is unknown. Manual analysis of the graphic-type data for the Tc value alone can add 2-5°C error to the final results. In order to determine the error of the system, we calibrate it by using standard samples (Ni, Nd$_2$Fe$_{14}$B and Ag (using DTA)) and used the results from these standard samples to treat the results of the samples. Nevertheless, the errors in Tc reported in this work could be as large as ±10°C.

$^{57}$Fe Mössbauer spectra were collected at room temperature in a standard transmission geometry using a $^{57}$CoRh source. The spectrometer was calibrated with an α-Fe foil. The Mössbauer spectra were fitted using a standard least-squares program.

Because of the multi-phase nature of some samples and the fact that every single phase in these samples comprises numerous magnetically inequivalent Fe sites, a program originally developed for the fitting of the spectra of amorphous materials was also used in order to analyze multi-phase samples in terms of a hyperfine field distribution.
REFERENCES


Chapter Three:

A NOVEL 3:22 PHASE IN THE HR-Fe-Si SYSTEM
(HR = Gd, Tb, Dy, Ho, Er, Tm and Lu)

3.1. INTRODUCTION

Recently, it was found that introducing interstitial atoms (N and C) into rare earth (R) transition metal (T) compounds, such as Sm$_2$Fe$_{17}$ and NdFe$_{14}$Ti, can dramatically improve their magnetic properties$^{1,2}$. For example, the R$_2$Fe$_{17}$N$_8$ nitrides with $\delta = 2.5$~$3$ have Curie temperatures ranging from 678 to 758 K, several hundred degrees higher than those of their parent R$_2$Fe$_{17}$ compounds (241~$477$ K). This opened up an alternative way to achieve the optimum magnetic properties and as a result, the previously ignored R$_2$Fe$_{17}$ series has attracted world-wide attention again. Since the Sm$_2$Fe$_{17}$N$_8$ nitride has even better intrinsic magnetic properties (Curie Temperature $T_c = 749$ K, $4\pi M_s = 15$ kG and $H_a = 14$ T)$^3$ $^4$ than the Nd$_2$Fe$_{14}$B compound ($T_c = 585$ K$^5$ $^4$, $4\pi M_s = 16$ kG$^6$ and $H_a = 7.3$ T$^7$), remarkable efforts have been made to realise Sm$_2$Fe$_{17}$N$_8$ magnets.

However, one of the main barriers making practical Sm$_2$Fe$_{17}$N$_8$ magnets is its poor thermal stability. It has been noticed that a partial substitution of Si for Fe in 2:17 stoichiometric or non-stoichiometric compounds improves the thermal stability of the Sm$_2$Fe$_{17}$N$_8$ phase$^8$. The decomposition temperature increases from $\sim 535^{\circ}$C for Sm$_2$Fe$_{17}$N$_8$ to $\sim 610^{\circ}$C for Sm$_2$Fe$_{15}$Si$_2$N$_8$.

In the present study, the phase formation in the Fe-rich corner of the R-Fe-Si system was investigated. We initiated the study by investigating a ternary phase with a composition RFe$_{4.45}$Si$_{1.52}$, whose formation had been reported by Bodak et al. in 1978$^9$. 43
They claimed that this phase adopts a tetragonal structure of the ZrFe$_4$Si$_2$-type (P4$_2$/mm). Our initial results (SEM, EDAX, XRD) on an as-cast DyFe$_{4.48}$Si$_{1.52}$ sample, however, showed that this composition forms multi-phase material (Figure 3-1). These phases were identified as (i) a tetragonal DyFeSi phase, (ii) a new phase with Dy : Fe : Si = 16 : 59 : 25 (at.%), corresponding to a Dy(Fe, Si)$_5$ composition and (iii) a dominant new phase with the R : Fe : Si ratio in the range of 12-15 : 74-78 : 10-12 (at.%), which we denote as R$_3$Fe$_{18.5}$Si$_{3.5}$—a 3-22 composition. Subsequent to this discovery, a systematic study was carried out in order to characterise this new 3:22 phase. Seven samples with the starting composition R$_3$Fe$_{18.5}$Si$_{3.5}$ (R = Gd, Tb, Dy, Ho, Er, Tm and Lu) were prepared. To compensate for the losses of the R content during the sample preparation, 10wt.% excess R was added in all the samples based on previous experience. Since the new 3:22 phase was identified in the as-cast sample, all the following studies are based on the as-cast samples.

![Figure 3-1: SEM microstructure photograph of the as-cast RFe$_{4.48}$Si$_{1.52}$ sample. It is multi-phase with (1) a DyFeSi phase (white phase), (2) a 1:5 phase (black phase) and (3) a new 3:22 phase (gray matrix phase).](image)
3.2. RESULTS AND DISCUSSION

3.2.1. SEM/EDAX AND X-RAY DIFFRACTION RESULTS

The novel 3:22 phase formed in all the 7 as-cast R$_3$Fe$_{18.3}$Si$_{3.5}$ samples. Figure 3-2(a-g) show their microstructure photographs. The samples with R = Gd, Tb, Dy, Ho and Er have a dominant matrix 3:22 phase with a small amount of RFeSi impurity in the form of dispersed fine grains whereas the samples with R = Tm and Lu formed approximately single 3:22 phase. EDAX analyses on the samples with R = Gd, Dy and Lu reveal a decreasing Si content in the 3:22 phase with increasing R atomic number. The Gd : Fe : Si ratio is 9.4 : 76.3 : 14.3 (±0.7at.%) for R = Gd and 12.2 : 77.2 : 10.6 (±0.7at.%) for R = Dy. For R = Lu, the R : Fe : Si ratio is 10.3 : 86.2 : 3.5 (±0.7at.%) which is quite different from those with R = Gd and Dy and is very similar to the Nd : Fe : Ti ratio observed for the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase$^{10}$

![Figure 3-2(1): SEM photograph of as-cast Gd$_3$Fe$_{18.5}$Si$_{3.5}$. It has a dominant matrix phase with some GdFeSi impurity (white phase).](image-url)
Figure 3-2(2): SEM microstructure photographs of as-cast (b) Tb$_3$Fe$_{18.5}$Si$_{3.5}$ and (c) Dy$_3$Fe$_{18.5}$Si$_{3.5}$. They have a dominant matrix phase with a small amount of RFeSi impurity.
Figure 3-2(3) SEM microstructure photographs of as-cast (d) $\text{Ho}_3\text{Fe}_{18.5}\text{Si}_{3.5}$ and (e) $\text{Er}_3\text{Fe}_{18.5}\text{Si}_{3.5}$. Both have a dominant matrix phase with a small amount of $\text{RFeSi}$ impurity.
Figure 2(4): SEM microstructure photographs of as-cast (f) $\text{Tm}_3\text{Fe}_{18.5}\text{Si}_{3.5}$ and (g) $\text{Lu}_3\text{Fe}_{18.5}\text{Si}_{3.5}$. They are roughly single phase.
Figure 3-3: Powder x-ray diffraction patterns of the $R_3Fe_{18.5}Si_{3.5}$ samples (Co $\text{K}\alpha$ radiation). Two types of patterns are apparent depending on $R$. The patterns with $R = \text{Gd}$ and $\text{Tb}$ is closely related to that of the rhombohedral $\text{Th}_2\text{Zn}_{17}$ (2:17-R) type structure and with $R = \text{Dy}$, $\text{Ho}$, $\text{Er}$, $\text{Tm}$ and $\text{Lu}$ they are related to the hexagonal $\text{Th}_2\text{Ni}_{17}$ (2:17-H) type structure.
The powder XRD patterns of all the $R_3Fe_{18.5}Si_{3.5}$ samples (Figure 3-3) have the principal XRD reflections associated with the hexagonal $TbCu_7$-type structure which is derived from the hexagonal $CaCu_5$ structure by a random dumb-bell replacement\(^{11}\). In addition, different superlattice reflections occur in the patterns, depending on the $R$ atom. Two distinct patterns are evident: (i) with $R = Gd$ and $Tb$, the patterns are characteristic of the rhombohedral $Th_2Zn_{17}$-type structure; (ii) with $R = Dy$, $Ho$, $Er$, $Tm$ and $Lu$, the patterns are very similar to that of the hexagonal $Th_2Ni_{17}$-type structure in which a characteristic reflection around $\theta = 40.5^\circ$ occurs. The reflections around $\theta = 41^\circ$ and $\theta = 49^\circ$ in the patterns with $R = Gd$, $Tb$, $Dy$, $Ho$, $Er$ and $Tm$ are the characteristic $(102)$ and $(112)$ reflections of the tetragonal $PbFCl$-type structure, which come from the $RFeSi$ impurity phase in these samples. It should be noted that a $CaCu_5$ type phase (with identical reflections to the $TbCu_7$ phase) has been reported for $Gd_2Fe_{15}Si_2$ by Yan et al.\(^{*'}\) and for $RFe_7Si_x$ ($R = Gd$ and $Er$, $0 < x < 2.5$) by Yuan et al.\(^{12}\).

### 3.2.2. $^{57}\text{Fe MÖSSBAUER RESULTS}$

$^{57}\text{Fe}$ Mössbauer spectroscopy has been used to determine the hyperfine parameters of the $^{57}\text{Fe}$ nuclei in the 3-22 compounds. Figure 3-4 shows the $^{57}\text{Fe}$ Mössbauer spectra of the $R_3Fe_{18.5}Si_{3.5}$ samples at 295 K. The spectra were well fitted with a minimum of 4 magnetic sextets with variable line-widths. At 295 K, the average hyperfine field of the new 3-22 phase ranges from 19.8 T ($R = Ho$) to 22.2 T ($R = Gd$).

Table 3-1 lists the average hyperfine field ($\mu_0<H_{hf}>$), the highest hyperfine field ($\mu_0H_{hf}$) out of the four subspectra and the relative area ($\sigma$) of this special subspectral component of the samples, derived from the fitting. One of the interesting parameters listed is the relative area ($\sigma$) of the spectral component with the largest hyperfine field.

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\(^{*'}\) Yan et al.

\(^{12}\) Yuan et al.
Figure 3-4: $^{57}$Fe Mössbauer spectra of the $R_3Fe_{18.5}Si_{3.5}$ samples at 295K. The dots and solid lines are experimental data and fitted curves, respectively.
Table 3-1: The average $^{57}$Fe hyperfine fields, the largest hyperfine field from the dumbbell atoms (at 295K) and relative areas of such dumb-bell subspectra ($\sigma$)

<table>
<thead>
<tr>
<th>$R_3Fe_{18.5}Si_{3.5}$</th>
<th>$\mu_0&lt;H_{hf}&gt;$ (±0.3 T)</th>
<th>$\mu_0H_{hf}$ (±0.3 T)</th>
<th>$\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = Gd$</td>
<td>22.2</td>
<td>27.3</td>
<td>4(2)</td>
</tr>
<tr>
<td>$Tb$</td>
<td>21.3</td>
<td>26.2</td>
<td>5(2)</td>
</tr>
<tr>
<td>$Dy$</td>
<td>21.0</td>
<td>26.0</td>
<td>6(2)</td>
</tr>
<tr>
<td>$Ho$</td>
<td>19.8</td>
<td>24.9</td>
<td>4(2)</td>
</tr>
<tr>
<td>$Er$</td>
<td>20.9</td>
<td>25.8</td>
<td>5(2)</td>
</tr>
<tr>
<td>$Tm$</td>
<td>19.8</td>
<td>24.3</td>
<td>9(2)</td>
</tr>
<tr>
<td>$Lu$</td>
<td>20.2</td>
<td>24.2</td>
<td>16(2)</td>
</tr>
</tbody>
</table>

Assuming that the new 3:22 phases have structures which, like the 2:17 phase, are derived directly from the CaCu$_5$-type structure by replacing a fraction of the R (Ca) atoms with T-T pairs (dumb-bells), we assign the subspectrum with the largest subspectral hyperfine field value to the Fe atoms at these dumb-bell sites, since these dumb-bell atoms have the shortest Fe-Fe distances and therefore the largest hyperfine interactions. Consequently, the $\sigma$ values can be used to represent the dumb-bell proportions in the 3:22 structures. In particular, $\sigma$ in $Lu_3Fe_{18.5}Si_{3.5}$ is 16(2)% which is larger than the ‘ideal’ 2:17 value of $\sigma_{2:17} = 11.8\%$. Givord et al.$^{13}$ have demonstrated that an excess of non-R metal is needed to stabilise the hexagonal 2:17 structure with heavy R elements, giving the general formula $R_{2-x}(2Fe)_xFe_{17}$ with $x = \frac{1}{6}$ for $R = Lu$ and $x = \frac{1}{5}$ for $R = Y$. These non-stoichiometric 2:17 structures contain a larger proportion of
dumb-bell sites than in the ‘ideal’ structure. In contrast to Lu$_2$Fe$_{18.5}$Si$_{3.5}$, the R$_3$Fe$_{18.5}$Si$_{3.5}$ compounds with $R = \text{Gd-Er}$ have a much smaller $\sigma$ ($\sim 5\%$) than the $\sigma_{2:17}$ value ($11.8\%$). In Tm$_3$Fe$_{18.5}$Si$_{3.5}$, $\sigma$ equals $9(2)\%$ which is close to $\sigma_{2:17}$.

3.2.3. DISCUSSION

There are two possible explanations for the observation of the smaller dumb-bell areas in the 3:22 compounds with $R = \text{Gd-Er}$; either (i) these compounds form a new structure with a different stoichiometry and therefore a lower dumb-bell proportion than that in the 2-17 structure or (ii) they have ‘ideal’ 2-17 structures with Si preferentially occupying the dumb-bell sites.

To distinguish between these two possibilities, we now consider the structural derivation of the 2:17 phases. As we know, a series of structures can be derived from the CaCu$_5$-type structure by replacing different fractions of the large $R$ atoms in 1:5 structure by pairs of smaller $T$-$T$ (dumb-bells) along the $c$-axis (the dumb-bell replacement). Examples are the 2:17 and 1:12 structures. This replacement process can be represented by a general formula

$$R_{1-x}T_5 + (T-T)_x \Rightarrow RT$$ \hspace{1cm} Equation 3-1

with $x = \frac{1}{5}$ corresponding to the 2:17 phase ($y = \frac{17}{2}$) and $x = \frac{1}{2}$ to the 1:12 phase ($y = 12$). Besides the 2:17 and 1:12 phases, Equation 3-1 also suggests the possible existence of other structures which can be derived from the 1:5 structure by different fractions of dumb-bell replacement, for example, $x = \frac{1}{4}$ corresponding to a 3:22 phase $x = \frac{2}{5}$ to a 3:29 phase and $x = \frac{5}{12}$ to a 1:10 phase, etc.. In the present case, the 3:22
stoichiometry exactly complies with a replacement of $\frac{1}{4}$ R atoms by dumb-bells.

Therefore, we propose that the 3:22 phase is an intermediate phase between the 1:5 and 2:17 phases and has a new structure which, like the 2:17 structures, can be derived from the 1:5 structure.

As mentioned above, replacing $\frac{1}{3}$ of the R sites in the 1:5 structure with dumb-bells results in the $R_2T_{17}$ structures. Two different replacement sequences, however, lead to two different 2:17 (the rhombohedral $Th_2Zn_{17}$-type and hexagonal $Th_2Ni_{17}$-type) structures, depending on the R atom. In the new 3:22 phases, two different structures are also evident depending on the R atom which, we believe, are due to the different dumb-bell replacement sequences as well. In the present work, we will concentrate on the structure formed in the Dy, Ho, Er, Tm and Lu systems.

To deduce the new 3:22 structure, we need to know the order of the dumb-bell replacement in the structure. Though the Equation 3-1 (or dumb-bell replacement) can easily describe the structural relationships between the various phases, it does not help in predicting the order of the dumb-bell replacement.

In the study of the structural relationships between the intermetallic compounds formed between transition metals, Kasper$^{15}$ found that by viewing the structures in terms of coordination polyhedra of nearest neighbours in conjunction with the scheme of ordering that was found to apply, the structural relationship of various transition metal phases, whose structural similarities had been noted previously although a general relationship among such phases had not been recognised, is readily explained.
The survey of the different structure types for phases containing only transition metals has shown that all of the structures studied by Kasper and Frank\textsuperscript{15 \hspace{1mm} 16} can be described in terms of the four coordination polyhedra with high coordination numbers, namely 12, 14, 15 and 16-fold coordination polyhedra. The topological and geometrical study shows that these coordination polyhedra have a common characteristic, that is, the ‘triangulated’ atomic arrangement on the surface of the coordination polyhedra. It follows, then, that the existence of only these four coordination polyhedra in the complex transition metal compounds is due to the fact that they are efficient space-filling arrangements.

Considering a special property of space-filling structures, namely the preponderance of tetrahedral interstices, perhaps the most satisfactory criterion for close-packing is the ratio of tetrahedral interstices relative to interstices of larger size. The tetrahedral interstice resulting from four spheres in contact is clearly the smallest achievable space-filling arrangement in 3 dimensions\textsuperscript{17}. Thus, the icosahedral group is denser than the hexagonal or cubic (FCC) close-packed configuration since the former contains only tetrahedral interstices while the latter contains octahedral interstices as well. As a corollary to this discussion, it follows that the coordination polyhedron of neighbouring atoms containing only triangular faces on the surface of the coordination polyhedra is preferred since this results in the tetrahedral groupings of triads of the atoms on the coordination shell together with the central atom. The 12, 14, 15, and 16-fold coordination polyhedra are those, though not the only ones, that fulfil this criterion and so are generally observed in the most transition metal compounds.

Using the coordination polyhedra of nearest neighbours in the structures of the 1:5, 2:17 and 1:12 phases, Frank and Kasper\textsuperscript{16} describe the transformation between
these structures as particularly large atoms (R) with 20-coordination shells being incorporated in place of pairs of 14-coordinated atoms (T), by local reversion to the normal CaZn$_5$ structure.

In the present study, our emphasis is on the phase formation between the rare earths (R) and transition metals (T), especially the possible new phases that have a structural relationship with the 1:5 structure according to Equation 3-1. Considering that the maximum fraction of R atoms that can be replaced by the dumb-bells in the 1:5 structure is $\frac{1}{2}$ (beyond this value, there will be dumb-bell atoms located at adjacent positions along the c-axis of the CaCu$_5$ structure, resulting in too short interatomic distances), we studied the 1:5 and 1:12 structures in terms of coordination polyhedra in these structures. We find that only three types of coordination polyhedra exist in these structures, the 20-fold coordination polyhedra for the large R atoms and 12, 14-fold coordination polyhedra for the small T atoms. The 12, 14-fold coordination polyhedra, as mentioned above, are close-packed arrangements. After studying the geometrical properties of the 20-fold coordination polyhedron, we noticed that it is also a close-packed configuration. In the 20-fold polyhedron, all the interstices are tetrahedral except two octahedral groupings, which is also a close-packed arrangement and is observed in the hexagonal or cubic close-packed configurations.

Following this result and by paying attention to the coordination shells of the particular large R atoms in the R-T compounds, it was then noticed that in fact all the R atoms in the compounds studied have 20 coordination neighbours. Examples are the famous Nd$_2$Fe$_{14}$B, CaCu$_5$, ThMn$_{12}$ and Th$_2$Ni$_{17}$ structures (Figure 3-5, 3-6 and 3-8). This observation is conceivable if one considers the large size difference between the
component atoms in these compounds. Figure 3-7 is parts of the period table showing the atomic radii of the interested elements. It shows that the atomic sizes of the R atoms are much larger than those of the T atoms, thus the atomic radium ratios in the R-T compounds are much larger than those in the compounds with only transition metals mentioned above. Consequently, a higher coordination number for the very large R atoms should be expected. In accordance with the concept due to Frank and Kasper\textsuperscript{16} and considering a coordination number larger than 16, 20 is the one preferred since it has the space-filling properties as the 12, 14, 15 and 16-fold coordination polyhedra mentioned above.

\textit{Figure 3-5: The Nd\textsubscript{2}Fe\textsubscript{14}B structure showing the CPRs.}

Based on the discussion above, it seems justifiable, then, to regard the R-T compounds studied as being determined by the geometrical requirement for sphere packing.
Figure 3-6: The 1:5 and 1:12 structures shown as stackings of the CPRs. They can be seen as simple stackings of CPRs along one direction. The only difference between them is the CPR constructions. Two types of CPRs exist in these structures—Type-I in the 1:5 structure and Type-II in the 1:12 structure. The Type-II is derived from the Type-I by replacing two R coordination atoms with two T atoms (the dumb-bell atoms).

The discussion above directed our attention to how the 20 coordination polyhedra around particular R atoms are incorporated in every single R-T structure. We noticed that actually all the known structures given by Equation 3-1, such as the 1:5, 2:17-H and 1:12 structures, can be seen as simple stackings of the 20-vertex coordination polyhedra formed by the 20 coordination neighbours around the large R atoms along one direction, with the difference between them only being the CPR constructions in the structures.
We will refer to this 20-vertex coordination polyhedron around R atoms as CPR hereafter.

<table>
<thead>
<tr>
<th>Transition metals</th>
<th>Transition metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 Ti 1.32, 2.00</td>
<td>23 V 1.22, 1.92</td>
</tr>
<tr>
<td>24 Cr 1.181, 1.85</td>
<td>25 Mn 1.17, 1.79</td>
</tr>
<tr>
<td>26 Fe 1.17, 1.72</td>
<td>27 Co 1.16, 1.67</td>
</tr>
<tr>
<td>28 Ni 1.15, 1.62</td>
<td></td>
</tr>
<tr>
<td>40 Zr 1.45, 2.16</td>
<td>41 Nb 1.34, 2.08</td>
</tr>
<tr>
<td>42 Mo 1.30, 2.01</td>
<td></td>
</tr>
<tr>
<td>72 Hf 1.44, 2.16</td>
<td>73 Ta 1.34, 2.09</td>
</tr>
<tr>
<td>74 W 1.30, 2.02</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-7: Parts of the period table showing the atomic sizes of the elements which are interested in the present work.

Figure 3-6 shows the CaCu5-type and ThMn12-type structures as CPR stackings. The main difference between these two structures is the constructions of the CPRs. In the CaCu5-type structure, the R atoms have eighteen T and two R coordination neighbours, which is an elongated 20-vertex polyhedron along the c-axis due to two large R(Ca) coordination atoms (referred to as Type-I CPR). In the ThMn12-type structure, all the 20 coordination neighbours of the R atoms are the small transition metal atoms. The CPR in this structure (referred to as Type-II) can be seen as a transformation of the Type-I by simply replacing two R co-ordinate atoms with two T atoms (dumb-bell atoms) followed by a minor atomic rearrangement.
The relationships between the CaCu5, Th2Ni17 and ThMn12 types of structures are shown in Figure 3-8. Their structural relationships are obvious from the CPR’s point of view. The three structures are similar CPR stackings along one direction. The main difference between them is the CPR types in each individual structure. The CaCu5-type and ThMn12-type structures are formed with exclusively Type-I and Type-II CPRs, respectively. The 2:17 structure, as an intermediate structure between 1:5 and 1:12, is formed with both Type-I and Type-II CPRs in the ratio of 1:2.

Figure 3-8: Atomic projections of the (a) CaCu5 structure along [110], (b) Th2Ni17 structure along [110] and (c) ThMn12 structure along [100]. All the structures can be seen as simple stackings of two different type CPRs along one direction.

As mentioned previously, besides the 2:17 and 1:12 structures, there is a possibility of other structures which can be derived from the 1:5 structure by replacing different fractions of the large R atoms with pairs of small transition metal atoms. This
is represented by the Equation 3-1 with \( x = \frac{1}{4} \) corresponding to the new 3:22 phase. If we consider the coordination shells of the particularly large R atoms in these structures, it appears that a coordination number of 20 for the R atoms is obligatory by the geometrical (or space-filling) requirements in the R-T structures studied. By implementing the 20-vertex CPRs into the structural derivation by Equation 3-1, in conjunction with the observation of the relationships between the 1:5, 2:17 and 1:12 structures, it seems justifiable that some of the structures given by Equation 3-1 are simple stackings of different proportions of the Type-I and Type-II CPR. In Table 3-2 we list some possible structures.

Table 3-2: Some of the possible phases whose structures can be derived from the 1:5 structure by the dumb-bell replacement. From the CPR point of view, these structures are constructed by simply stacking different proportions of the Type-I and Type-II CPRs.

<table>
<thead>
<tr>
<th>Possible Phase</th>
<th>Dumb-bell fraction in the structure (x)</th>
<th>The proportion of Type-I CPRs</th>
<th>The proportion of Type-II CPRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3:22</td>
<td>1/4</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>2:17-H</td>
<td>1/3</td>
<td>1/3</td>
<td>2/3</td>
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<td>5:46</td>
<td>3/8</td>
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</tr>
<tr>
<td>1:10</td>
<td>5/12</td>
<td>1/6</td>
<td>5/6</td>
</tr>
<tr>
<td>1:12</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
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</tbody>
</table>

In fact, a phase with a 3:22 composition was reported quite some time ago. It has a tetragonal Pu\(_2\)Zn\(_{22}\)-type structure with the space group I4\(_1\)/amd\(^{18}\)\(^{19}\) which is shown in Figure 3-9. Although no direct structural relationship between this 3:22 phase and 1:5
phase is apparent from the dumb-bell replacement point of view, it is clearly a member of the structural series listed in Table 3-2 in terms of the CPRs in these structures. The relationships between the Pu$_3$Zn$_{22}$ structure and the CaCu$_5$, Th$_2$Ni$_{17}$ and ThMn$_{12}$ structures are schematically illustrated in Figure 3-10. For easier demonstration of the relationships among these structures, no details of each structure but only the frameworks of the CPR stackings in these structures are shown in the figure. The Pu$_3$Zn$_{22}$-type structure has the same CPR stacking characteristics as the other three structures and is a simple stacking of both types of CPR.

The Pu$_3$Zn$_{22}$-type phase, like 2:17, has an intermediate structure between the 1:5 and 1:12 structures. Stacking $\frac{1}{3}$ layers of the Type-I CPRs and $\frac{2}{3}$ layers of the Type-II...
CPRs leads to the Th$_2$Ni$_{17}$-type structure and stacking $\frac{1}{2}$ layers of the Type-I CPRs and $\frac{1}{2}$ layers of the Type-II CPRs forms the Pu$_3$Zn$_{22}$-type structure. However, there is an essential difference in the forms of the CPR stacking between the Pu$_3$Zn$_{22}$ and Th$_2$Ni$_{17}$-type structures. The atomic arrangements along the [001]$_{1:5}$ and [110]$_{1:5}$ directions in the Type-I CPR are very different because of the two large R coordination atoms. The atomic arrangements along these two directions in the Type-II CPR, however, are approximately identical. Therefore, there are two alternative ways to align the Type-I

![Diagram showing the relationships between the CaCu$_5$, Th$_2$Ni$_{17}$, ThMn$_{12}$, and Pu$_3$Zn$_{22}$ structures in the forms of the CPR stacking.](image)

Figure 3-10: Schematic illustration of the relationships between the CaCu$_5$, Th$_2$Ni$_{17}$, ThMn$_{12}$, and Pu$_3$Zn$_{22}$ structures in the forms of the CPR stacking. All the structures have similar CPR stacking characteristics.
CPRs over the Type-II CPR in a real structure without introducing a large difference in the atomic arrangement in the stacking area. In the Th$_2$Ni$_{17}$ structure, all the Type-I CPRs align along the same direction. In the Pu$_3$Zn$_{22}$ structure, however, the alignment of the Type-I CPRs changes by 90° every other Type-I CPR layer. Because of this CPR stacking sequence, the relationship between the Pu$_3$Zn$_{22}$ and CaCu$_5$ structures is not as apparent as the relationships between Th$_2$Ni$_{17}$ and CaCu$_5$ or ThMn$_{12}$ and CaCu$_5$ from the dumb-bell replacement point of view.

![Diagram](image)

**Figure 3-11:** Illustration of the atomic arrangement in the Pu$_3$Zn$_{22}$ structure and its relationships with the CaCu$_5$, structures. (a) The atomic projection of the CaCu$_5$ structure along its c-axis. (b) The atomic projection of the Pu$_3$Zn$_{22}$ structure along its a-axis. (c) A demonstration of the atomic rearrangement occurring on the sliding planes.
The relationship between the CaCu₅-type and Pu₃Zn₂₂-type structures is illustrated in Figure 3-11. The derivation of the Pu₃Zn₂₂ structure from the CaCu₅ structure involves two steps, (1) replacing \( \frac{1}{4} \) of large Ca atoms with two small Cu atoms (dumbbells) in the CaCu₅ structure along its c axis (Figure 3-11a) and (2) shifting every \( 2^*a_{1.5} \) block atoms a distance \( \frac{1}{2}a_{1.5} \) along the \([10\bar{1}]_{1.5}\) direction. After this shift, the atoms on the sliding plane—(110)₁₁₅ have to be reorganised to accommodate both sides. It is worth noting that after this atomic rearrangement, the atomic arrangement on these (110)₁₁₅ planes becomes exactly the same as that on the (1\( \bar{1} \)0)₁₁₅ plane.

Figure 3-12: (a) Proposed structure for the new \( R_3(Fe_{1.5}Si_{22}) \) phase (\( R = Dy, Ho, Er, Tm \) and Lu) showing the dumb-bell replacement sequence. (b) Stacking of CPR layers in the proposed 3:22 structure
The structure of the new $R_3(Fe_{1-x}Si_x)_{22}$ phase is different from the $Pu_3Zn_{22}$ structure. Based on the discussion above and applying the CPR concept, we propose a possible crystal structure for the $R_3(Fe_{1-x}Si_x)_{22}$ phase with $R = Dy, Ho, Er, Tm$ and $Lu$. This structure is a stacking of two layers of the Type-I CPRs, two layers of the Type-II CPRs and then one layer of the Type-I CPR and one layer of the Type-II CPRs which is illustrated in Figure 3-12(b). This atomic arrangement forms an orthorhombic structure with the possible space group Pmm2 (No. 25) The relationship of the lattice parameters of the 1:5 and new 3:22 structure is:

$$a_{3:22} = \sqrt{3}a_{1:5}$$
$$b_{3:22} = 2c_{1:5}$$
$$c_{3:22} = 3a_{1:5}$$

Figure 3-13: Powder x-ray diffraction pattern of the $Dy_3Fe_{18.5}Si_{3.5}$ sample (Co Ka radiation) and the calculated diffraction pattern based on the proposed orthorhombic 3:22 structure. Since there is some DyFeSi impurity in the sample, its calculated diffraction pattern (with PbFCl-type structure) is also shown in the figure.
Based on this proposed structure and the indexation of the experimental powder x-ray diffraction data of the Dy$_3$Fe$_{18.5}$Si$_{3.5}$ sample, we calculated the theoretical powder x-ray diffraction pattern of the new 3:22 phase which is shown in Figure 3-13 as solid sticks. From the figure it can be seen that the calculated diffraction pattern basically matches the experimental results. Since we did not refine the atomic positions in the proposed structure, however, the intensities of the calculated reflections do not match those of the experimental pattern very well. The lattice parameters of the R$_3$(Fe, Si)$_{22}$ phases (R = Dy, Ho, Er, Tm and Lu) calculated from the indexation of the x-ray results based on the proposed structure are listed in Table 3-3. Because the structures for the R$_3$Fe$_{18.5}$Si$_{3.5}$ compounds with R = Gd and Tb are still unknown, we indexed these two compounds in terms of the TbCu$_7$-based XRD.

Table 3-3: The lattice parameters of the new R$_3$Fe$_{18.5}$Si$_{3.5}$ compounds from a TbCu$_7$-based XRD indexation for R = Gd and Tb and a proposed orthorhombic structure based XRD indexation for R = Dy, Ho, Er and Lu. Their Curie temperatures (from TGA) are also shown.

<table>
<thead>
<tr>
<th>R$<em>3$Fe$</em>{18.5}$Si$_{3.5}$</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>T$_c$ (±10 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Gd</td>
<td>4.900(4)</td>
<td></td>
<td>4.136(8)</td>
<td>549</td>
</tr>
<tr>
<td>Tb</td>
<td>4.895(3)</td>
<td></td>
<td>4.123(4)</td>
<td>521</td>
</tr>
<tr>
<td>Dy</td>
<td>8.426(4)</td>
<td>8.280(6)</td>
<td>14.594(9)</td>
<td>493</td>
</tr>
<tr>
<td>Ho</td>
<td>8.426(4)</td>
<td>8.274(8)</td>
<td>14.594(9)</td>
<td>486</td>
</tr>
<tr>
<td>Er</td>
<td>8.409(1)</td>
<td>8.266(2)</td>
<td>14.564(8)</td>
<td>497</td>
</tr>
<tr>
<td>Tm</td>
<td>8.357(1)</td>
<td>8.280(6)</td>
<td>14.475(1)</td>
<td>467</td>
</tr>
<tr>
<td>Lu</td>
<td>8.357(1)</td>
<td>8.280(9)</td>
<td>14.474(9)</td>
<td>481</td>
</tr>
</tbody>
</table>
The magnetic ordering temperatures $T_c$ of the $R_3Fe_{18.5}Si_{3.5}$ compounds, determined by TGA, are also listed in Table 3-3. The highest value of $T_c$ is for $R = \text{Gd}$ (549K) and the lowest for Tm (467K). The $T_c$ values of the $R_3Fe_{18.5}Si_{3.5}$ compounds are much higher than those of the $R_2Fe_{17}$ series (476K for Gd$_2$Fe$_{17}$ and 275K for Tm$_2$Fe$_{17}$). The substitution of Fe by Si in R-T intermetallics always enhances the magnetic ordering temperature at low concentrations, as widely reported in the literature\textsuperscript{11, 20}. This enhancement of $T_c$ was previously ascribed by Strnat\textsuperscript{21} to a preferential occupancy by the substituting element (Si) into the dumb-bell sites, thereby removing the negative exchange associated with the dumb-bell sites. However, previous Mössbauer studies of Tm$_2$Fe$_{15}$Si$_2$ by Gubbens et al.\textsuperscript{20} gave no indication of such preferential occupancy. An alternative explanation, proposed by Yan et al.\textsuperscript{11} on the basis of an X-ray refinement, is that the partial substitution of Fe by Si modifies the atomic position parameters in these 2:17 structures, which in turn enlarges the interatomic distances in the dumb-bells.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-14.png}
\caption{The lattice parameters and the magnetic ordering temperature ($T_c$) of the new 3:22 phases}
\end{figure}
Based on the proposed structure for the new $R_3Fe_{18.5}Si_{3.5}$ compounds, the EDAX results and the relative area of the dumb-bell component ($\sigma$) obtained from the Mössbauer results, we can investigate the preferential site occupancy shown by Si in these structures. For $Gd_3(Fe_{1-x}Si_x)_{22}$ and $Dy_3(Fe_{1-x}Si_x)_{22}$, the calculated fractions of dumb-bell sites occupied by Si are 62(20)% and 42(20)%. The values are about 3-4 times larger than the value of 16% expected for a random occupation using our stoichiometry $R_3Fe_{18.5}Si_{3.5}$.

Thus, there is a strong preferential occupancy of the dumb-bell sites by Si in the $3:22$ structures. This result support the explanation given by Strnat$^{21}$ for the enhancement of $T_c$ by Si substitution as being due to a reduction of the negative exchange effects associated with the rather small interatomic distances at the dumb-bell sites.

### 3.3. CONCLUSIONS

Using a combination of SEM/EDAX, powder x-ray diffraction, $^{57}$Fe Mössbauer spectroscopy and TGA, we have investigated the formation of a novel ternary intermetallic compound in the Fe-rich end of the R-Fe-Si systems ($R = Gd, Tb, Dy, Er, Ho, Tm$ and $Lu$), namely the $3:22$ phase. It is an intermediate phase between the $1:5$ and $2:17$ phases and, like the $2:17$ phase, it crystallises in two different structures depending on the $R$ atom. With $R = Gd$ and $Tb$, it has a structure closely related to the rhombohedral $Th_2Zn_{17}$-type structure and with $R = Dy, Er, Ho, Tm$ and $Lu$, it crystallises in a structure closely related to the hexagonal $Th_2Ni_{17}$-type structure. In terms of the replacement of $R$ atoms by T-T dumb-bells in $CaCu_5$, the new $3:22$
structure corresponds to a $\frac{1}{4}$ replacement of the large R atoms in the CaCu$_5$ structure by pairs of the small transition metal atoms (dumb-bells) along the c axis.

In the study of the structure of the 3:22 phase, a fruitful approach is to consider the coordination shells around the particular large R atoms in the R-T phases, which correspond to a 20-fold coordination polyhedron. The exclusive observation of the 20-fold coordination polyhedra around the R atoms (CPR) in the R-T compounds can be explained by its geometrical and topological characteristic, having the space-filling property. By incorporating the CPR concept into the derivation of the new 3:22 structure, a new structural derivation method—a CPR stacking method—was developed and used. From the CPR point of view, all the CaCu$_5$, Th$_2$Ni$_{17}$, ThMn$_{12}$ and new 3:22 structures can be seen as simple stackings of the 20-vertex CPRs along one direction. Based on this CPR model, a likely structure for the new 3:22 phase was proposed, which is orthorhombic with a possible space group Pmm2. Single crystal diffraction would be required to resolve this point.

Using Mössbauer spectroscopy, a very strong preferential occupation of the dumb-bell sites by Si in these has been observed in the $R_3{(Fe_{1-x}Si_x)_{22}}$ compounds for $R = $ Gd and Dy. This explains the Curie temperature in this series, with regard to the effect of the Si
REFERENCES


17 A. H. Boerdick, Philips Research Reports, 7, p303 (1953).


Chapter Four:

A NEW Nd₃(Fe₁₋ₓTiₓ)₉ PHASE AND ITS STRUCTURE

4.1. INTRODUCTION

As mentioned in Chapters 1 and 3, the absorption of nitrogen or carbon by the iron-rich rare-earth intermetallic compounds such as Sm₂Fe₁₇ and NdFe₁₁Ti has a dramatic effect on the intrinsic magnetic properties of such compounds. The high Curie temperatures coupled with the strong uniaxial anisotropy make these nitrides (Sm₂Fe₁₇N₈ and NdFe₁₁TiN₉) very promising for technological application as high performance permanent magnets.

Sm₂Fe₁₇N₈ crystallizes in the rhombohedral Th₂Zn₁₇-type (2:17-R) structure and NdFe₁₁TiN₉ crystallizes in the tetragonal ThMn₁₂-type (1:12-T) structure. Both are derived from the hexagonal CaCu₅-type structure by replacing a fraction of the large R(Ca) atoms with pairs of smaller transition metal atoms (dumb-bells) and this process is given by Equation 3-1 with \( x = \frac{1}{3} \) corresponding to the Th₂Zn₁₇-type structure and \( x = \frac{1}{2} \) corresponding to the ThMn₁₂-type structure.

Besides these two structure, some other rare-earth (R)—transition metal (T) structures also provide examples of such structural derivation, such as the hexagonal TbCu₇-type structure (1:7 phase, space group P6/mmm) and the orthorhombic ScFe₆Ga₆-type structure (1:12-O phase, space group Immm)\(^{1,3}\). The 1:7-type structure is
basically a disordered version of the 2:17-H and 2:17-R structures and the 1:12-O structure corresponds to $x = \frac{1}{2}$ in Equation 3-1.

In addition to the above phases, Equation 3-1 also indicates the possibility of other structures derived from the CaCu$_5$ structure with different proportions of large R(Ca) atoms being replaced by small dumb-bell atoms, such as a 3:22 phase ($x = \frac{1}{4}$), a 3:29 phase ($x = \frac{2}{5}$) and a 9:94 phase ($x = \frac{7}{16}$). In Chapter 3, we reported the formation of the 3:22 phase in the R-Fe-Si systems (R = Gd, Tb, Dy, Ho, Er, Tm and Lu), which is an intermediate phase between the 1:5 and 2:17 phases.

When searching for new Fe-based compounds with potentials for use as starting materials for practical permanent magnets, a high Fe content in the compounds is desirable, since this can result in higher magnetization and Curie temperature. However, it should be noted that the maximum $x$ value in Equation 3-1 is $\frac{1}{2}$. Beyond this value, there will be dumb-bell atoms located at adjacent positions along the $c$-axis of the CaCu$_5$ structure, resulting in too short interatomic distances. Therefore, in searching for other possible phases foreshadowed by Equation 3, we started by investigating the possible existence of intermediate phases between the 2:17 and the 1:12 phases. In fact, a phase with a 2:19 composition had been reported by S. J. Collocott, et. al in the Nd-Fe-Ti system$^{10}$.

In the present study we also selected the Nd-Fe-Ti system, based on two considerations: (1) in order to optimize the intrinsic magnetic properties of permanent magnet phases, the best R-T combination is Nd-Fe, since this maximizes the net
magnetization and can produce the necessary uniaxial anisotropy, (2) it is well-known that the 1:12 phase does not exist in any R-T binary systems and a small amount of a third element such as Ti, V, Cr, Mo, Al, Si, W is essential to stabilize the 1:12-T structure in the rare earth-transition metal systems.

In this study, three Nd-Fe-Ti samples with starting compositions Nd$_7$Fe$_{40.7}$Ti$_{1.2}$ ($7$-42), Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ (3-22) and Nd$_5$Fe$_{42.4}$Ti$_{3.6}$ (5-46), which correspond to \( x = \frac{1}{8}, \frac{2}{8}\) and \( \frac{3}{8} \) in Equation 3-1, respectively, were prepared by arc-melting the pure elements in an Ar atmosphere. Based on our previous experience, 7 wt.% excess Nd was added to compensate for the Nd losses during the arc melting. Annealing was carried out in a quartz tube under an Ar atmosphere at 1100°C for 3 days. All samples were characterized with x-ray diffraction, SEM, EDAX and room temperature Mössbauer spectroscopy.

4.2. RESULTS AND DISCUSSION

Table 4-1(a): The compositions (EDAX) and crystal structures of the matrix phase formed in the as-cast and annealed Nd$_7$Fe$_{40.7}$Ti$_{1.2}$, Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ and Nd$_5$Fe$_{42.4}$Ti$_{3.6}$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of the matrix phase Nd : Fe : Ti (±0.6 at.%)</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>7$Fe$</em>{40.7}$Ti$_{1.2}$</td>
<td>annealed 10.3 : 87.2 : 2.5 as-cast 10.7 : 86.8 : 2.5</td>
<td>Th$<em>2$Zn$</em>{17}$</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{20.8}$Ti$_{1.2}$</td>
<td>annealed 8.8 : 85.4 : 5.8 as-cast 9.7 : 85.7 : 4.6</td>
<td>monoclinic TbCu$_5$-type</td>
</tr>
<tr>
<td>Nd$<em>5$Fe$</em>{42.4}$Ti$_{3.6}$</td>
<td>annealed 7.4 : 85.4 : 7.2 as-cast 7.4 : 85.5 : 7.1</td>
<td>ThMn$_{12}$</td>
</tr>
</tbody>
</table>

75
The EDAX results show that the Nd : (Fe + Ti) ratios of the principal phases in all the three samples are much lower than the starting compositions, see Table 4-1(a), indicating that extra Nd was burnt out during the arc-melting process. The compositions of the matrix phases in the Nd$_7$Fe$_{40.7}$Ti$_{1.2}$ and Nd$_5$Fe$_{42.4}$Ti$_{3.6}$ samples correspond to 2:17 and 1:12, respectively. In the Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ sample, however, two novel phases with the Nd : (Fe + Ti) ratios 9:94 and 3:29 crystallized in the as-cast and annealed samples, respectively.

Table 4-1 (b): The lattice parameters of the matrix phase and average hyperfine fields (room temperature) of as-cast and annealed Nd$_7$Fe$_{40.7}$Ti$_{1.2}$, Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ and Nd$_5$Fe$_{42.4}$Ti$_{3.6}$. Since the structure of the new phase in the as-cast Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ sample is still unknown but shows a relationship with the 1:7 structure, we index it in terms of the 1:7 structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>$\mu_0 &lt;H_{hf}&gt;$ (±0.3T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>7$Fe$</em>{40.7}$Ti$_{1.2}$ annealed</td>
<td>8.59(4)</td>
<td>12.50(5)</td>
<td></td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{20.8}$Ti$_{1.2}$ annealed</td>
<td>10.64(1)</td>
<td>8.59(1)</td>
<td>9.74(8)</td>
<td>96.92(8)</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>as-cast</td>
<td>4.94(2)</td>
<td>4.18(9)</td>
<td></td>
<td>21.2</td>
</tr>
<tr>
<td>Nd$<em>5$Fe$</em>{42.4}$Ti$_{3.6}$ annealed</td>
<td>8.55(9)</td>
<td>4.77(8)</td>
<td></td>
<td></td>
<td>22.9</td>
</tr>
</tbody>
</table>

4.2.1. THE Nd$_7$Fe$_{40.7}$Ti$_{1.2}$ SAMPLE

The as-cast Nd$_3$Fe$_{40.7}$Ti$_{1.2}$ sample is multi-phase, comprising a dominant matrix 2:17 phase and a small amount of α-Fe(Ti) and a Nd-rich phase (Nd : Fe : Ti = 33.9~70.9 : 28.1~64.4 : 0.8~1.6) (Figure 4-1 (a)). The composition of the matrix 2:17 phase is Nd : Fe : Ti = 10.7 : 86.8 : 2.5 (±0.6 at.%).
Figure 4-1: SEM photographs of (a) as-cast and (b) annealed Nd$_7$Fe$_{40.7}$Ti$_{1.2}$. The as-cast sample is multi-phase, comprising a dominant matrix 2:17 phase, a small amount of $\alpha$-Fe(Ti) (the dark phase inside the matrix grains) and a Nd-rich intergranular impurity phase. After annealing, most of the impurities disappeared and the grains of matrix 2:17 phase grew much bigger.
Figure 4-2: Powder X-ray diffraction patterns of (a) annealed Nd$_{7}$Fe$_{40.7}$Ti$_{1.2}$, (b) as-cast and (c) annealed Nd$_{3}$Fe$_{20.8}$Ti$_{1.2}$ and (d) Nd$_{5}$Fe$_{42.4}$Ti$_{3.6}$ (Cu Kα radiation). The stick patterns represent the calculated powder diffraction patterns in terms of (a) Th$_{2}$Zn$_{17}$, (b) TbCu$_{7}$ (c) monoclinic 3:29 and (d) ThMn$_{12}$ structures. The peaks unmatched by the theoretical pattern in (b) are superlattice peaks of the new phase in the sample.
Figure 4-3: $^{57}$Fe Mössbauer spectra (at room temperature) of (a) annealed Nd$_{7}$Fe$_{40.7}$Ti$_{1.2}$, (b) as-cast, (c) annealed Nd$_{3}$Fe$_{20.8}$Ti$_{1.2}$, and (d) annealed Nd$_{3}$Fe$_{42.4}$Ti$_{3.6}$. Solid lines represent the theoretical fits.
After annealing, the sample was homogenized and most impurities disappeared. Figure 4-1 (b) shows the SEM photograph of the annealed sample. It is composed of approximately a single matrix 2:17 phase. The composition of the 2:17 phase (Nd : Fe : Ti = 10.3 : 87.2 : 2.5 (±0.5 at.%) ) is practically unchanged by the annealing process. The main result of the annealing is a combination of α-Fe(Ti) and the Nd-rich phase into the 2:17 phase and a growth of the 2:17 grains. The XRD patterns of both the as-cast and annealed samples have the characteristic reflections of the rhombohedral Th$_2$Zn$_7$ structure (Figure 4-2(a)). The lattice parameters of the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_7$ phase in the annealed sample are listed in Table 4-1.

The Mössbauer spectra of both the as-cast and annealed samples are characteristic of the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_7$ phase. Figure 4-3 (a) shows the Mössbauer spectrum of the annealed sample. The average hyperfine field at room temperature for the annealed sample is 18.9 (±0.2) T. The largest subspectral hyperfine field is 21.7 (±0.3 T), which we assign to the dumb-bell sites because of their shortest Fe-Fe distance.

4.2.2. THE Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ SAMPLE

The as-cast Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ sample has a microstructure similar to that of the as-cast Nd$_3$Fe$_{40.7}$Ti$_{1.2}$ sample but with much finer matrix grains. The sample is composed of (i) a dominant matrix phase, (ii) a fine grain intergranular phase (of order 3μm) with the 2:17 composition and (iii) a small amount of α-Fe(Ti) inside the matrix grains (see Figure 4-4 (a)). The composition of the matrix phase detected by EDAX is Nd : Fe : Ti = 8.8 : 85.4 : 5.8. It is neither 2:17 nor 1:12 but intermediate between them. Its stoichiometry corresponds to a 9:94 phase (i.e. $x = \frac{7}{16}$ in Equation 3-1).
Figure 4-4: SEM photographs of (a) as-cast and (b) annealed Nd$_3$Fe$_{20.8}$Ti$_{1.2}$. The as-cast sample is multi-phase comprising a dominant matrix phase (with a 9:94 composition) and some impurities (α-Fe and 2:17). After annealing, the matrix phase grew much larger and its composition changed from 9:94 to 3:29. The α-Fe and 2:17 impurities disappeared and a small amount of the 1:12 phase formed.
The powder XRD pattern of this new phase (Figure 4-2 b) shows all the strong peaks of a typical TbCu$_7$ (1:7) structure with several weak superlattice peaks. Since the crystal structure of the new matrix phase is unknown, we indexed it in terms of the TbCu$_7$-type structure and the values of the lattice parameters from the indexation are listed in Table 1. The TbCu$_7$-type structure is basically a disordered version (in terms of the sequence of the dumb-bell replacement) of the hexagonal and rhombohedral 2:17 structures. It is commonly observed as a main phase (composition close to 1:9) in rapidly-quenched or mechanically-alloyed samples$^{3-9}$.

After annealing, the grains of the matrix phase grew much larger (Figure 4-4(b)). Nd$_5$(Fe$_{1-x}$Ti$_x$)$_{17}$ disappeared and a small amount of Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ formed, along with some free α-Fe(Ti) precipitates. EDAX result reveals that the composition of the matrix phase changed from Nd : Fe : Ti = 8.8 (±0.9 at.%): 85.4 (±1.2 at.%): 5.8 (±0.6 at.%) to Nd : Fe : Ti = 9.7 (±0.5 at.%): 85.7 (±0.7 at.%): 4.6 (±0.4 at.%) upon annealing. The latter corresponds to a stoichiometry of 3:29 ($x = \frac{2}{5}$ in Equation 3-1) and is very close to the composition of the 2:19 phase (9.4 : 86.5 : 4.1) reported by Collocott, et al.$^{10}$.

Consistent with the EDAX result, the powder x-ray diffraction pattern of the annealed sample (Figure 4-2(c)) shows that the matrix phase is neither Nd$_5$(Fe$_{1-x}$Ti$_x$)$_{17}$ nor Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ and also differs from the 9:94 phase in the as-cast sample. The pattern has all the characteristic reflections of the CaCu$_3$-type structure plus several superlattice reflections, indicating another new phase formed after annealing, whose structure, like the Nd$_5$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases, is closely related to the CaCu$_3$-type structure.
The Mössbauer spectra of the as-cast and annealed Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ samples at room temperature are shown in Figure 4-3(a) and (c). The analysis of these two spectra employed three sextets with variable line-widths. Including extra subspectra in the fitting procedure had little effect on the average hyperfine field. The calculated fits are shown in Figure 4-3(a) and (c) as solid lines. The average hyperfine fields obtained from these fits are 20.7 (±0.3)T and 21.2 (±0.2)T for the as-cast and annealed samples, respectively. The fact that the average hyperfine fields in 3:29 and 9:94 are almost identical indicates some similarity between these two new phases.

4.2.3. THE Nd$_5$Fe$_{42.4}$Ti$_{3.6}$ SAMPLE

Similar to the as-cast Nd$_3$Fe$_{40.7}$Ti$_{1.2}$ and Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ sample, the as-cast Nd$_5$Fe$_{42.4}$Ti$_{3.6}$ sample is multi-phase, consisting of a dominant matrix phase with a small amount of $\alpha$-Fe(Ti) and some intergranular 2:17 phase (Figure 4-4(a)). The EDAX result shows that the matrix phase is very inhomogeneous. The central part of the matrix grains has the composition of essentially a 1:12 ratio. The border area of the matrix grains, however, has a 9:94 composition. The average $^{57}$Fe hyperfine field of the as-cast sample at room temperature is 22.9 (±0.3)T.

After annealing, the sample homogenized to approximately single phase tetragonal Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ with a very small amount of $\alpha$-Fe(Ti) remaining (Figure 4-5(b)). The powder XRD pattern shows the characteristic reflections of the tetragonal 1:12 structure (Figure 4-2(d)). The lattice parameters of the Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase are listed in Table 4-1. The fit to the Mössbauer spectrum, using three sextets with variable line-widths, yields an average hyperfine field of 25.2 (±0.3)T (Figure 4-3(d)).
Figure 4-5: SEM photographs of (a) as-cast and (b) annealed Nd₅Fe₄₂.₄Ti₃.₆. The microstructure of the as-cast sample is similar to that of as-cast Nd₃Fe₂₀.₈Ti₁.₂. It comprises a dominant matrix phase with small amounts of α-Fe and 2:17 impurities. The matrix phase is very inhomogeneous with the composition varying over a wide range. After annealing, the α-Fe disappeared and virtually single phase 1:12 formed with a small amount of the 3:29 phase.
Because of the multi-phase nature of the samples and the fact that the individual phases comprise numerous magnetically-inequivalent Fe sites, such as the 2:17 and 1:12 phases, in the Mössbauer analysis we used a program employing a distribution of hyperfine field. In figure 4-6 we show the distribution of the $^{57}$Fe hyperfine field in both the as-cast and annealed Nd$_7$Fe$_{40.7}$Ti$_{1.2}$, Nd$_3$Fe$_{20.8}$Ti$_{1.2}$ and Nd$_3$Fe$_{42.4}$Ti$_{3.6}$ samples, derived from the analysis. The field distributions in the as-cast and annealed Nd$_7$Fe$_{40.7}$Ti$_{1.2}$ samples are virtually identical, except that the small peak centered around
32 T, which is from the α-Fe(Ti) impurity in the as-cast sample, disappeared after annealing. This observation is consistent with the SEM results mentioned above.

The hyperfine field distributions of the as-cast and annealed Nd₃Fe₂₀.₈Ti₁₂ samples (Figure 4-6 (b)) show a small shift of the main component centered around 20.2T towards higher values upon annealing, indicating a phase transition from 9:94 to 3:29. This result is in agreement with the fits using the least-squares program. The α-Fe(Ti) peak around 32T is substantially larger after annealing, as can be seen from the spectrum (Figure 4-3 (c)) and the distribution (Figure 4-6 (b)).

The hyperfine field distribution of the as-cast Nd₅Fe₄₂₄Ti₃₆ samples shows that 9:94 is the dominant phase in the sample. After annealing a drastic change in the hyperfine field distribution was observed. A large shift of the peak position from ~20T to ~24.2T occurred, reflecting the formation of single phase 1:12 (see Figure 4-6(c)). The combination of XRD and Mössbauer Spectroscopy clearly shows the consolidation of the 1:12-T phase upon annealing in this sample.

4.2.4. THE STRUCTURE OF THE NEW Nd₃(Fe₁ₓTiₓ)₂₉ PHASE

Our results have shown that besides the well known Nd₂(Fe₁ₓTiₓ)₁₇ and Nd(Fe₁ₓTiₓ)₁₂ phases, two new phases also crystallize in the Nd-Fe-Ti system. The Nd : (Fe+Ti) ratios of these two novel phases lie between 2:17 and 1:12 and are close to 9-94 and 3-29, respectively. Like the 2:17 and 1:12, the x-ray diffraction patterns of these two new phases comprise all the characteristic reflections of the hexagonal 1:5 structure, indicating that they have close structural relationships with the 1:5 structure. If the structures of these two new phases, like the 2:17 and 1:12 structures, can be derived from the CaCu₂-type structure with the difference being in the dumb-bell stacking
sequence and dumb-bell content, according to Equation 3-1, the 9:94 and 3:29 phases correspond to $\frac{7}{16}$ and $\frac{2}{5}$ of the large rare-earth atoms being substituted by the smaller transition-metal dumb-bell atoms in the 1:5 structure, respectively. Thus, the structural series which can be derived from 1:5, by the dumb-bell replacement, so far is 1:5, 1:7, 3:22, 2:17, 3:29, 9:94 and 1:12.

A similar structural derivations have been observed in the RFe$_6$Sn$_6$ series of compounds$^{12-13}$. New long-range-ordered related structures were observed, which consist of different intergrowths of HfFe$_6$Ge$_6$-type and ScFe$_6$Ga$_6$-type structural slabs. From the disordered version of the YCo$_6$Ga$_6$ structure, there are several possible derived structure-types with orthorhombic symmetry and different long-range ordering.

The powder X-ray diffraction pattern of the new 9:94 phase can be indexed in terms of the 1:7 structure for most of the reflections, indicating that there is a close relation between the real structure of 9-94 and the 1:7-type structure.

In order to fix the initial atomic positions in the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ structure, Li et. al$^{14}$, by viewing the possible structure relationship between the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ structure and the well known CaCu$_5$, Th$_2$Zn$_{17}$ and ThMn$_{12}$ structures, proposed a structure for the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase, which is monoclinic with the space group P2$_1$/c (No. 14). Recently, it is believed that the 3:29 phase has a space group A$_2$/m instead of P2$_1$/c$^{15}$.

It is well known that the R$_2$Fe$_{17}$ phase can crystallize in two different structures depending on the R atom. The rhombohedral Th$_2$Zn$_{17}$-type structure is formed with R = Y, Pr, Nd, Sm and the hexagonal Th$_2$Ni$_{17}$-type structure is formed with R = Dy, Er, Ho,
Tm and Lu. For R = Gd and Tb, R₂Fe₁₇ can crystallize in both the rhombohedral and hexagonal structures. The Th₂Zn₁₇-type and Th₂Ni₁₇-type structures are derived from the 1:5 structure by replacing \( \frac{1}{3} \) of the large R atoms with pairs of transition metal atoms (dumb-bells), but with different replacement sequences. After a systematic search for the new 3:29 phases in the R-Fe-Ti systems with R=Y, Pr, Nd, Sm, Gd, Tb, Dy and Ho, we found that in the ternary R-Fe-Ti systems, the Nd₃(Fe₁₋ₓTiₓ)₂₉-type 3:29 phases only crystallizes in the systems where the rhombohedral Th₂Zn₁₇-type 2:17 forms. In the systems where the 2:17 phase crystallizes in the hexagonal Th₂Ni₁₇-type structure another novel intermediate phase with a different structure forms, which will be discussed in the following chapters. Consequently, this suggests that the new Nd₃(Fe₁₋ₓTiₓ)₂₉ structure should have a close structural relationship with the Th₂Zn₁₇-type structure. This result supports the structural model proposed by Li, et al.

In Chapter 3 we demonstrated that by viewing the 1:5, 2:17 and 1:12 structures in terms of the coordination polyhedra around the particularly large rare earth atoms (CPR), these structures can be simply described as stackings of the 20-vertex CPRs. It is followed, then, that the relationships of these structures can also be easily explained upon consideration of the CPRs. By employing these relationships, the possible structure for the 3:22 phase was proposed.

A similar simple relationship exists between the new Nd₃(Fe₁₋ₓTiₓ)₂₉ structure and the 1:5, 2:17 and 1:12 structures in terms of the CPRs which is shown in Figure 4-7 and 4-8. All the structures are simple stackings of 20-vertex CPR with the differences being mainly inside the CPR constructions. As an intermediate structure between the Th₂Zn₁₇ and ThMn₁₂ structures, the Nd₃(Fe₁₋ₓTiₓ)₂₉ structure is an arrangement of the two types
of CPR formed in the $\text{Th}_2\text{Zn}_{17}$ and $\text{ThMn}_{12}$ structures alternately along the $c$-axis of the $\text{Th}_2\text{Zn}_{17}$ cell. In this structure there are the 2:17 segment and the 1:12 segment alternately following one another, as illustrated in Figure 4-8.

Based on the structural relationship between the 1:5 and new 3:29 structures, the lattice parameters for the new $\text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase can be derived from those of the 1:5 phase according to following equations\(^{14}\):

\[
\begin{align*}
    a &= \sqrt{(2a_{1:5})^2 + c_{1:5}^2} \\
    b &= \sqrt{3}a_{1:5} \\
    c &= \sqrt{a_{1:5}^2 + (2c_{1:5})^2} \\
    \beta &= \arctan\left(\frac{a_{1:5}}{c_{1:5}}\right) + \arctan\left(\frac{a_{1:5}}{2c_{1:5}}\right)
\end{align*}
\]

\((4-1)\)
Figure 4-8: Schematic representation of the atomic arrangement and the CPR stacking sequence in the new 3-29 structure.

Figure 4-9: The structure for the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase and its relationship with the CaCu$_5$ structure.
It is known that the 1:12 phase does not exist in any binary R-Fe system and a third element T, such as Ti, V, Cr, Mn, W, Mo, Al and Si, is essential to stabilize the 1:12 structure. In the case of the new Nd₃(Fe₁₋ₓTiₓ)₂₉ phase, the third element Ti is also essential in stabilizing the 3:29 structure. The role of the third element in stabilizing the 1:12 and 3:29 phases remains unclear so far.

Although the R(Fe₁₋ₓTx)₁₂ phases can crystallize with different T, such as T= Ti, V, Cr, Mn, Al, W, Mo and Si, the amount of the T element required to stabilize such phases differ with each specific T element. The prevalent observation is that the larger the size of the T atom (see Figure 3-5), the lower the T content in the R(Fe₁₋ₓTx)₁₂ phase. Thus, it appears to us that the atomic size factor might play a key role in the stabilization of the 1:12 phases, and, accordingly, the 3:29 phases.

A goal of crystallography has long been to find rules that might enable one to predict which phase may be formed when different metals are melted together. Much work has been done in this area. Some factors which have been extensively used for the treatment of alloys consisting of two or three components during the past decades are size (geometrical factor), electro-chemical factors and valence electron concentration\(^{16,17}\). The strength of the influence of each factor on the structures chosen by an alloy system is dependent on the difference between the elemental components, regarding that particular factor.

The size factor is the characteristic of the structures in which there occur a range of interatomic distances that are incompatible with the usual atomic radii. Many results have shown that the stoichiometric formula and the structure type of many intermetallic compounds are largely fixed by geometrical factors\(^{16,18}\).
The size factor (or geometric factor) is, in fact, associated with close-packed atomic arrangement with respect to the crystallographic topology. If one considers the atoms as touching spheres, the close-packed structures are the those that fill the space best and have the highest possible coordination number. For example, with *identical* spheres a local density higher than that of the hexagonal or cubic (FCC) close-packed arrangements can be achieved by a configuration based on an icosahedron. This configuration includes 33 spheres, 13 of which include the icosahedron and the central sphere and the remaining 20 are placed above the 20 triangular faces of the icosahedron. In fact, such a configuration appears commonly in the transition metal compounds. However, it is not possible geometrically to perpetuate such a configuration without introducing holes which are larger than the sphere size. This need not be the situation, however, for unequal size spheres packed together. Assuming larger spheres are available to fill the holes resulting from the arrangement of the icosahedral groups, this would have coordination numbers larger than 12. Actually, the occurrence of high coordination numbers (≥12) have been generally observed in the transition metal compounds in which the sites with higher coordination number than 12 provide the position for the large atoms in the compounds. However, it has been shown that only the coordinations that satisfy the closed-packed atomic arrangement, such as the 12, 14, 15 and 16-fold coordinations, were generally observed in the actual structures. These coordination polyhedra have a ‘triangular’ atomic arrangement on the surface of the polyhedron sphere. Thus, the ‘triads’ of atoms on the surface together with the central one form the densest tetrahedral packing in 3-d space.
Pertaining to the spherical packing inside the 'triangular' coordination polyhedra mentioned above, a geometrical study of these coordination polyhedra showed that except for the regular icosahedron which can be constructed by the equal spheres, the other polyhedra with coordination numbers higher than 12 cannot be realized with identical spheres. For CN=14, 12 out of the 14 coordination spheres may be the same but differ from the central one, and the two coordination spheres along the six-fold axis must be different from the other twelve. The situation is more complex for CN=15. Not all spheres surrounding the central one are equivalent, but the central one is larger than most of the spheres on the surface. The polyhedron for CN=16 is a compact one achieved by utilizing two kinds of spheres with a radius ratio of 1.23. The larger sphere at the center is surrounded by a tetrahedral arrangement of four other large spheres and twelve smaller spheres making contact with one another. With the coordinations higher than 12, the interstices are then distorted rather than regular tetrahedra, and on the surface of the coordination polyhedra there appear triangular, but not equilateral, faces.

In the case of 20-vertex CPR, a similar condition exists. In the 1:12 structure, the CPR involves 3 different R-T interatomic distances and 6 different T-T interatomic distances.

It has been reported that in the RFe_{12-x}T_x (T = Ti, V, Cr, Mn, Mo, W and Al, et al) phases, the 8f and 8j sites are occupied completely by iron atoms while the 8i site is populated by both Fe and T atoms. An exception occurs when T = Si which prefers the 8f and 8j sites in RFe_{10}Si_2. The shortest R-T distances in the CPR of the RFe_{12-x}T_x structure occur between R atoms and the T atoms at the 8i sites. Progressively larger R-T distances are involved for the 8f and 8j sites, respectively. Since the metallic radii of the T elements, except for Si, are substantially larger than that of Fe (see Figure 3-5).
one might expect the T atoms to preferentially occupy the 8j sites rather than the 8i sites. However, on the basis of average T-T distances on the surface of the CPR (2.49Å, 2.69Å and 2.57Å for the 8f, 8j and 8i sites in Yfe11Ti, respectively), the 8i site is expected to be preferred over the 8f or 8j sites for larger T atoms than Fe32. This latter argument seems to be in accordance with the observed preferential occurrences in these systems.

The site preference occupation by the third element in the 1:12 phase can be easily explained in terms of the coordination polyhedra in the structure. Extending the consideration to the coordination polyhedra around the transition metal atoms on the surface of the 20-vertex CPR, there are basically 2 different coordinations, 12 for the 8j and 8f atoms and 15 for the 8i atoms, in the 1:12 structure. It is, then, conceivable that the 8i sites should be preferred by the large T atoms over the 8j and 8f sites, since the former has a higher coordination number and so more able to accommodate the larger atoms. From the space-filling point of view, this site occupation also results in a better space-filling. It follows that Si, which is smaller than Fe, should prefer the 8f and 8j sites. This is in fact observed in LuFe10Si22. It should be noted that in accordance with a consideration due to Frank and Kasper, all the three coordination polyhedra in the 1:12 structure can be regarded as having space-filling properties.

In the 1:5 structure, there are only two coordination numbers, 20 for the large R atoms and 12 for the small T atoms. The 20-vertex CPR (Type-I) in this structure has 3 interatomic distances between the central R atom and the 20 coordination atoms and 3 interatomic distances among the coordination atoms. The largest interatomic distance is between the central R and two R coordination neighbors, which stretches the Type-I
CPR along these two R directions (the $c_{1,5}$ direction). In the 1:12 structure, the two furthest R coordination neighbors in the Type-I CPR are replaced by two much closer transition metal neighbors. After the replacement, the atomic positions in the CPRs are adjusted accordingly and the CPRs (Type-II) become more symmetric. In accordance to the discussion due to Kasper and Frank, the Type-II CPR is a more densely-packed arrangement than the Type-I CPR. However, without the third element with a different atomic size the Type-II CPR cannot be realized because of the geometrical restraint.

The systematic study of the Nd-Fe-Ti system based on the samples with different compositions (the details will be reported in the following chapter) shows that the Ti content of the Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase is constant around 7.2 at.%. If this Ti content is that required to satisfy the size factor mentioned above to construct the Type-II CPRs in the Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ structure, the 3:29 phase, having half Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ structural units and half Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$ structural units, should have a Ti content equal to the average of the 1:12 and 2:17 Ti contents, which is $\frac{1}{2} \times 2.5 \text{ at} \% + \frac{1}{2} \times 7.2 \text{ at} \% = 4.8 \text{ at} \%$. Comparing this with the EDAX result on the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase (Ti$_{3:29}$ = 4.6 at.%), we see clearly that the calculated Ti content for 3:29 phase matches the experimental result very well.

In summary, the large atomic size ratio of the rare earth and transition metal components in the R-T phases resolves 20 coordination neighbors for the large R atoms, which is a dense-packing arrangement in accordance with a consideration due to Boerdijk$^{19}$. However, forming these 20-fold coordination polyhedra geometrically requires unequal spheres at the 20 coordination sites. Consequently, for the 1:12 structure in which all the 20 coordination sites are occupied by transition metal atoms,
there is a requirement for a third element (transition metal) with a size different from Fe to meet this geometrical factor. For the new \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) structure the same situation applies. The third element is essential to form the structure. We believe that the \( 3:29 \) phase, like the \( 1:12 \) phase, should also exist in the other R-Fe-T systems with \( T = V, Al, Cr, Mn, Mo \) and \( W \), but has different \( T\% \), depending on the atomic size of \( T \) atom. In fact, the \( 3:29 \) phase has been reported in the systems with \( T = V^{24}, Cr, Mn^{25-26}, Mo^{27} \) systems.

A similar phase to our \( 3:29 \) phase was reported in the \( R_2(\text{Fe}_{0.9}\text{V}_{0.09})_{17} \) system\(^{26,28} \). These authors gave an orthorhombic indexation with lattice parameters \( a, b \) and \( c \) being five times those of the basic \( 1:5 \) structure, in a so-called ortho-hexagonal setting of the crystallographic coordinates. The typical XRD peak observed at about \( 2\theta \sim 39.5^\circ \) evident in Figure 2-l(b) is also present in the new R-Fe-V phase.

4.3. CONCLUSION

The formation of two new ternary intermetallic phases in the Fe rich end of the Nd-Fe-Ti phase diagram, namely \( 9:94 \) with a \( \text{TbCu}_7 \) derived structure and \( 3:29 \) with a new monoclinic structure has been investigated. Both structures can be derived from the \( \text{CaCu}_5 \) structure by replacing a fraction of R (Ca) atoms with T-T dumb-bells. Replacing \( \frac{7}{16} \) and \( \frac{2}{5} \) of the R atoms in the \( \text{CaCu}_5 \) structure by dumb-bells leads to the formation of the new \( 9:94 \) and \( 3:29 \) structures, respectively. The practical structural relationships between the \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) phase and the \( 1:5, 2:17 \) and \( 1:12 \) phases are very simple in terms of the CPR. \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) is an intermediate phase between the rhombohedral
2:17 and the tetragonal 1:12 phases. Its structure can be obtained by a 1:1 stacking of the rhombohedral 2:17 and tetragonal 1:12 structural segments.

Similarly to the 1:12 phase, the 3:29 phase does not crystallize in the binary system, a third element (Ti) is required to stabilize it. The role of the third element can be explained by the geometrical construction of the CPR in the 3:29 and 1:12 phases. The construction of the 20-vertex CPR requires spheres with different sizes at the 20 coordination sites to achieve dense-packing.
REFERENCES


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Chapter Five

PHASE FORMATION IN THE Nd-Fe-Ti SYSTEM

5.1. INTRODUCTION

In searching for Fe-based rare-earth permanent magnet materials, the R$_2$Fe$_{17}$ have phases always been attractive since they are the most Fe-rich compounds among the rare-earth iron binaries found so far$^{1,2}$. Unfortunately, the Curie temperatures of these R$_2$Fe$_{17}$ compounds are very low (200-480 K) and their anisotropies are easy-plane. The other attractive and widely studied R-rich compounds are the pseudo-binary R-Fe-M series and one of the most important among them is R(Fe$_{1-x}$M$_x$)$_{12}$$^{3,4}$. The SmFe$_{11}$Ti compound has strong uniaxial anisotropy and a high Curie temperature comparable to those of Nd$_3$Fe$_{14}$B$^{5,6}$. Recently it has been found that by introducing interstitial atoms, such as H$^{7,8}$, C$^{9,10,11}$ and N$^{12}$, into the R$_2$Fe$_{17}$ compounds, their Curie temperatures can be substantially increased and with R = Sm, Sm$_2$Fe$_{17}$X$_8$ exhibits an easy c-axis anisotropy when $\delta > 0.5$ for X = C$^{13}$ or $\delta > 0.8$ for X = N$^{14}$. The intrinsic magnetic properties of Sm$_2$Fe$_{17}$N$_8$, such as room temperature anisotropy field (14 T) and Curie temperature (749 K), are even better than those of Nd$_3$Fe$_{14}$B$^{12,15}$. Introducing interstitial C and N atoms in the R(Fe$_{1-x}$M$_x$)$_{12}$ compounds also improves their intrinsic magnetic properties$^{16}$. The excellent intrinsic magnetic properties (high Curie temperatures coupled with strong uniaxial anisotropy) have made the nitrides and carbides of the 2:17 (such as Sm$_2$Fe$_{17}$N$_8$ and Sm$_2$Fe$_{17}$C$_{10}$) and the 1:12 (such as NdFe$_{11}$TiN$_6$ and NdFe$_{11}$TiC$_n$) phases very promising candidates for application as high performance permanent magnets$^{15,17}$. 
In our initial work reported in preceding chapter, a new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ (3:29) phase was identified. It is an intermediate phase between the rhombohedral Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and tetragonal Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases. The structure of this new 3:29 phase is a simple 1:1 stacking of the rhombohedral Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and tetragonal Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ structural units. Magnetic studies have shown that both the magnetization and Curie temperature of the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase are slightly larger than those of the 2:17 phase\textsuperscript{118}. This fact suggests that the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase might be used as a starting material to produce new nitride permanent-magnets whose performance, ultimately, may supersede that of the Sm$_2$Fe$_{17}$N$_5$ phase.

Subsequent to this result, a detailed study of the R corner of the Nd-Fe-Ti system was undertaken in order to better comprehend the phase formation in the R corner of the Nd-Fe-Ti system, especially around the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$, Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases. In this chapter we will report the results of this study. Since the third element Ti plays a key role in stabilizing the novel Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases as described in the previous chapter, the emphasis of this study is placed on the phase formation in the R corner of the Nd-Fe-Ti system as a function of Ti content.

5.2. RESULTS AND DISCUSSION

Samples of (Nd$_{1-x}$Ti$_x$)Fe$_5$ with $x = 0.0$, 0.1, 0.146, 0.2, 0.25, 0.268, 0.3, 0.333, 0.35, 0.4, 0.419, 0.45 and 0.5 were prepared by arc-melting the pure elements (>99.9%) 5 times. To compensate for Nd loss during arc-melting, 7 wt.% excess Nd was added in each sample. All the samples were then annealed at three different temperatures, 850°C, 950°C and 1070°C, respectively, for a period of 3 days under an Ar atmosphere. They were characterized by (1) powder x-ray diffraction (XRD), (2) scanning electron
microscopy (SEM) with non-standard energy disperse x-ray analysis (EDAX), (3) room temperature $^{57}$Fe Mössbauer spectroscopy and (4) a modified thermo-gravimetric analysis (TGA).

5.2.1. THE AS-CAST SAMPLES:

All the as-cast samples have the similar microstructures which are multi-phase comprising a dominant matrix phase with some $\alpha$-Fe(Ti) and an intergranular impurity phase. The main differences in terms of their microstructures are the grain sizes of the matrix phases. The higher the Ti content, the finer the grains of the matrix phase. SEM photographs of the six representative $(\text{Nd}_{1-x}\text{Ti}_x)$Fe$_3$ samples with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 are shown in Figure 1.

Mössbauer analysis gives a relative spectral area contribution from the $\alpha$-Fe(Ti) impurities of 20(5)% for $x < 0.25$ and $x \geq 0.40$. The amount of $\alpha$-Fe(Ti) impurities for $0.25 \leq x \leq 0.40$ corresponds to a 8(4)% relative spectral area.

The EDAX analyses, which are listed in Table 5-1, show that the matrix phases in the samples with low Ti ($< 2.0$) or high Ti ($> 4.0$) contents are generally homogeneous. They have a 2:17 composition in the low Ti samples and a 1:12 composition in the high Ti samples. Contrary to the samples with either high or low Ti content, the matrix phases in the samples with intermediate Ti content are very inhomogeneous and their compositions cover a wide range between 2:17 and 1:12. The central parts of the matrix grains have relatively high Ti and low Nd contents—approaching a Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ composition. Towards the boundary regions of the matrix grains the Ti content decreases and the Nd content increases and around the edges of the matrix grains the composition is close to a 2:17.
Figure 5-1(1): SEM photographs of the as-cast \((Nd_{1-x}Ti_x)Fe_5\) samples with \(x = 0\) and 0.1. They are multi-phase with a dominant matrix \(Nd_2(Fe_{1-x}Ti_x)_{17}\) phase, some \(\alpha\)-Fe and a Nd-rich phase.
Figure 5-1(2): SEM photographs of the as-cast $(\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$ samples with $x = 0.2$ and 0.3. The matrix phases are finer than those in the sample with $x=0$ and 0.1. EDAX shows that the matrix phases in these samples have very inhomogeneous compositions.
Figure 5-1 (3): SEM photographs of the as-cast (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples with $x = 0.4$ and 0.5. They have similar micro-structures as the samples with intermediate Ti content, but the matrix phases in these samples are generally homogenous with a 1:12 composition.
Table 5-1: EDAX results of the matrix phase and the phase content in the (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples

<table>
<thead>
<tr>
<th>Samples $(Nd_{1-x}Ti_x)Fe_5$</th>
<th>Composition of Matrix Phase Nd : Fe : Ti (EDAX)</th>
<th>Impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0.00$</td>
<td>10.46 : 89.54 : 0.00</td>
<td>$\alpha$-Fe &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.05</td>
<td>10.47 : 88.81 : 0.72</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.10</td>
<td>10.66 : 87.95 : 1.39</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.146</td>
<td>10.4-10.8 : 86.5-87.2 : 2.4-2.7</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.20</td>
<td>10.5-10.9 : 86.3-86.4 : 2.8-3.0</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.25</td>
<td>8.6-9.9 : 85.1-86.5 : 4.0-6.2</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase</td>
</tr>
<tr>
<td>0.286</td>
<td>8.6-9.9 : 85.1-86.1 : 3.9-6.2</td>
<td>$\alpha$-Fe(Ti) &amp; Nd-rich phase + 2:17</td>
</tr>
<tr>
<td>0.30</td>
<td>9.6-9.8 : 84.6-86.1 : 4.1-5.6</td>
<td>$\alpha$-Fe(Ti) &amp; 6:23 + 2:17</td>
</tr>
<tr>
<td>0.35</td>
<td>9.4-10.0 : 85.2-85.6 : 4.8-5.1</td>
<td>$\alpha$-Fe(Ti) &amp; 6:23 + Nd-rich phase</td>
</tr>
<tr>
<td>0.40</td>
<td>7.5-10.7 : 83.1-85.8 : 4.6-8.5</td>
<td>$\alpha$-Fe(Ti) &amp; 6:23 + 2:17</td>
</tr>
<tr>
<td>0.416</td>
<td>7.3-7.5 : 85.3-85.6 : 7.1-7.2</td>
<td>$\alpha$-Fe(Ti) &amp; 9.8-10.4 : 84.9-86.4 : 3.8-4.7</td>
</tr>
<tr>
<td>0.45</td>
<td>7.4-8.8 : 82.9-84.2 : 7.4-8.7</td>
<td>$\alpha$-Fe(Ti) &amp; 11.6 : 83.3 : 5.0</td>
</tr>
<tr>
<td>0.50</td>
<td>7.4-7.6 : 84-84.8 : 7.8-8.4</td>
<td>$\alpha$-Fe(Ti) &amp; 9.4 : 84.9 : 5.7 (3:29)</td>
</tr>
</tbody>
</table>
The inhomogeneous nature of the samples with intermediate Ti content can also be observed clearly from the TGA data of these samples. Figure 3-2 shows the TGA trace of four samples with \( x = 0.1, 0.3, 0.4, 0.45 \). The data reveal that the samples with low or high Ti contents are virtually single-phase. The samples with low Ti content comprise approximately single phase \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) and the samples with high Ti content formed roughly single phase \( \text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \). The samples with intermediate Ti content, however, are very inhomogeneous. Unlike the samples with low or high Ti contents, the magnetization of these samples decreases gradually as the temperature increases, indicating that their magnetic ordering temperatures cover a broad range from the \( T_c \) of the \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase to that of the \( \text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) phase.

![Figure 3-2: TGA data of the \( (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 \) samples with \( x = 0.1, 0.3, 0.4 \) and 0.45.](image)

\[ \text{Figure 5-2: TGA data of the } (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 \text{ samples with } x = 0.1, 0.3, 0.4 \text{ and } 0.45. \]
Figure 5-3: Powder x-ray diffraction patterns of the as-cast \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) samples with \(x = 0.0, 0.1, 0.2, 0.3, 0.4\) and 0.5 (Co Ka radiation). The bar patterns are calculated patterns of the 2:17, 1:7 and 1:12 structures based on the indexation of the experimental results.
The powder x-ray diffraction results are consistent with the SEM/EDAX analyses and the TGA results. Figure 5-3 shows the typical powder x-ray diffraction patterns of the as-cast samples with \( x = 0.0, 0.1, 0.2, 0.3, 0.4 \) and 0.5. The patterns of the samples with low Ti and high Ti content have the characteristic reflections of the rhombohedral \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) and the tetragonal \( \text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) structures, respectively. The patterns of samples with intermediate Ti content are neither the \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) type nor the \( \text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) type but have all the characteristic reflections of a \( \text{TbCu}_7 \)-type structure with some superlattice peaks. The lattice parameters of the matrix phases deduced from the x-ray diffraction results of the samples with \( x = 0.0, 0.1, 0.2, 0.3, 0.4 \) and 0.5 are listed in Table 5-2. Since the structure of the matrix phases in the samples with intermediate Ti content is unknown, we simply index them in terms of a \( \text{TbCu}_7 \)-type structure.

**Table 5-2: The matrix phases formed in the as-cast \( \text{(Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 \) samples with \( x = 0.0, 0.1, 0.2, 0.3, 0.4 \) and 0.5 and their lattice parameters. Since the matrix phase formed in the samples with intermediate Ti content has not been clearly identified, we indexed their patterns in terms of the 1:7-type structure.**

<table>
<thead>
<tr>
<th>(Nd(_{1-x})Ti(_x))Fe(_5)</th>
<th>Phase</th>
<th>Lattice Parameters</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=0.00</td>
<td>2:17-R</td>
<td>8.569(1)</td>
<td>12.474(0)</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>2:17-R</td>
<td>8.598(2)</td>
<td>12.485(7)</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>1:7</td>
<td>4.957(2)</td>
<td>4.171(3)</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>1:7</td>
<td>4.950(1)</td>
<td>4.182(3)</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>1:12</td>
<td>8.575(5)</td>
<td>4.192(8)</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1:12</td>
<td>8.592(1)</td>
<td>4.188(4)</td>
<td></td>
</tr>
</tbody>
</table>

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There two possible explanations for the inhomogeneous nature of the samples with intermediate Ti content, (1) some intermediate phases, like Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{29}$, exist between Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ and have compositions and magnetic ordering temperatures between those of Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$, or (2) the matrix phases in those samples have many defects on an atomic scale developed from the rapid cooling during sample preparation and these defects make Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ present quite inhomogeneously.

In order to further analyze the phases formed in the samples, room temperature $^{57}$Fe Mössbauer spectra were collected. Because of the inhomogeneous and multi-phase nature of the as-cast samples and the fact that the individual phases in the samples comprise numerous magnetically-inequivalent Fe sites (e.g. Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$), the spectra were fitted using the program developed by Le Caër and Dubois$^{19}$, which employs a distribution of hyperfine field. Figure 5-4 shows the $^{57}$Fe Mössbauer spectra of the samples with $x = 0.146$, 0.3 and 0.45. The solid lines in the spectra are the fitted results. The hyperfine field distributions deduced from these fits for the three samples are shown in Figure 5-4. The hyperfine field distributions clearly indicate a shift towards higher field with increasing Ti content. The multi-phase nature of these samples is reflected in both the widths and asymmetries of the hyperfine field distributions.

To estimate the relative amounts of each possible phase in the samples, the hyperfine field distributions were in turn fitted using a superposition of several simple Lorentzian lines, each corresponding to an individual phase. This process of fitting the hyperfine field distributions is by no means rigorous since there is no reason to suppose
Figure 5-4: $^{57}$Fe Mössbauer spectra of the as-cast \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) samples with (a) \(x = 0.146\), (b) \(x = 0.30\) and (c) \(x = 0.4\) at 295K.
that such distributions should be Lorentzian. Nevertheless, such fits may give some information on the relative amount of the various possible phase components in a sample.

Figure 5-5: Hyperfine field distributions of the as-cast \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) samples with (a) \(x = 0.146\), (b) \(x = 0.30\) and (c) \(x = 0.45\).

Using the fitting of the hyperfine field distributions, the analysis of the spectra of all thirteen samples of \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) suggests that there are essentially four components present in these samples, with hyperfine fields around 16.1, 19.6, 25.4 and 31.2T, respectively. The relative amounts of each component present in a sample are a function of the Ti content. As shown in Figure 5-6, there are roughly three phase regions. For \(x \leq 0.1\), the sample is pre-dominantly the \(\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}\) phase, whereas for \(x \geq 0.4\), the
sample is pre-dominantly the Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase. In the intermediate range $0.1 < x < 0.4$, the dominant component is a new phase which attains a maximum content with a Ti content around $x = 0.3$.

![Figure 5-6: The dependence of the relative fitted sub-spectral areas deduced from the hyperfine field distributions of the component phases on the Ti concentration $x$ in the (Nd$_{1-x}$Ti$_x$)$_5$Fe$_5$ samples.](image)

A similar result has been reported in the melt-spun Nd$_{7.7}$Fe$_{92.3}$Ti$_x$ samples$^{20}$. With $x = 2.8$, and $x \geq 7.7$ the 2:17 and 1:12 formed as main phases in the as-cast samples. However, with $x = 4.6$, the 7:1 phase showed as a dominant one.

### 5.2.2. THE ANNEALED SAMPLES

As mentioned above, the results from the as-cast samples showed that all the sample s are multi-phases and the matrix phases in the samples with intermediate Ti content are quite inhomogeneous. Their compositions and magnetic ordering temperatures cover a wide range between those of the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases. Considering the solidification procedure, we know that this multi-phase and
inhomogeneous nature in the as-cast samples are resulted from the thermodynamical and kinetic conditions of the different stages during the cooling procedure. They reflect that this system has very completed phase diagram around the compositions studied.

In order to better understand the thermal-equilibrium phase formation at different temperatures, the samples were annealed at 850°C, 950°C and 1070°C, respectively, for a period of 3 days and then quenched to the room temperature. Since only the Nd$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase crystallizes in the annealed samples with low Ti content, the following discussion will focus on the samples with intermediate and high Ti contents.

5.2.2.1. The samples annealed at 850°C

The matrix phases in all the samples annealed at 850°C are rhombohedral Nd$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$. No Nd$_{3}$(Fe$_{1-x}$Ti$_{x}$)$_{29}$ or Nd(Fe$_{1-x}$Ti$_{x}$)$_{12}$ formed at this temperature. This indicates that the 3:29 and 1:12 phases are unstable below 850°C in the Nd-Fe-Ti system, which is agreed with the results reported by Jang$^{20}$ and Margarian$^{21}$, et. al. Figure 5-7 shows the powder x-ray diffraction patterns of the samples with $x$ = 0.2, 0.3, 0.4 and 0.5 annealed at 850°C for 3 days. All the patterns have the characteristic reflections of the rhombohedral Nd$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ structure with a few weak peaks from the Nd(Fe$_{1-x}$Ti$_{x}$)$_{2}$ and α-Fe(Ti) (or Fe$_{2}$Ti in the sample with high Ti content) impurities.

The SEM/EDAX results are consistent with the x-ray diffraction results. Figure 5-8 shows the SEM photographs of four samples with $x$ = 0.1, 0.3, 0.4 and 0.5. They comprise a dominant matrix Nd$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase and two impurity phases, one in the form of dispersed precipitates and one in the intergranular regions. The EDAX results (listed in Table 5-2) reveal that the compositions of the matrix Nd$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase in all these samples is approximately the same, independent of the starting compositions.
Figure 5-7: Powder x-ray diffraction patterns of the 850°C annealed (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples with $x = 0.2$, 0.3, 0.4 and 0.5 (Co $K\alpha$ radiation). The solid bars are the calculated reflection patterns based on the indexation of the experimental data in terms of the rhombohedral 2:17 structure.
Figure 5-8(1): SEM photographs of the 850°C annealed (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples with $x = 0.1$ and 0.3. They comprise a dominant 2:17 matrix phase and a small amount of impurities.
Figure 5-8(2): SEM photographs of the ($Nd_{1-x}Ti_x$)Fe$_5$ samples (with $x = 0.4$ and $0.5$) annealed at 850°C for 3 days. They comprise a dominant matrix $Nd_2(Fe_{1-x}Ti_x)_17$ phase and a small amount of 1:3 and Fe$_2$Ti impurities.
Different starting compositions only cause different amounts or type of impurities. In the samples with low Ti content, the impurity phases are $\alpha$-Fe(Ti) (precipitates) and a Nd-rich phase with a Nd : (Fe+Ti) $\approx$ 1:1 (intergranular phase). In the samples with high Ti content, $\alpha$-Fe is replaced by Fe$_2$Ti and the Nd-rich phase changed to Nd(Fe$_{1-x}$Ti$_x$)$_3$.

Table 5-3: The compositions (EDAX results) and the lattice parameters of the matrix Nd$_2$(Fe$_{1-x}$Ti$_x$)$_7$ phase formed in the 850°C annealed (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples with $x$ = 0.2, 0.3, 0.4 and 0.5.

<table>
<thead>
<tr>
<th>(Nd$_{1-x}$Ti$_x$)Fe$_5$</th>
<th>Composition (EDAX) Nd : Fe : Ti (± 0.6 at.%)</th>
<th>Lattice parameters a (Å) c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0.2$</td>
<td>10.6 : 86.3 : 3.1</td>
<td>8.583(2) 12.501(2)</td>
</tr>
<tr>
<td>0.3</td>
<td>10.6 : 86.1 : 3.3</td>
<td>8.591(1) 12.495(7)</td>
</tr>
<tr>
<td>0.4</td>
<td>10.6 : 85.3 : 4.1</td>
<td>8.590(4) 12.483(2)</td>
</tr>
<tr>
<td>0.5</td>
<td>10.3 : 85.7 : 4.0</td>
<td>8.601(2) 12.483(9)</td>
</tr>
</tbody>
</table>

Although the samples with intermediate and high Ti content have very similar microstructures there is a variance in the samples with $x = 0.3$–0.4. The EDAX results from these samples indicate that the impurity phase in the form of a dispersed precipitate in these samples is neither $\alpha$-Fe(Ti) nor Fe$_2$Ti, but a phase with a composition of Nd : R : Ti = 8.3–9.2 : 81.9–84.3 : 6.4–9.2. Based on the composition, this could be another intermediate phase between Nd$_2$(Fe$_{1-x}$Ti$_x$)$_7$ and Nd(Fe$_{1-x}$Ti$_x$)$_12$. However, because the amount of this phase is too small, its identification cannot be completed.
Based on our XRD, SEM and EDAX results, in Figure 5-8 we show the Fe corner of the isothermal phase diagram of the Nd-Fe-Ti system at 850°C. This diagram is by no means rigorous and is only based on the results of the very limited number of samples used in the present work. However, it basically gives the information of the phase formation around R corner of the Nd-Fe-Ti system at this temperature. The dotted lines and the grey mark in the figure represent the possible new phase identified by the SEM/EDAX results.

\[ \text{Fe}_2\text{Ti} \]

Figure 5-9: The Fe corner of the isothermal phase diagram of the Nd-Fe-Ti system at 850°C. The dotted line and the gray mark represent the possible new phase identified by the SEM/EDAX results.

5.2.2.2. The samples annealed at 950°C

Annealing at 950°C for 3 days produced the same results as the 850°C annealing procedure in all samples except that with \( x = 0.5 \). Figure 3-9 shows the SEM
photographs of several typical samples annealed at 950°C (x = 0.25, 0.3, 0.35, 0.4 and 0.5). All the samples are multi-phase, consisting of a matrix phase and small amounts of impurity phases. The EDAX analysis revealed that, like the results of the 850°C annealed samples, the dominant matrix phases in all the samples have approximately the same 2:17 composition (see Table 5-3). The different starting compositions only induce different types or different amounts of impurity phases. Only a Nd-rich impurity phase exists in the samples with low Ti content. As the Ti content increases, another impurity phase in the form of a finely scattered precipitate is produced. This impurity phase is identified by EDAX as Fe$_2$Ti in the samples with high Ti content. However, in the samples with 0.3≤x<0.4 this phase has a composition Nd : R : Ti = 8.3 ~ 9.2 : 81.9 ~ 84.3 : 6.4 ~ 9.2, which is identical to that of the possible new phase identified in the 850°C annealed samples with the same Ti content range. The starting compositions of the samples with x = 0.3~0.4 are Nd : R : Ti = 10.0 ~ 11.7 : 83.3 : 5 ~ 6.7, which are close to the composition of the possible new phase. However, the amounts of the new phase formed in these samples are very small. One possible explanation could be that this phase has very slow formation kinetics.

The sample with x = 0.5 has a different micro-structure from all the other samples. It consists of three phases, (1) a dominant matrix phase with a composition Nd : R : Ti = 10.3 : 86.2 : 3.5 (close to the composition of the Nd$_2$(Fe$_{1.3}$Ti$_{0.7}$) phase), (2) a very small amount of the intergranular impurity phase with a composition Nd : R : Ti = 9.2~9.6 : 86.0~86.5 : 4.0~4.7—a 3:29 ratio and (3) a very small amount of the Fe$_2$Ti impurity in the form of finely dispersed precipitates.
Figure 5-10(1): SEM photographs of the 950°C annealed (Nd$_{1-x}$Ti$_x$)Fe$_5$ samples with $x = 0.25$ and 0.3. They comprise a dominant matrix Nd$_2$(Fe$_{1-x}$Ti$_x$)$_7$ phase and some Nd(Fe$_{1-x}$Ti$_x$)$_3$, impurities.
Figure 5-10(2): SEM photographs of the 950°C annealed $(\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$ samples with $x = 0.35$ and 0.4. They are multi-phase with a dominant matrix $\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ phase, some $\text{Fe}_2\text{Ti}$ and a very small amount of $\text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_3$ impurities.
Figure 5-10(3): SEM photographs of the 950°C annealed \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) samples with \(x = 0.45\) and 0.5. The sample with \(x = 0.45\) has a similar microstructure to the samples with \(x = 0.35\) and 0.4, but with more \(\text{Fe}_2\text{Ti}\) precipitated. The sample with \(x = 0.5\) has a totally different microstructure from all the other samples.
Figure 5-11: Powder x-ray diffraction patterns of the 950°C annealed \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5\) samples with \(x = 0.25, 0.286, 0.3, 0.333, 0.35, 0.4, 0.45, 0.5\). (Co Kα radiation). The stick patterns are calculated \(\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_17\) diffraction patterns.

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The powder x-ray diffraction results of the \( (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 \) samples with \( x = 0.25, 0.286, 0.3, 0.333, 0.4, 0.45 \) and 0.5 are shown in Figure 5-11. The patterns of all these samples, except that with \( x = 0.5 \), have the characteristic reflections of the rhombohedral \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_17 \) structure, which is consistent with the SEM/EDAX results. The lattice parameters of the main \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_17 \) phase in these samples deduced from the x-ray results are listed in Table 5-4.

**Table 5-4: The compositions (EDAX results) and lattice parameters of the matrix phase in the 950°C annealed \( (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 \) samples with \( x = 0.25, 0.286, 0.30, 0.333, 0.35, 0.375, 0.40, 0.45 \) and 0.5. Since the structure of the matrix phase for \( x = 0.5 \) sample is still unknown, we did not index it.**

<table>
<thead>
<tr>
<th>( (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5 )</th>
<th>Composition (EDAX) Nd : Fe : Ti (± 0.7 at %)</th>
<th>Lattice Parameters a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.25 )</td>
<td>10.5 : 85.8 : 3.7</td>
<td>8.601(1)</td>
<td>12.519(1)</td>
</tr>
<tr>
<td>0.286</td>
<td>10.6 : 85.7 : 3.7</td>
<td>8.604(4)</td>
<td>12.476(4)</td>
</tr>
<tr>
<td>0.30</td>
<td>10.5 : 85.8 : 3.7</td>
<td>8.594(5)</td>
<td>12.492(8)</td>
</tr>
<tr>
<td>0.333</td>
<td>10.2 : 85.2 : 4.6</td>
<td>8.595(1)</td>
<td>12.505(5)</td>
</tr>
<tr>
<td>0.35</td>
<td>10.4 : 85.5 : 4.1</td>
<td>8.598(1)</td>
<td>12.485(7)</td>
</tr>
<tr>
<td>0.375</td>
<td>10.5 : 85.3 : 4.2</td>
<td>8.595(3)</td>
<td>12.488(3)</td>
</tr>
<tr>
<td>0.40</td>
<td>10.5 : 85.8 : 3.7</td>
<td>8.592(4)</td>
<td>12.487(3)</td>
</tr>
<tr>
<td>0.45</td>
<td>10.1 : 85.6 : 4.3</td>
<td>8.600(2)</td>
<td>12.479(8)</td>
</tr>
<tr>
<td>0.50</td>
<td>10.0 : 86.4 : 3.6</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

The x-ray diffraction pattern of the \( (\text{Nd}_{0.5}\text{Ti}_{0.5})\text{Fe}_5 \) sample is different from those of all the other samples. In this pattern, although all the characteristic reflections of the \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_17 \) phase exist, there are also several other peaks. In order to analyze the
structure of the matrix phase formed in the (Nd₀.₅Ti₀.₅)Fe₅ sample, the powder x-ray
diffraction pattern was analyzed using the LAZY PULVERIX program. Figure 5-12
shows the experimental and the calculated theoretical powder diffraction patterns of the
Nd₂(Feₓ₋₅Tiₓ)₁₇ and Nd(Feₓ₋₅Tiₓ)₁₂ phases. From the figure it can be seen that the
experimental diffraction pattern includes all the characteristic reflections of the
rhombohedral Nd₂(Feₓ₋₅Tiₓ)₁₇ and tetragonal Nd(Feₓ₋₅Tiₓ)₁₂ structures. Besides these
reflections, there are some additional reflections (marked with arrows) which cannot be
indexed to any known phase in this system. If this sample is multi-phase with both
Nd₂(Feₓ₋₅Tiₓ)₁₇ and Nd(Feₓ₋₅Tiₓ)₁₂ phases, according to the intensity of the reflections at
2θ = 42.4° and 42.8°, which correspond to the (300) reflection of Nd₂(Feₓ₋₅Tiₓ)₁₇ and the
(301) reflection of Nd(Feₓ₋₅Tiₓ)₁₂, respectively, the sample should comprise at least 30-
40% the Nd(Feₓ₋₅Tiₓ)₁₂ phase. However, this is inconsistent with the SEM/EDAX
results, which show that this sample only has one dominant phase and no trace of the
Nd(Feₓ₋₅Tiₓ)₁₂ phase was identified.

The data from the TGA analysis are consistent with the SEM/EDAX results (see
Figure 5-13). Although the TGA result shows a trace of the Nd(Feₓ₋₅Tiₓ)₁₂ phase in this
sample, the amount of the Nd(Feₓ₋₅Tiₓ)₁₂ phase is very small. This small amount of the
Nd(Feₓ₋₅Tiₓ)₁₂ phase is impossible to generate the strong 1:12-like reflections observed
in the x-ray diffraction pattern. Thus, the 1:12-like reflections must be contributed by
another phase. The only phase which can provide such strong reflections in this sample
is the main matrix phase. Based on this discussion and the fact that several extra peaks
marked by the arrows in the diffraction pattern cannot be indexed to any known phase in
Nd-Fe-Ti systems, we conclude that the matrix phase in this sample is a new phase with
a structure which is related to the rhombohedral Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and tetragonal Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ structures.

Figure 5-12: Powder x-ray diffraction pattern of the 950°C annealed (Nd$_{0.5}$Ti$_{0.5}$)Fe$_5$ sample and the calculated theoretical powder diffraction patterns of the Nd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases. (Co Kα radiation). The peaks marked with arrows cannot be indexed to any known phase in the Nd-Fe-Ti system.

Figure 5-13: TGA result of the 950°C annealed (Nd$_{0.5}$Ti$_{0.5}$)Fe$_5$ sample. The result shows that sample is virtually single phase with a trace of Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ impurity.
5.2.2.3. The samples annealed at 1070°C

After annealing the samples at 1070°C for 3 days, the SEM/EDAX results (Figure 5-14) show that although Nd₂(Fe₁₋ₓTiₓ)₁₇ is still the dominant phase in the low Ti content samples (x ≤ 0.25), Nd₃(Fe₁₋ₓTiₓ)₂₉ and Nd(Fe₁₋ₓTiₓ)₁₂ start to form in the samples with intermediate Ti content (x > 0.25) and became the dominant phase in the higher Ti content samples. Because of the formation of Nd₃(Fe₁₋ₓTiₓ)₂₉ and Nd(Fe₁₋ₓTiₓ)₁₂, the microstructures of the samples annealed at this temperature are totally different from those of the samples annealed at 850°C and 950°C. The compositions of the Nd₂(Fe₁₋ₓTiₓ)₁₇, Nd₃(Fe₁₋ₓTiₓ)₂₉ and Nd(Fe₁₋ₓTiₓ)₁₂ phases, from the EDAX results, are listed in Table 5-5. Like the Nd₂(Fe₁₋ₓTiₓ)₁₇ phase formed in the samples annealed at 850°C and 950°C, all the Nd₂(Fe₁₋ₓTiₓ)₁₇, Nd₃(Fe₁₋ₓTiₓ)₂₉ and Nd(Fe₁₋ₓTiₓ)₁₂ phases in these samples have very well defined stoichiometric composition ratio and show little to no solubility.

The x-ray diffraction results are consistent with the SEM results. Figure 5-15 shows the powder x-ray diffraction patterns of the samples with x = 0.0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5. The patterns of the samples with x < 0.25 have the characteristic reflections of the rhombohedral Nd₂(Fe₁₋ₓTiₓ)₁₇ phase and the patterns of the samples with x ≥ 0.286 reveal that the Nd₃(Fe₁₋ₓTiₓ)₂₉ phase started to become the dominant phase and remains as the dominant phase in all the samples with intermediate and high Ti content, but as the Ti content increases, the amount of the Nd(Fe₁₋ₓTiₓ)₁₂ phase increases accordingly, which is indicated by the intensity of the characterized (0 0 2) and (2 0 2) reflections of Nd(Fe₁₋ₓTiₓ)₁₂ in the diffraction patterns (marked with arrows). Table 5-4 lists the lattice parameters of the main phase in the samples with x = 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5.
Figure 5-14(1): SEM photographs of the 1070°C annealed samples with $x = 0.25$ and 0.3. In the sample with $x = 0.25$, the \( \text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase is the main phase with a small amount of the \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) phase. As the Ti content increases, the \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) phase becomes the dominant phase and the \( \text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) phase also starts to precipitate in the sample with $x = 0.30$. 

Figure 5-14(2): SEM photographs of the 1070°C annealed Nd$_{0.6}$Ti$_{0.4}$Fe$_5$ and Nd$_{0.5}$Ti$_{0.5}$Fe$_5$ samples. The dominant phase in these samples is Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$. As the Ti content increases, more Nd(Fe$_{1-x}$Ti$_x$)$_{12}$ formed.
Table 5-5: EDAX results of $\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$, $\text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ and $\text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12}$ formed in the samples with $x = 0.3, 0.333, 0.375, 0.4$ and $0.5. (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$.

<table>
<thead>
<tr>
<th>$(\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$</th>
<th>Phase</th>
<th>Composition (EDAX) $\text{Nd} : \text{Fe} : \text{Ti} (\pm 0.7 \text{ at.%})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0.30$</td>
<td>$\text{Nd}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17}$</td>
<td>10.5 : 85.9 : 3.6</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}<em>3(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{29}$</td>
<td>9.5 : 85.6 : 4.9</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}(\text{Fe}_{1-x}\text{Ti}<em>x)</em>{12}$</td>
<td>7.9 : 84.7 : 7.4</td>
</tr>
<tr>
<td>$0.333$</td>
<td>$\text{Nd}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17}$</td>
<td>10.3 : 86.4 : 3.3</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}<em>3(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{29}$</td>
<td>9.5 : 86.0 : 4.5</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}(\text{Fe}_{1-x}\text{Ti}<em>x)</em>{12}$</td>
<td>7.8 : 84.5 : 7.7</td>
</tr>
<tr>
<td>$0.375$</td>
<td>$\text{Nd}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17}$</td>
<td>10.5 : 85.6 : 3.9</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}<em>3(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{29}$</td>
<td>9.3 : 85.5 : 5.2</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}(\text{Fe}_{1-x}\text{Ti}<em>x)</em>{12}$</td>
<td>7.9 : 84.4 : 7.7</td>
</tr>
<tr>
<td>$0.40$</td>
<td>$\text{Nd}<em>3(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{29}$</td>
<td>9.6 : 85.1 : 5.3</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}(\text{Fe}_{1-x}\text{Ti}<em>x)</em>{12}$</td>
<td>7.8 : 84.6 : 7.6</td>
</tr>
<tr>
<td>$0.50$</td>
<td>$\text{Nd}<em>3(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{29}$</td>
<td>9.7 : 85.2 : 5.1</td>
</tr>
<tr>
<td></td>
<td>$\text{Nd}(\text{Fe}_{1-x}\text{Ti}<em>x)</em>{12}$</td>
<td>8.0 : 84.2 : 7.8</td>
</tr>
</tbody>
</table>

Table 5-6: The lattice parameters of the matrix phases in the 1070°C annealed $(\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$ samples with $x = 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45$ and $0.5. (\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$.

<table>
<thead>
<tr>
<th>$(\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_5$</th>
<th>Phase</th>
<th>Lattice Parameters $\text{a (Å)}$, $\text{b (Å)}$, $\text{c (Å)}$, $\beta(\degree)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0.10$</td>
<td>2:17</td>
<td>8.593(2) 12.499(9)</td>
</tr>
<tr>
<td>0.20</td>
<td>2:17</td>
<td>8.599(5) 12.493(9)</td>
</tr>
<tr>
<td>0.25</td>
<td>2:17</td>
<td>8.590(3) 12.518(2)</td>
</tr>
<tr>
<td>0.30</td>
<td>3:29</td>
<td>10.710(5) 8.544(1) 9.687(6) 97.704(6)</td>
</tr>
<tr>
<td>0.35</td>
<td>3:29</td>
<td>10.761(2) 8.562(0) 9.832(2) 96.923(2)</td>
</tr>
<tr>
<td>0.40</td>
<td>3:29</td>
<td>10.756(2) 98.584(9) 9.709(9) 97.856(3)</td>
</tr>
<tr>
<td>0.45</td>
<td>3:29</td>
<td>10.755(0) 8.578(7) 9.732(1) 97.670(9)</td>
</tr>
<tr>
<td>0.50</td>
<td>3:29</td>
<td>10.775(0) 8.598(2) 9.733(9) 97.799(5)</td>
</tr>
</tbody>
</table>
Figure 5-15: Powder x-ray diffraction patterns of 1070°C annealed \((\text{Nd})_{1-x}\text{Ti}_x\text{Fe}_5\) samples with \(x = 0.0, 0.1, 0.2, 0.25, 0.30, 0.333, 0.35, 0.40, 0.45\) and 0.50. (Co Kα radiation)
5.3. CONCLUSIONS

Our systematic study of the Nd-Fe-Ti system with samples of \((\text{Nd}_{1-x}\text{Ti}_x)\text{Fe}_3\) \((x = 0.0, 0.1, 0.146, 0.2, 0.25, 0.268, 0.3, 0.333, 0.35, 0.4, 0.419, 0.45\) and 0.5) revealed that there are four primary phases in this system and the third element Ti plays a key role in the stabilization of these phases.

In the as-cast samples, only the \(\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}\) or \(\text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12}\) phases formed in the samples with low or high Ti contents. The dominant matrix phases in the samples with intermediate Ti content are very inhomogeneous and their compositions cover a broad range continuously from the 2:17 composition to the 1:12 composition. The x-ray results show a 1:7 associated diffraction pattern indicating that a new phase with a 1:7 related structure exists in these samples.

The phase formation at the Fe-rich corner of the Nd-Fe-Ti system at 900°C and 1100°C was reported by Jang\(^{20}\) and Margarian\(^{31}\), et. al. They pointed out that the 1:12 and 3:29 phases do not stabilize below 900°C. Our results show that they still do not stabilize at up to 950°C. In order to obtain the pure \(\text{Nd}_2(\text{Fe}_{1-x}\text{Ti}_x)_{29}\) phase, annealing at temperature above 1070°C is necessary. However, to prepare pure \(\text{Nd}(\text{Fe}_{1-x}\text{Ti}_x)_{12}\), the annealing temperature has to be even higher.

It should be noted that there is no 2:17, 3:29 and 1:12 co-existence region in the 1100°C phase diagram given by Margarian, et. al. This contradicts the results obtained in our samples with mediate and high Ti content. In these samples, it is common observation that the three phases co-exist in the same samples.
Although the Nd₃(Fe₁₋ₓTiₓ)₂₉ and Nd(Fe₁₋ₓTiₓ)₁₂ phases do not crystallize in the samples annealed at relatively low temperatures, 850°C and 950°C, the results showed the trace of some other possible new phases between 2:17 and 1:12. One of these phases has a composition Nd : R : Ti = 8.3~9.2 : 81.9~84.3 : 6.4~9.2, which, if it exists, must have a very slow formation speed. Another phase has a composition Nd : R : Ti = 10.25 : 86.0~86.22 : 3.53. Its structure is closely related to the Th₂Zn₁₇ and ThMn₁₂ structures.
REFERENCES


Chapter Six

PHASE FORMATION AND TRANSFORMATION IN THE Fe CORNER OF THE Gd-Fe-Ti SYSTEM

6.1. INTRODUCTION

Depending on R, the $R_2T_{17}$ phase crystallizes in two different structures resulting from different dumb-bell replacement sequences. The rhombohedral Th$_2$Zn$_{17}$-type 2:17 phase crystallizes in the ‘light’ rare-earth and Y, Gd, Tb systems and the hexagonal Th$_2$Ni$_{17}$-type 2:17 phase crystallizes in the ‘heavy’ rare-earth systems.

In Chapters 3 and 4, the existence of two novel phases, namely $R_3(Fe_{1-x}Si_x)_{22}$ ($R$ = Gd, Tb, Dy, Ho, Er, Tm and Lu) and Nd$_3(Fe_{1-x}Ti_x)_{29}$, were reported. $R_3(Fe_{1-x}Si_x)_{22}$ is an intermediate phase between the 1:5 and 2:17 phases and, like the 2:17 phase, it also crystallizes in two different structures depending on R. In the systems with R = Gd and Tb, it has a structure closely related to the rhombohedral Th$_2$Zn$_{17}$-type structure and in the systems with R = Dy, Ho, Er, Tm and Lu, its structure is intimately related to the hexagonal Th$_2$Ni$_{17}$-type structure. In the dumb-bell replacement point of view, the 3:22 structures correspond to a replacement of $\frac{1}{4}$ large R atoms with pairs of the transition metal atoms (dumb-bells) in the 1:5 structure. Two different structures are resulted from different replacement orders. In terms of the coordination shells of the particularly large R atoms (CPR), the structure of the 3:22 phase with R = Dy, Ho, Er, Tm and Lu is intermediate between the Th$_2$Ni$_{17}$-type 2:17 and 1:12 structures and is a simple 2:1 stacking of hexagonal Th$_2$Ni$_{17}$-type and ThMn$_{12}$-type structural units.
The novel Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase has been identified as an intermediate phase between the rhombohedral 2:17 and tetragonal 1:12 phases. It crystallizes generally in the LR-Fe-T systems (LR = Nd$^{1,2}$, Pr$^3$, Sm$^4$, and Y$^5$; T = Ti, V, Cr, Mn$^{6,7}$ and Mo$^8$), where the 2:17 phase crystallizes in the rhombohedral Th$_2$Zn$_{17}$-type structure. Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ has a monoclinic structure with space group of A2/m$^9$ and is formed simply by a 1:1 stacking of the rhombohedral 2:17 and tetragonal 1:12 structural units.

As mentioned above, the R$_3$(Fe$_{1-x}$Si$_x$)$_{29}$ phase undergoes a change of structure correlated with that undergone by the 2:17 phase from the rhombohedral structure to the hexagonal structure as R changes from Gd, Tb to Dy. The Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase was identified only in the 'light' rare-earth systems where the 2:17 phase crystallizes in the rhombohedral structure. This raises the question as to whether the R$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase also crystallizes in the "heavy" rare earth systems but undergoes a structural change as R changes from 'light' rare earth elements to 'heavy' rare earth elements, resulting in another novel intermediate structure between the hexagonal 2:17 and tetragonal 1:12 structures.

In an attempt to identify the possible intermediate phases between the 2:17-H and 1:12-T phases, the Gd-Fe-Ti, Tb-Fe-Ti and Dy-Fe-Ti systems were selected based on two considerations: (1) the R$_2$M$_{17}$ phase will change the structure from the Th$_2$Zn$_{17}$-type to the Th$_2$Ni$_{17}$-type when R changes from Gd, Tb to Dy, (2) as in the 1:12-T phase, the new 3:29 phase does not exist in binary R-Fe systems and a third element (Ti) is essential to stabilize its structure. In this chapter, we will report the results of our systematic study of the Gd-Fe-Ti system. In the following two chapters the results on the Tb-Fe-Ti and Dy-Fe-Ti systems will be presented.
6.2. RESULTS AND DISCUSSIONS

Samples with starting compositions $\text{Gd}_{10.5}\text{Fe}_{86}\text{Ti}_{3.5}$, $\text{Gd}_{8.5}\text{Fe}_{86}\text{Ti}_{5.5}$, $\text{Gd}_{8.5}\text{Fe}_{85}\text{Ti}_{1.5}$, $\text{Gd}_{8.5}\text{Fe}_{82}\text{Ti}_{9.5}$, $\text{Gd}_{8.5}\text{Fe}_{80.5}\text{Ti}_{11}$, $\text{Gd}_{7.5}\text{Fe}_{86}\text{Ti}_{6.5}$, $\text{Gd}_{7.5}\text{Fe}_{85}\text{Ti}_{7.5}$ and $\text{Gd}_{7.5}\text{Fe}_{84}\text{Ti}_{8.5}$ were prepared by arc-melting the pure Gd, Fe and Ti metals (>99.9%) with 10 wt.% excess Gd. The selected samples were annealed at 1000°C, 1090°C, respectively, for a period of 3 days. All the samples were characterized by XRD, SEM/EDAX, Mössbauer spectroscopy and TGA.

![Figure 6-1: Powder x-ray diffraction patterns of the (a) 1000°C annealed $\text{Gd}_{10.5}\text{Fe}_{86}\text{Ti}_{3.5}$ (2:17R with some 1:3 impurity) and (b) 1090°C annealed $\text{Gd}_{8.5}\text{Fe}_{86}\text{Ti}_{5.5}$ (3:29) samples (Cu Kα radiation). Solid bars are the calculated diffraction patterns of 2:17R and 3:29 based on the indexation of the experimental data.](image)
Figure 6-2: Powder x-ray diffraction patterns of (a) as-cast Gd$_{7.5}$Fe$_{85}$Ti$_{7.5}$ (1:12-T), (b) 1000°C annealed Gd$_{7.5}$Fe$_{85}$Ti$_{7.5}$, (new P$_{1}$1$_{2}$ phase, the arrows indicate its structural difference from the 1:12 structure) and (c) 1000°C annealed Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$, (1:11) (Co Ka radiation). In the Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$ sample some Gd(Fe$_{1-x}$Ti$_{x}$)$_{12}$ impurity is present. Solid bars are the calculated diffraction patterns based on the indexation of the experimental data.
Our results show that at least five intermetallic compounds exist in the Fe corner of the ternary Gd-Fe-Ti system above 1000°C. Besides the well known 2:17, 1:12 and 1:11 phases, two novel phases have been identified as a new Nd₃(Fe₁₋ₓTiₓ)₂₉-type Gd₃(Fe₁₋ₓTiₓ)₂₉ phase and a new tetragonal 1:12 related phase (P₁₁₂). Figure 6-1 shows the powder x-ray diffraction patterns (Cu Kα radiation) of the Gd₃(Fe₁₋ₓTiₓ)₁₇ and Gd₃(Fe₁₋ₓTiₓ)₂₉ phases obtained in the 1000°C annealed Gd₁₀.₅Fe₆₆Ti₅₃ and 1090°C annealed Gd₈.₅Fe₄₆Ti₅₅ samples. Figure 6-2 shows the powder x-ray diffraction patterns (Co Kα radiation) of the Gd(Fe₁₋ₓTiₓ)₁₂, P₁₁₂ and Gd(Fe₁₋ₓTiₓ)₁₁ phases obtained in the as-cast Gd₇₅Fe₈₅Ti₇₅ and 1000°C annealed Gd₈₅Fe₈₄Ti₇₅ and Gd₈₅Fe₈₀₅Ti₇₅ samples. The compositions (EDAX results), lattice parameters and magnetic ordering temperatures Tc of those phases are listed in Table 6-1.

Table 6-1: Phases formed in the Fe corner of the Gd-Fe-Ti system and their compositions, lattice parameters and magnetic ordering temperatures (Tc).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition Gd : Fe : Ti (±0.6 at.%)</th>
<th>Structure</th>
<th>Lattice Parameters a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β(°)</th>
<th>Tc (±10K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:17</td>
<td>9.7 : 86.4 : 3.9</td>
<td>Th₂Zn₁₇</td>
<td>8.561(3)</td>
<td>-</td>
<td>12.476(3)</td>
<td>-</td>
<td>504</td>
</tr>
<tr>
<td>3:29</td>
<td>9.1 : 85.7 : 5.2</td>
<td>Nd₃(Fe,Ti)₂₉</td>
<td>10.640(9)</td>
<td>8.565(8)</td>
<td>9.737(5)</td>
<td>97.017(1)</td>
<td>524</td>
</tr>
<tr>
<td>1:12</td>
<td>7.2<del>7.9 : 84.1</del>86.1 : 6.7~8.4</td>
<td>ThMn₁₂</td>
<td>8.543(7)</td>
<td>-</td>
<td>4.793(4)</td>
<td>-</td>
<td>601</td>
</tr>
<tr>
<td>P₁₁₂</td>
<td>6.9<del>7.1 : 84.8</del>86.0 : 6.9~8.3</td>
<td>unknown</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>612</td>
</tr>
<tr>
<td>1:11</td>
<td>7.8 : 81.3 : 10.9</td>
<td>BaCd₁₁</td>
<td>8.237(7)</td>
<td>-</td>
<td>4.848(3)</td>
<td>-</td>
<td>&lt;RT</td>
</tr>
</tbody>
</table>
6.2.1. THE Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ PHASE

The SEM/EDAX and XRD results reveal that the as-cast and $1000^\circ$C annealed Gd$_{10.5}$Fe$_{86}$Ti$_{3.5}$ samples formed a dominant matrix Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase (>90 vol.%) with a very small amount of impurity phase in the intergranular regions (see Figure 6-4). The powder x-ray diffraction patterns of both the as-cast and annealed samples have the characteristic reflection pattern of the rhombohedral Th$_2$Zn$_{17}$-type structure. The composition of the rhombohedral Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase obtained by EDAX analysis is Gd : Fe : Ti = 9.7(±0.6) : 86.2(±0.5) : 3.9(±0.4) and the composition of the impurity phase in the intergranular area is Gd : Fe : Ti = 18.8(±0.5) : 78.5(±0.7) : 2.5(±0.5). No trace of the hexagonal Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase was identified in this study. Thus, the hexagonal 2:17 phase does not crystallize in the Gd-Fe-Ti systems under the conditions employed in this work.

![SEM photograph of the as-cast Gd$_{10.5}$Fe$_{86}$Ti$_{3.5}$ sample.](image)

(a) as-cast Gd$_{10.5}$Fe$_{86}$Ti$_{3.5}$

*Figure 6-3(1): SEM photograph of the as-cast Gd$_{10.5}$Fe$_{86}$Ti$_{3.5}$ sample. It comprises a dominant matrix 2:17 phase with small amounts of the Gd$_6$(Fe$_{1-x}$Ti$_x$)$_{23}$/Gd(Fe$_{1-x}$Ti$_x$)$_3$ impurities in the intergranular area.*

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Figure 6-3(2): SEM photograph of 1000°C annealed Gd$_{10.5}$Fe$_{86}$Ti$_{3.5}$. It has a similar microstructure to that of the as-cast sample with a dominant matrix 2:17 phase and small amounts of impurities. Annealing homogenized the matrix phase.

The Curie temperature and average $^{57}$Fe hyperfine field (at room temperature) of this Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ are 504(±10)K and 20.0(±0.2)T, respectively. Its lattice parameters deduced from the x-ray diffraction data are $a = 8.561(3)$Å and $c = 12.476(3)$Å.

6.2.2. THE Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ PHASE

Figure 6-5 shows the SEM photographs of the as-cast and 1080°C annealed Gd$_8.5$Fe$_{86}$Ti$_{5.5}$ samples. The as-cast sample is multi-phase with approximately equal amounts of the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases. After annealing the sample became virtually single phase with only a very small amount of impurities. The EDAX results show that the dominant matrix phase of the annealed sample has a composition Gd : Fe : Ti = 9.1 : 85.7 : 5.2(±0.4 at.%), which is similar to that observed in the novel Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase reported in Chapter 4 (Nd : Fe : Ti = 9.4 : 86.5 : 4.1), but has a slightly higher Ti content. The impurities in this sample were identified as Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Gd(Fe$_{1-x}$Ti$_x$)$_{12}$.  

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Figure 6-4: SEM photographs of the as-cast and 1080°C annealed Gd$_{8.5}$Fe$_{86}$Ti$_{5.5}$ samples. The as-cast sample is multi-phase with approximately equal amounts of Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Gd(Fe$_{1-x}$Ti$_x$)$_{12}$. After annealing, the sample became virtually single phase Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ with a very small amount of Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ impurities.
The powder x-ray diffraction data of the annealed sample shows the characteristic reflections of the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$-type structure (see Figure 6-1(b)). Therefore, the novel Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$-type 3:29 phase also crystallizes in the Gd-Fe-Ti system. This result is readily understandable. As an intermediate phase between the rhombohedral 2:17 and tetragonal 1:12 phases, the 3:29 phase is formed simply by the alternate stacking of the rhombohedral Th$_2$Zn$_{17}$ and tetragonal ThMn$_{12}$ structural units. In the Gd-Fe-Ti system, Gd$_3$(Fe$_{1-x}$Ti$_x$)$_29$ crystallizes in the rhombohedral Th$_2$Zn$_{17}$-type structure and consequently, the formation of the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_29$ phase is expected.

As mentioned in Chapter 4, the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$ phase, like the tetragonal 1:12 phase, does not stabilize in any binary R-Fe systems and a specific amount of third element, Ti, is essential to stabilize the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$ structure. The role of the third element (Ti) in stabilizing this structure is an atomic size effect. Since the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$-type structure contains half of the rhombohedral Th$_2$Zn$_{17}$-type structural units and half of the tetragonal ThMn$_{12}$-type structural units, the amount of the third element (Ti) needed to stabilize the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_29$-type structure, as discussed in Chapter 4, should be around $\frac{1}{2} \times Ti\%_{1:12} + \frac{1}{2} \times Ti\%_{2:17}$. In the Gd-Fe-Ti system, the Ti contents determined by the EDAX results are 3.9 at.% for the Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase and 6.7 ~ 8.4 at.% for the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase. Considering that a 6.7 at.% Ti content is sufficient to stabilize the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ structure, the Ti content for the new Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase will be about $\frac{1}{2} \times 3.9 \text{ at.}\% + \frac{1}{2} \times 6.7 \text{ at.}\% = 5.25 \text{ at.}\%$. Comparing with the EDAX result (5.2 at%), the calculated Ti content for the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase matches the
experimental results well. Thus, the slightly higher Ti content observed in Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ is vital in stabilizing this Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ compound.

6.2.3. THE Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ PHASE

Approximately single-phase Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ was obtained in the as-cast Gd$_{7.5}$Fe$_{86}$Ti$_{6.5}$, Gd$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Gd$_{7.5}$Fe$_{84}$Ti$_{8.5}$ samples. Figure 6-6 shows the SEM microstructure photographs of these samples. All three as-cast samples are approximately single phase with only a very small amount of impurities in the intergranular area. The EDAX results of the matrix phases in these samples are listed in Table 6-2. Although the compositions of the matrix phases in these samples are slightly different, the powder x-ray diffraction patterns of all three samples are the same (see Figure 6-7). All the patterns are characterized by the typical reflections of the ThMn$_{12}$-type structure. Table 6-2 lists the lattice parameters of the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ formed in these three samples. The lattice parameters are slightly different because of different compositions.

![SEM photograph of the as-cast (a) Gd$_{7.5}$Fe$_{86}$Ti$_{6.5}$ sample. It is approximately single phase with only a very small amount of impurities (<8 vol.%).](image)

Figure 6-5(1): SEM photograph of the as-cast (a) Gd$_{7.5}$Fe$_{86}$Ti$_{6.5}$ sample. It is approximately single phase with only a very small amount of impurities (<8 vol.%).
Figure 6-5(2): SEM photographs of the as-cast (b) Gd\textsubscript{7.5}Fe\textsubscript{85}Ti\textsubscript{7.5} and (c) Gd\textsubscript{7.5}Fe\textsubscript{84}Ti\textsubscript{8.5} samples. They are approximately single phase with a very small amount of impurities in the intergranular area.
Figure 6-6: Powder x-ray diffraction patterns of the as-cast (a) Gd$_{7.5}$Fe$_{8.5}$Ti$_{6.5}$, (b) Gd$_{7.5}$Fe$_{8.5}$Ti$_{7.5}$ and (c) Gd$_{7.5}$Fe$_{8.5}$Ti$_{8.5}$ samples with Co Kα radiation. All the patterns show the characteristic reflections of the ThMn$_{12}$-type structure (refer to figure 6-2a).
Table 6-2: The compositions (EDAX) and the lattice parameters of the Gd(Fe_{1-x}Ti_x)_{12} phases formed in the as-cast Gd_{75}Fe_{85}Ti_{17.5}, Gd_{75}Fe_{85}Ti_{17.5} and Gd_{75}Fe_{85}Ti_{17.5} samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (EDAX) Gd : Fe : Ti (at.%)</th>
<th>Lattice parameters a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd_{75}Fe_{86}Ti_{6.5}</td>
<td>7.2(±0.5) : 86.1(±0.5) : 6.7(±0.1)</td>
<td>8.5418(6)</td>
<td>4.7996(1)</td>
</tr>
<tr>
<td>Gd_{75}Fe_{84}Ti_{8.5}</td>
<td>7.5(±0.4) : 84.6(±0.5) : 7.9(±0.3)</td>
<td>8.5437(3)</td>
<td>4.7933(8)</td>
</tr>
<tr>
<td>Gd_{75}Fe_{84}Ti_{8.5}</td>
<td>7.5(±0.4) : 84.1(±0.2) : 8.4(±0.3)</td>
<td>8.5499(8)</td>
<td>4.8001(8)</td>
</tr>
</tbody>
</table>

6.2.4. A NEW ALTERNATIVE 1:12 PHASE

After annealing the Gd_{75}Fe_{86}Ti_{6.5}, Gd_{75}Fe_{85}Ti_{7.5} and Gd_{75}Fe_{84}Ti_{8.5} samples at 1000°C and 1100°C for three days, the SEM results revealed that the annealed samples remained virtual single phase and the annealing procedures simply homogenized the samples. Figure 6-8 shows the SEM photographs of the 1000°C annealed samples. The compositions of the matrix phases in these three annealed samples, determined by EDAX, are Gd : Fe : Ti = 7.1(±0.3) : 86.3(±0.3) : 6.6(±0.2) for Gd_{75}Fe_{86}Ti_{6.5}, Gd : Fe : Ti = 7.1(±0.1) : 85.9(±0.2) : 6.9(±0.2) for Gd_{75}Fe_{85}Ti_{7.5} and Gd : Fe : Ti = 6.9(±0.2) : 84.8 (±0.7) : 8.3(±0.5) for Gd_{75}Fe_{84}Ti_{8.5}.

Comparing with the EDAX results of the as-cast samples, the composition of the matrix phase in the annealed samples is approximately the same as those of the Gd(Fe_{1-x}Ti_x)_{12} phase formed in the as-cast samples. However, the powder x-ray diffraction results show that, after annealing, the tetragonal Gd(Fe_{1-x}Ti_x)_{12} phase is transformed into a new phase with a structure closely related to the tetragonal 1:12 structure.
Figure 6-7(1): SEM microstructure photographs of the 1000°C annealed Gd$_{7.5}$Fe$_{86}$Ti$_{6.5}$ and Gd$_{7.5}$Fe$_{85}$Ti$_{7.5}$ samples. They are virtually single phase.
Figure 6-7(2): SEM microstructure photograph of 1000°C annealed Gd7.5Fe84Ti8.5.

Figure 6-8 shows the powder x-ray diffraction patterns of the samples annealed at 1000°C for 3 days. From the patterns, it can be seen that between 2θ = 20 ~ 70° (with Co Kα radiation), all the characteristic reflections of the ThMn12-type structure exist. However, in addition to these characteristic tetragonal 1:12 peaks two extra reflections at 2θ = 33.3° and 66.5° are apparent. These two peaks can not be indexed to any known phases nor to the oxidizes in the system. Combining the fact that the samples are roughly single phase, it can be concluded that a new phase formed upon annealing. The similarity of the x-ray diffraction patterns of the new phase and the tetragonal Gd(Fe1-xTi12 phase suggests that these two phases should have very similar structures. We shall refer to this new phase as P1:12, since it has an approximately the same composition as the tetragonal 1:12 phase and its structure is also closely related to the tetragonal 1:12 structure.

The 1100°C annealed Gd7.5Fe86Ti6.5, Gd7.5Fe85Ti7.5 and Gd7.5Fe84Ti8.5 samples show the same results as the 1000°C annealed samples mentioned above. After annealing, the tetragonal 1:12 phase transformed into the new P1:12 phase.
Figure 6-8: Powder x-ray diffraction patterns of the 1000°C annealed Gd$_{7.5}$Fe$_{86.0}$Ti$_{18.5}$, Gd$_{7.5}$Fe$_{85}$Ti$_{17.5}$ and Gd$_{7.5}$Fe$_{84}$Ti$_{18.5}$ samples (Co Kα radiation). Peaks marked with arrows are superlattice reflections. In (c) we also show the calculated pattern of tetragonal 1:12 structure in order to compare the difference between the new $P_{112}$ phase and the tetragonal 1:12 phase.
Thus, in the Gd-Fe-Ti system, the tetragonal Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase only stabilizes in the as-cast samples. After annealing it transforms into a new phase with a new structure that is closely related to the tetragonal 1:12 structure. This suggests that in the composition range used in this work, the new P$_{1:12}$ structure is more stable than the tetragonal 1:12 structure in the Gd-Fe-Ti system.

Although the new P$_{1:12}$ phase, like the tetragonal Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase, stabilizes in a composition range, its structure modifies slightly as the Ti content changes. This is reflected in the intensity of its two characteristic reflections at $2\theta=33.3^\circ$ and $66.5^\circ$. From figure 9-8 it can be seen clearly that the characteristic peaks of the P$_{1:12}$ phase in the pattern of the Gd$_{7.5}$Fe$_{86}$Ti$_{6.5}$ sample (with low Ti content) are barely visible. As the Ti content increased, the intensity of these two peaks increased accordingly.

As we already mentioned above, the ThMn$_{12}$-type phase does not crystallize in the binary R-Fe systems and a third element, such as Ti, V, Si, Al, Mo and W, is essential to stabilize it. In the present work, although the structure of the new P$_{1:12}$ phase is unknown, the results clearly show that the third element Ti plays a very important role in stabilizing this new structure.

The magnetic ordering temperature ($T_c$) of the new phase derived from TGA results is 512 (±10) K that is nearly the same as that of the tetragonal Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase. This also indicates the close relationship between these two phases.

6.2.5. THE 1:11 PHASE

Although the new P$_{1:12}$ phase can stabilize over quite a broad Ti content range, this phase is replaced by the tetragonal Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ phase (with the BaCd$_{11}$-type structure) if the Ti content is too high.
Figure 6-9: SEM photographs of (a) as-cast and (b) annealed Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$. Both comprise a dominant matrix phase with a small amount of impurity phases in the intergranular regions.
Figure 6-9 shows the SEM photographs of the as-cast and 1000°C annealed Gd₈₅Fe₈₀₅Ti₁₁ samples. The as-cast sample is virtually single phase with a dominant matrix phase ( >95 vol.% ) and very small amounts of Fe₂Ti and a Gd-rich impurity phase in the intergranular area. The EDAX results give the composition of the matrix phase as Gd : Fe : Ti = 7.2(±0.2) : 83.2(±0.3) : 9.6(±0.2)—approximately a 1:12 composition ratio, but with a very high Ti content. The composition of the phase in the boundary area is Gd : Fe : Ti = 28.8(±1.2) : 68.8(±0.4) : 2.4(±0.8) —approximately a 6:23 composition ratio.

The powder x-ray diffraction pattern of the as-cast Gd₈₅Fe₈₀₅Ti₁₁ sample is shown in Figure 6-10. Because the matrix phase and the impurity phase have compositions close to the 1:12 and 6:23 ratios, respectively, the calculated powder x-ray diffraction patterns of the Gd(Fe₁ₓTiₓ)₁₂ and Gd₆(Fe₁ₓTiₓ)₂₃ phases are shown in Figure 6-10 in order to analyze the sample. The results indicate that the diffraction pattern of this sample cannot be indexed as a combination of the Gd(Fe₁ₓTiₓ)₁₂ and Gd₆(Fe₁ₓTiₓ)₂₃ phases, but rather a combination of the tetragonal 1:12 and 1:3 phases. Thus, the calculated diffraction pattern of the Gd(Fe₁ₓTiₓ)₃ phases is shown in Figure 6-10 as well. It can be seen that the experimental diffraction pattern also cannot be indexed as a combination of the Gd(Fe₁ₓTiₓ)₁₂ and Gd(Fe₁ₓTiₓ)₃ phases. There are two inconsistencies if one considers the sample a mixture of the Gd(Fe₁ₓTiₓ)₁₂ and Gd(Fe₁ₓTiₓ)₃ phases. First, if this x-ray diffraction pattern is indexed as a combination of the Gd(Fe₁ₓTiₓ)₁₂ and Gd(Fe₁ₓTiₓ)₃ phases, there should be a strong (1 0 7) reflection at 31.4° from the 1:3 phase, but no such reflection is evident in the experimental diffraction pattern. Second, if the peaks at 34.4° and 40.5° are from the (0 1 6) and (1 1
6), (116) reflections of Gd(Fe, Ti) phase, the sample should contain more than 15% of the Gd(Fe, Ti) phase according to the relative intensities of these reflections. However, SEM clearly shows that the sample has less than 5% of the Gd-rich boundary phase. Combining the SEM/EDAX and powder x-ray diffraction results, it appears that the matrix phase in this sample may be a new phase. The same results were also observed in the as-cast samples with high Ti content in the Tb-Fe-Ti and Dy-Fe-Ti systems. In the following two chapters this phase will be further discussed.

Figure 6-10: Powder x-ray diffraction pattern of the as-cast Gd,5Fe80,5Ti11 sample. The solid bars underneath are the calculated diffraction patterns of the Gd(Fe, Ti)12, Gd(Fe, Ti)3 and Gd(Fe, Ti)23 phases.
After annealing, the Fe$_7$Ti impurity disappeared and the sample became two phases with a dominant Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ matrix phase and a small amount of an intergranular impurity phase. The composition of the Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ phase from EDAX is Gd : Fe : Ti = 7.8 : 81.3 : 10.9 (±0.6 at.%). The impurity phase in the intergranular regions has a composition of Gd : Fe : Ti = 9.2 : 85.8 : 5.0 (±0.8 at.%), which is identical to that of Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$.

Figure 6-2(c) is the powder x-ray diffraction pattern of the annealed Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$ sample that has the characteristic reflections of the BaCd$_{11}$-type structure with several peaks from the impurity phase. The lattice parameters of the Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ phase, derived from the x-ray diffraction data, are $a = 8.2401(9)$Å and $c = 4.8407(2)$Å. The magnetic ordering temperature of the Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ is below room-temperature and thus could not be determined by TGA.

6.3. CONCLUSIONS

Our study has shown that there are at least 5 ternary phases in the Fe corner of the Gd-Fe-Ti ternary system. Besides the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$, the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ and the Gd(Fe$_{1-x}$Ti$_x$)$_{11}$ phases, two new phases have been identified as the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and P$_{1:12}$ phases.

Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, like Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, is an intermediate phase between the rhombohedral Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$, and tetragonal Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phases and has the monoclinic Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type structure. The formation of the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase in the Gd-Fe-Ti system is consistent with the fact that Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$ crystallizes in the rhombohedral Th$_2$Zn$_{17}$-type structure.
The third element Ti plays a key role in stabilizing Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, which can be seen by the fact that the Ti content needed to stabilize Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ is equal to $\frac{1}{2} \cdot $ Ti$_{2:17}$ + $\frac{1}{2} \cdot $ Ti$_{1:12}$, since the 3:29 structure is a simple 1:1 stacking of the rhombohedral 2:17 and tetragonal 1:12 structural units.

The P$_{1:12}$ phase has a structure that is closely related to that of the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase. The difference between these two structures are the characteristic superlattice peaks of the P$_{1:12}$ phase at 2$\theta$ = 33.3° and 66.5° (Co Kα radiation). The compositions of the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phases are approximately identical. They stabilize over the same Ti content range. However, the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase was found to stabilize in the as-cast samples and after annealing the Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ phase transforms into the new P$_{1:12}$ phase. The Ti atoms also play a key role in this structural transformation, which is reflected in the intensity of the characteristic superlattice peaks of the P$_{1:12}$ phase. As the Ti content decreases, the intensities of the characteristic superlattice peaks of the P$_{1:12}$ phase decrease accordingly.

Considering the x-ray diffraction and the SEM/EDAX results, in figure 6-11 we present the Fe corner of the isothermal phase diagram of the Gd-Fe-Ti ternary system at 1000°C. This phase diagram is not an accurate representation, because it is solely based on SEM, EDAX and XRD results from our limited samples mentioned above.

The magnetic ordering temperatures determined by thermo-gravimetric analysis (TGA) for all the samples are given in Table 6-1. As observed in other R-Fe-Ti$^{1,6}$ systems, the magnetic ordering temperature ($T_c$) increases in the order 2:17R $\Rightarrow$ 3:29 $\Rightarrow$ 1:12 $\Rightarrow$ P$_{1:12}$. The Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase has a $T_c$ between the Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$ and the
Gd(Fe_{1-x}Ti_x)_{12} reflecting the fact that the novel 3:29 phase is an intermediate phase between those two phases. The Curie temperature of the new P_{1:12} phase is nearly the same as that of the Gd(Fe_{1-x}Ti_x)_{12} phase, which, together with the x-ray diffraction results suggests that both phases are closely related with each other.

Figure 6-11: The Fe corner of the 1000(C isothermal ternary phase diagram of the Gd-Fe-Ti system. This phase diagram is only a schematic representation and solely based on the SEM/EDAX and x-ray diffraction results of our limited number of samples.
REFERENCES


Chapter Seven:

PHASE FORMATION AND TRANSFORMATION IN
THE Fe CORNER OF THE Tb-Fe-Ti SYSTEM

7.1. INTRODUCTION

In the previous chapters we have reported two new phases, an \(R_3(\text{Fe}_{1-x}\text{Si}_x)_{22}\) phase \((R = \text{Gd, Tb, Dy, Er, Ho, Tm and Lu})\) and a \(R_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}\) phase \((R = \text{Nd and Gd})\). \(R_3(\text{Fe}_{1-x}\text{Si}_x)_{22}\) \((3:22)\) is an intermediate phase between the 1:5 and 2:17 phases and, like the 2:17 phase, undergoes a change of structure correlated with that undergone by \(R_2T_{17}\) as \(R\) changes from Gd, Tb to Dy (Chapter 3).

The \(R_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}\) \((3:29)\) phase is an intermediate phase between the hexagonal \(\text{Th}_2\text{Ni}_{17}\)-type 2:17 and 1:12 phases. So far it has been observed generally in the ‘light’ rare-earth systems, such as the \(\text{Pr-Fe-Ti}\), \(\text{Nd-Fe-Ti}\), and \(\text{Sm-Fe-Ti}\) systems, as-well as \(\text{Y-Fe-Ti}\) system \(^5\), where the 2:17 phase crystallizes in the rhombohedral \(\text{Th}_2\text{Zn}_{17}\)-type structure.

The results above consequently lead to the question of whether the 3:29 phase also crystallizes in the “heavy: rare earth systems but, like the 2:17 and 3:22 phases, undergoes a structural change as \(R\) changes from the “light” rare earths to “heavy” rare-earths, resulting in a new intermediate structure between the hexagonal \(\text{Th}_2\text{Ni}_{17}\)-type and tetragonal \(\text{ThMn}_{12}\)-type structures.

To identify the possible new phase between the hexagonal 2:17 and tetragonal 1:12 phases, the Gd-Fe-Ti, Tb-Fe-Ti and Dy-Fe-Ti systems have been selected
considering that the structure of the $R_{2}T_{17}$ phase transforms from rhombohedral to hexagonal, as $R$ changes from Gd to Tb and Dy. The results of the systematic study on the Gd-Fe-Ti system (reported in Chapter 6) show that in the ternary Gd-Fe-Ti system, the Gd$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase crystallizes in the rhombohedral structure and accordingly the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase was identified in this system. In this chapter we will report the results of our systematic study on the Tb-Fe-Ti system.

Besides Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, another new phase was also observed in the Gd-Fe-Ti system. This new phase has a similar composition as Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ and its structure is closely related to Gd(Fe$_{1-x}$Ti$_x$)$_{12}$. This structural derivation of the tetragonal 1:12 phase has not been observed in any “light” rare earth systems.

Thus, succeeding the results of the Gd-Fe-Ti system, the focus of this study has been extended to include the following questions: (i) what does Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ crystallize in? (ii) does the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase or some other new intermediate phases between 2:17 and 1:12 exist in this system? (iii) does P$_{1;12}$ also crystallize in the Tb-Fe-Ti system?

In order to study this system, samples with starting compositions Tb$_{10.5}$Fe$_{89.5}$, Tb$_{10.5}$Fe$_{88}$Ti$_{1.5}$, Tb$_{10.5}$Fe$_{87}$Ti$_{2.5}$, Tb$_{10.5}$Fe$_{86.5}$Ti$_{3}$, Tb$_{8.5}$Fe$_{89}$Ti$_{2.5}$, Tb$_{8.5}$Fe$_{88}$Ti$_{3.5}$, Tb$_{8.5}$Fe$_{86}$Ti$_{5.5}$, Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$, Tb$_{7.5}$Fe$_{90}$Ti$_{2.5}$, Tb$_{7.5}$Fe$_{88}$Ti$_{4.5}$, Tb$_{7.5}$Fe$_{87}$Ti$_{5.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ (with 10 wt.% excess of Tb) were prepared. Annealing was carried out at 3 different temperatures, 1000°C, 1090°C and 1100°C, respectively, in a vacuumed quartz tube under a partial Ar atmosphere for a period of 3 days. The samples were characterized by (i) powder x-ray diffraction (XRD) with Co or Cu Kα radiation, (ii) SEM equipped with EDAX and (iii) modified TGA for Tc measurement.
7.2. RESULTS AND DISCUSSION

Our systematic study based on these samples shows that the phase formation in this system is more complicated than the other systems that have been studied. There are at least 7 phases crystallizing in the Fe corner of the Tb-Fe-Ti system. They were identified as (1) rhombohedral $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ (2:17-R), (2) hexagonal $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ (2:17-H), (3) the new $\text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$-type $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ (3:29) phase, (4) another new intermediate phase between 2:17 and 1:12 which is presumably an phase related to the hexagonal 2:17 phase, (5) the tetragonal $\text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12}$ phase, (6) the new $P_{1:12}$ phase that has been identified in the Gd-Fe-Ti system and (7) $\text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{11}$. Both the Tb and Ti contents play key roles in the stabilization and transformation of these phases.

7.2.1. THE $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ PHASE

As with all the other R-Fe-Ti systems that have been reported in the previous chapters, the samples with relatively high Tb and low Ti contents form the $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ phase. However, in contrast to the Nd-Fe-Ti and Gd-Fe-Ti systems, $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ can crystallize in both the rhombohedral $\text{Th}_2\text{Zn}_{17}$-type and hexagonal $\text{Th}_2\text{Ni}_{17}$-type structures, depending on the Tb and Ti contents.

Figure 7-1 shows the SEM photographs of the $\text{Tb}_{10.5}\text{Fe}_{89.5}$, $\text{Tb}_{10.5}\text{Fe}_{88}\text{Ti}_{1.5}$, $\text{Tb}_{10.5}\text{Fe}_{87}\text{Ti}_{2.5}$, $\text{Tb}_{8.5}\text{Fe}_{89}\text{Ti}_{2.5}$ and $\text{Tb}_{8.5}\text{Fe}_{88}\text{Ti}_{3.5}$ samples annealed at 1100°C for 3 days. The results reveal that the $\text{Tb}_{10.5}\text{Fe}_{89.5}$, $\text{Tb}_{10.5}\text{Fe}_{88}\text{Ti}_{1.5}$, $\text{Tb}_{8.5}\text{Fe}_{89}\text{Ti}_{2.5}$ and $\text{Tb}_{8.5}\text{Fe}_{88}\text{Ti}_{3.5}$ samples comprise only one dominant matrix phase together with a small amount of an impurity phase (about 5~15 vol.%) in the intergranular regions and the $\text{Tb}_{10.5}\text{Fe}_{87}\text{Ti}_{2.5}$ sample has two principal phases with a small amount of a third impurity phase.
Figure 7-1(1): SEM microstructure photographs of the (a) T\textsubscript{b}10.5Fe\textsubscript{89.5} and (b) T\textsubscript{b}10.5Fe\textsubscript{88.0}Ti\textsubscript{1.5} samples annealed at 1100°C for 3 days. They comprise a dominant matrix phase and a small amount of impurities.
Figure 7-1(2): SEM photographs of the (c) Tb$_{10.5}$Fe$_{87.0}$Ti$_{2.5}$ and (d) Tb$_{8.5}$Fe$_{89.0}$Ti$_{2.5}$ samples annealed at 1100°C for 3 days. The Tb$_{10.5}$Fe$_{87.0}$Ti$_{2.5}$ sample contains two main phases and a small amount of third impurity phase. The Tb$_{8.5}$Fe$_{89.0}$Ti$_{2.5}$ sample comprises one dominant phase with a small amount of impurity.
Figure 7-1(3): SEM photograph of the Tb$_{8.5}$Fe$_{88.0}$Ti$_{3.5}$ samples annealed at 1100°C for 3 days. It is similar to the Tb$_{10.5}$Fe$_{89.5}$, Tb$_{10.5}$Fe$_{88}$Ti$_{1.5}$, Tb$_{8.5}$Fe$_{89}$Ti$_{2.5}$ samples, containing a dominant matrix phase with some impurity.

The powder x-ray diffraction patterns of the Tb$_{10.5}$Fe$_{89.5}$, Tb$_{10.5}$Fe$_{88}$Ti$_{1.5}$, Tb$_{10.5}$Fe$_{87}$Ti$_{2.5}$, Tb$_{8.5}$Fe$_{89}$Ti$_{2.5}$ and Tb$_{8.5}$Fe$_{88}$Ti$_{3.5}$ samples are shown in Figure 7-2. Two distinct patterns are evident depending on the composition: (1) the patterns of the samples with relatively high Tb and low Ti contents (Tb$_{10.5}$Fe$_{89.5}$ and Tb$_{10.5}$Fe$_{88}$Ti$_{1.5}$) show the characteristic reflections of the rhombohedral Th$_2$Zn$_{17}$-type structure (2:17-R) with few extra weak peaks from the Tb$_6$(Fe$_{1-x}$Ti$_x$)$_{23}$ and α-Fe impurities; (2) the patterns of the samples with relatively low Tb and high Ti contents (Tb$_{8.5}$Fe$_{89}$Ti$_{2.5}$ and Tb$_{8.5}$Fe$_{88}$Ti$_{3.5}$) show the characteristic reflections of the hexagonal Th$_2$Ni$_{17}$-type structure (2:17-H). Consistent with the SEM results, the pattern of the Tb$_{10.5}$Fe$_{87}$Ti$_{2.5}$ sample exhibits both the characteristic reflections of the rhombohedral and hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phases.
Figure 7-2: Powder x-ray diffraction patterns of the 1100°C annealed Tb$_{10.5}$Fe$_{89.5}$, Tb$_{10.5}$Fe$_{88}$Ti$_{1.5}$, Tb$_{10.5}$Fe$_{87}$Ti$_{2.5}$, Tb$_{8.5}$Fe$_{89}$Ti$_{2.5}$ and Tb$_{8.5}$Fe$_{88}$Ti$_{3.5}$ samples (Co Kα radiation). The bar patterns are the calculated diffraction results of 2:17-R and 2:17-H.
Therefore, unlike in the Gd-Fe-Ti system, both the rhombohedral and hexagonal 2:17 phases crystallize in the Tb-Fe-Ti system, but what structure \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) adopts depends on both the Tb and Ti contents. The rhombohedral \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase favors a relatively high Tb and low Ti contents whereas the hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase only crystallizes in those samples with a relatively low Tb and high Ti content.

Table 7-1: The lattice parameters and Curie temperatures of the rhombohedral \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) and hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phases formed in the \( \text{Tb}_{10.5}\text{Fe}_{89.5} \), \( \text{Tb}_{10.5}\text{Fe}_{88}\text{Ti}_{1.5} \), \( \text{Tb}_{8.5}\text{Fe}_{89}\text{Ti}_{2.5} \) and \( \text{Tb}_{8.5}\text{Fe}_{88}\text{Ti}_{3.5} \) samples annealed at 1100°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Lattice Parameters</th>
<th>Tc (±10 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Tb}<em>{10.5}\text{Fe}</em>{89.5} )</td>
<td>( \text{Th}<em>2\text{Zn}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} )</td>
<td>( a(\text{Å}) ) 8.5180(2), ( c(\text{Å}) ) 12.4091(4)</td>
<td>402</td>
</tr>
<tr>
<td>( \text{Tb}<em>{10.5}\text{Fe}</em>{88}\text{Ti}_{1.5} )</td>
<td>( \text{Th}<em>2\text{Zn}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} )</td>
<td>( a(\text{Å}) ) 8.5204(4), ( c(\text{Å}) ) 12.4180(9)</td>
<td>408</td>
</tr>
<tr>
<td>( \text{Tb}<em>{10.5}\text{Fe}</em>{87}\text{Ti}_{2.5} )</td>
<td>( \text{Th}<em>2\text{Zn}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} ) &amp; ( \text{Th}<em>2\text{Ni}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} )</td>
<td>( a(\text{Å}) ) 8.5237(4), ( c(\text{Å}) ) 12.4238(7)</td>
<td>431</td>
</tr>
<tr>
<td>( \text{Tb}<em>{8.5}\text{Fe}</em>{89}\text{Ti}_{2.5} )</td>
<td>( \text{Th}<em>2\text{Ni}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} )</td>
<td>( a(\text{Å}) ) 8.4723(0), ( c(\text{Å}) ) 8.3654(8)</td>
<td>436</td>
</tr>
<tr>
<td>( \text{Tb}<em>{8.5}\text{Fe}</em>{88}\text{Ti}_{3.5} )</td>
<td>( \text{Th}<em>2\text{Ni}</em>{17}\text{-type} \text{Tb}<em>2(\text{Fe}</em>{1-x}\text{Ti}<em>x)</em>{17} )</td>
<td>( a(\text{Å}) ) 8.4722(8), ( c(\text{Å}) ) 8.3659(2)</td>
<td>448</td>
</tr>
</tbody>
</table>

The lattice parameters, derived from the powder x-ray diffraction results, and magnetic ordering temperatures, from the TGA results, of the rhombohedral and tetragonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phases formed in the various Tb-Fe-Ti samples are listed in Table 7-1. Since both phases can stabilize in a narrow composition range, their lattice parameters and magnetic ordering temperatures (Tc) change slightly as composition changes. Generally, hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) has relatively higher Tc than rhombohedral \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \).
7.2.2. THE Tb(Fe<sub>1-x</sub>Ti<sub>x</sub>)<sub>12</sub> PHASE

In our first attempt to identify the possible new intermediate phases between the 2:17 and 1:12 phases in the Tb-Fe-Ti system, the samples with Tb<sub>7.5</sub>Fe<sub>88</sub>Ti<sub>4.5</sub>, Tb<sub>8.5</sub>Fe<sub>86</sub>Ti<sub>5.5</sub> and Tb<sub>7.5</sub>Fe<sub>87</sub>Ti<sub>5.5</sub> compositions were selected based on the following considerations:

1) The Tb:(Fe+Ti) ratio for the new possible intermediate phases should be between 2:17 and 1:12. Because our initial results show that the Tb<sub>2</sub>(Fe<sub>1</sub>,Ti<sub>x</sub>)<sub>17</sub> phase always crystallizes with a lower Tb content than a Tb:(Fe+Ti) = 2:17 ratio, however, we intentionally chose relatively lower Tb contents in our samples.

2) The Ti contents of these possible phases should also lie between those of the 2:17 and 1:12 phases, as in the 3:29 phase. In most of the R-Fe-Ti systems, the Ti contents are 2-4 at.% for the 2:17 phase and 6.5-8 at.% for the 1:12 phase, as reported in previous chapters.

However, the SEM/EDAX and x-ray diffraction results from these samples revealed that no intermediate phases between the 2:17 and 1:12 phases crystallize in this composition range. The samples formed either Tb<sub>2</sub>(Fe<sub>1</sub>,Ti<sub>x</sub>)<sub>17</sub> or Tb(Fe<sub>1</sub>,Ti<sub>x</sub>)<sub>12</sub> and P<sub>12</sub>-the new phase that has been first identified in the Gd-Fe-Ti system (Chapter 6), depending on the composition and annealing temperatures.

The powder x-ray diffraction patterns of the Tb<sub>7.5</sub>Fe<sub>88</sub>Ti<sub>4.5</sub>, Tb<sub>8.5</sub>Fe<sub>86</sub>Ti<sub>5.5</sub> and Tb<sub>7.5</sub>Fe<sub>87</sub>Ti<sub>5.5</sub> samples annealed at 1000°C and 1100°C are shown in Figure 7-3. Three types of patterns are evident in these samples, depending on the composition and annealing temperature. The diffraction pattern of the Tb<sub>8.5</sub>Fe<sub>86</sub>Ti<sub>5.5</sub> sample annealed at 1000°C has the characteristic reflections of the hexagonal Th<sub>2</sub>Ni<sub>17</sub>-type structure with
Figure 7-3: Powder x-ray diffraction patterns of the Tb$_{7.5}$Fe$_{88}$Ti$_{4.5}$, Tb$_{8.5}$Fe$_{86}$Ti$_{5.5}$ and Tb$_{7.5}$Fe$_{87}$Ti$_{5.5}$ samples annealed at 1000°C and 1100°C (Co Kα). The bar patterns are the calculated diffraction results of the hexagonal 2:17 and tetragonal 1:12 structures.
few weak reflections from the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ impurity. This indicates that the hexagonal 2:17 phase can stabilize with a quite high Ti content in the Tb-Fe-Ti system. The lattice parameters of this hexagonal 2:17 phase derived from the powder x-ray diffraction data are $a=8.4823(2)$Å and $c=8.3694(9)$Å. They are slightly larger than those of the hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase formed in the Tb$_{85}$Fe$_{89}$Ti$_{25}$ and Tb$_{85}$Fe$_{88}$Ti$_{35}$ samples due to its relatively higher Ti content.

With such a high Ti content, however, this Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase can only stabilize at relatively low temperatures. When the annealing temperature reaches 1100°C, the Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase decomposes and the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phase forms instead. Besides annealing temperature, either reducing Tb content or further increasing the Ti content also reduces the stability of the Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase and transforms it to the tetragonal Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phase or the new P$_{1;12}$ phase.

Table 7-2: The lattice parameters and magnetic ordering temperatures ($T_c$) of the phases formed in the Tb$_{75}$Fe$_{88}$Ti$_{4.5}$, Tb$_{85}$Fe$_{86}$Ti$_{5.5}$ and Tb$_{75}$Fe$_{87}$Ti$_{5.5}$ samples annealed at 1000°C and 1100°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Temp. (°C)</th>
<th>Phase</th>
<th>Lattice Parameters (Å)</th>
<th>$T_c$ (±10K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$<em>{75}$Fe$</em>{88}$Ti$_{4.5}$</td>
<td>1000</td>
<td>1:12-T</td>
<td>a = 8.5141(9)</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1:12-T</td>
<td>c = 4.7867(0)</td>
<td>550</td>
</tr>
<tr>
<td>Tb$<em>{85}$Fe$</em>{86}$Ti$_{5.5}$</td>
<td>1000</td>
<td>2:17-H</td>
<td>a = 8.5157(0)</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1:12-T(P$_{1;12}$ trace)</td>
<td>c = 4.7872(9)</td>
<td>554</td>
</tr>
<tr>
<td>Tb$<em>{75}$Fe$</em>{87}$Ti$_{5.5}$</td>
<td>1000</td>
<td>1:12-T(P$_{1;12}$ trace)</td>
<td>a = 8.4823(2)</td>
<td>554</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>P$_{1;12}$</td>
<td>c = 4.7869(4)</td>
<td>558</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phases have the structures that are closely related to each other, therefore very similar powder x-ray diffraction patterns, it is very hard to distinguish them precisely merely from the powder x-ray diffraction data. Nevertheless, the result in Figure 7-3 clearly reveals the tendency to form the P$_{1:12}$ phase with increasing Ti content and annealing temperature. As the Ti content and the annealing temperature increase, the intensity of the characteristic superlattice reflection of the P$_{1:12}$ phase at $\theta=33.5^\circ$ (Co Ke) increases accordingly, suggesting that the P$_{1:12}$ phase is more stable at high temperature with high Ti content in this system. The converse is true for the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phase.

Since the x-ray diffraction patterns of the 1100°C annealed Tb$_{75}$Fe$_{88}$Ti$_{45}$ and Tb$_{75}$Fe$_{87}$Ti$_{15}$ samples have the characteristic reflections of the tetragonal 1:12 and P$_{1:12}$ phases, respectively, the SEM photographs of these two samples are shown in Figure 7-4. The Tb$_{75}$Fe$_{87}$Ti$_{15}$ sample is virtually single phase and the Tb$_{75}$Fe$_{88}$Ti$_{45}$ sample is approximately single phase with only a very small amount of Tb(Fe$_{1-x}$Ti$_x$)$_3$ impurity. The matrix phases in both samples are very homogeneous. The compositions of the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phases from the EDAX analysis in these two samples are Tb : Fe : Ti = 7.2(±0.4 at.%) : 88.0(±0.5 at.%) : 4.8(±0.2 at.%) and 7.6(±0.4 at.%) : 86.9(±0.5 at.%) : 5.5(±0.2 at.%), respectively. Comparing with the Nd-Fe-Ti and Gd-Fe-Ti systems, the amounts of the third element (Ti) required to stabilize the 1:12 and P$_{1:12}$ structures are much lower in the Tb-Fe-Ti system.

Further work on the Tb$_{85}$Fe$_{84}$Ti$_{7.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$, Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ and Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ samples shows that both the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phases also stabilize in the higher Ti content range.
Figure 7-4: SEM photographs of the (a) Tb$_{7.5}$Fe$_{88}$Ti$_{4.5}$ and (b) Tb$_{7.5}$Fe$_{87}$Ti$_{5.5}$ samples annealed at 1100°C.
Figure 7-5 shows the SEM microstructure photographs of the as-cast \( \text{Tb}_{8.5}\text{Fe}_{84.0}\text{Ti}_{7.5} \), \( \text{Tb}_{7.5}\text{Fe}_{85.0}\text{Ti}_{7.5} \), \( \text{Tb}_{8.5}\text{Fe}_{82.0}\text{Ti}_{9.5} \) and \( \text{Tb}_{7.5}\text{Fe}_{83.0}\text{Ti}_{9.5} \) samples. Except for the \( \text{Tb}_{8.5}\text{Fe}_{84.0}\text{Ti}_{7.5} \) sample, which consists of two principal phases and a small amount of a third phase in the intergranular regions, the other three samples are roughly single phase with only a very small amount of impurities in the intergranular area. The compositions of the principal matrix phases formed in these four samples are listed in Table 7-3.

The TGA results are consistent with the SEM results (Figure 7-6). The TGA traces of the \( \text{Tb}_{8.5}\text{Fe}_{82.0}\text{Ti}_{9.5} \), \( \text{Tb}_{7.5}\text{Fe}_{85.0}\text{Ti}_{7.5} \) and \( \text{Tb}_{7.5}\text{Fe}_{83.0}\text{Ti}_{9.5} \) samples appear single phase with only a hint of the \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_3 \) impurity. The \( \text{Tb}_{8.5}\text{Fe}_{84.0}\text{Ti}_{7.5} \) sample, however, comprises two principal phases with a small amount of the \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_3 \) impurity. The Curie temperatures of the main phases in these samples are listed in Table 7-3.

Figure 7-7 shows the powder x-ray diffraction patterns of the as-cast \( \text{Tb}_{8.5}\text{Fe}_{84.0}\text{Ti}_{7.5} \), \( \text{Tb}_{7.5}\text{Fe}_{85.0}\text{Ti}_{7.5} \), \( \text{Tb}_{8.5}\text{Fe}_{82.0}\text{Ti}_{9.5} \) and \( \text{Tb}_{7.5}\text{Fe}_{83.0}\text{Ti}_{9.5} \) samples. The patterns of the \( \text{Tb}_{7.5}\text{Fe}_{85.0}\text{Ti}_{7.5} \) and \( \text{Tb}_{7.5}\text{Fe}_{83.0}\text{Ti}_{9.5} \) samples show the characteristic reflections of the \( \text{P}_{112} \) phase and the pattern of the \( \text{Tb}_{8.5}\text{Fe}_{84.0}\text{Ti}_{7.5} \) has the characteristic reflections of both the \( \text{P}_{112} \) and hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_17 \) phases with a few weak peaks from the \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_3 \) impurity. The pattern of the \( \text{Tb}_{8.5}\text{Fe}_{82.0}\text{Ti}_{9.5} \) sample, however, is different from those of the other three samples. It is similar to the powder x-ray diffraction pattern of the as-cast \( \text{Gd}_{8.5}\text{Fe}_{80.0}\text{Ti}_{11} \) sample reported in Chapter 6 (see Figure 6-10). The characteristic reflection of the \( \text{P}_{112} \) phase at \( \theta = 28.8^\circ \) (Cu K\(\alpha \) radiation) does not exist in this pattern, but several other extra reflections appeared, such as the reflections at \( \theta = 23.7^\circ , 34.5^\circ , 38.2^\circ , 40.8^\circ \) and \( 52.8^\circ \), which are marked with the arrows in Figure 7-7. These extra peaks cannot be indexed to any known phases formed in the Tb-Fe-Ti system.
Figure 7-5: SEM photographs of the as-cast \( \text{Tb}_{8.5}\text{Fe}_{84}\text{Ti}_{7.5} \) and \( \text{Tb}_{7.5}\text{Fe}_{85}\text{Ti}_{7.5} \) samples. \( \text{Tb}_{8.5}\text{Fe}_{84}\text{Ti}_{7.5} \) comprises two principal phases and \( \text{Tb}_{7.5}\text{Fe}_{85}\text{Ti}_{7.5} \) is approximately single phase with only a small amount of impurities in the intergranular area.
Figure 7-5(2): SEM photographs of the as-cast (c) Tb8.5Fe82Ti9.5 and (d) Tb7.5Fe85Ti9.5 samples. They are almost single phase with only a very small amount of impurities in the intergranular area.
Figure 7-6: TGA traces of the as-cast Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$, Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ and Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ samples.
Figure 7-7: Powder x-ray diffraction patterns of the as-cast (b) Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$, (c) Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$, (d) Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$, and (e) Tb$_{8.5}$Fe$_{83}$Ti$_{9.5}$, samples (Cu Kα). The solid bars are the calculated diffraction pattern of the 1:3 phase. The peaks marked with arrows cannot be indexed to any known phases in the system, indicating a possible new phase formed in the sample.
Table 7-3: The compositions and Curie temperatures of the principle phases formed in the as-cast Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$, Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ and Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase Content</th>
<th>Composition (EDAX) Tb : Fe : Ti (at.%)</th>
<th>$T_c$ (TGA) (±10K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$<em>{8.5}$Fe$</em>{84}$Ti$_{7.5}$</td>
<td>P$_{1:12}$ 2:17-H</td>
<td>6.8(±0.2) : 85.7(±0.3) : 7.5(±0.2)</td>
<td>556</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.4(±0.4) : 85.3(±0.2) : 6.3(±0.3)</td>
<td>464</td>
</tr>
<tr>
<td>Tb$<em>{7.5}$Fe$</em>{85}$Ti$_{7.5}$</td>
<td>P$_{1:12}$</td>
<td>7.6(±0.3) : 85.3(±0.3) : 7.1(±0.3)</td>
<td>558</td>
</tr>
<tr>
<td>Tb$<em>{8.5}$Fe$</em>{82}$Ti$_{9.5}$</td>
<td>Unclear</td>
<td>6.9(±0.5) : 84.3(±0.8) : 8.8(±0.9)</td>
<td>557</td>
</tr>
<tr>
<td>Tb$<em>{7.5}$Fe$</em>{83}$Ti$_{9.5}$</td>
<td>P$_{1:12}$</td>
<td>6.6(±0.2) : 85.8(±0.6) : 7.6(±0.7)</td>
<td>555</td>
</tr>
</tbody>
</table>

As the SEM and TGA results shown, the Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ sample is almost single phase with only a very small amount of impurity. Combining the SEM/EDAX, x-ray diffraction and the TGA results, it is likely that the matrix phase in this sample is a new phase with a new structure. This new phase, as the P$_{1:12}$ phase, has a very similar magnetic ordering temperature to that of the Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ phase. The similarity of the powder x-ray diffraction patterns of the tetragonal Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ phase and the new phase suggests that both the structures should have a close structural relationship.

As mentioned above, the 1:12-T phase can stabilize with a very low Ti content in the Tb-Fe-Ti system and as the Ti content increases, the Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ phase transforms to a new P$_{1:12}$ phase with a structure that is closely related to the structure of Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$. Here we see that further increasing Ti content will result another possible structural transformation.
After annealing the samples at 1000°C and 1100°C for 3 days, the SEM results (see Figure 7-8) show that the microstructures of the Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Tb$_{7.5}$Fe$_{85}$Ti$_{9.5}$ samples remained almost the same as those in the as-cast samples. The Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Tb$_{7.5}$Fe$_{85}$Ti$_{9.5}$ samples remained approximately single phase and the Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$ sample still comprises two principal phases. The annealing procedure only homogenizes them. In the Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ sample, however, annealing leads to the decomposition of the matrix phases in the as-cast samples.

The powder x-ray diffraction patterns of the Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Tb$_{7.5}$Fe$_{85}$Ti$_{9.5}$ samples annealed at 1000°C and 1100°C (Figure 7-9) show that the matrix P$_{1:12}$ phase changed to the Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ phase in Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and remained unchanged in Tb$_{7.5}$Fe$_{85}$Ti$_{9.5}$ after annealing. As the results show above, approximately single P$_{1:12}$ phase formed in the annealed Tb$_{7.5}$Fe$_{85}$Ti$_{5.5}$ sample, which has a lower Ti content than the Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ sample. The crystallization of the nearly single phase tetragonal Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ in the Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ sample infers that the Ti content itself is not the only factor affecting the structural transformation between the tetragonal 1:12 and P$_{1:12}$ phases.

Similarly to the as-cast sample, the powder x-ray diffraction pattern of the Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$ sample annealed at 1100°C (Figure 7-10) shows the characteristic reflections of both the hexagonal Tb$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ and tetragonal Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$ phases. Because of the decomposition of the matrix phase, however, the pattern of the annealed Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ sample is totally different from its as-cast counterpart. The single matrix phase in the as-cast sample decomposed into three phases upon annealing, which were identified as (i) Tb(Fe$_{1-x}$Ti$_{x}$)$_{12}$, (ii) Tb(Fe$_{1-x}$Ti$_{x}$)$_{11}$ and (iii) Tb(Fe$_{1-x}$Ti$_{x}$)$_{3}$. Table 7-4 lists the phases formed in these samples and their compositions.
Figure 7-8(1): SEM photographs of the (a) Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, (b) Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ samples annealed at 1090°C.
Figure 7-8(2): SEM photographs of the (c) Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ and (d) Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ samples annealed at 1090°C.
Figure 7-9: Powder x-ray diffraction patterns of the Tb$_{7.5}$Fe$_{85}$Ti$_{9.5}$ and Tb$_{7.5}$Fe$_{82}$Ti$_{9.5}$ samples annealed at 1000°C and 1100°C (Co Kα). The Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ samples have the characteristic reflections of the 1:12 structure and the Tb$_{7.5}$Fe$_{82}$Ti$_{9.5}$ samples show the characteristic reflections of the P$_{11_2}$ phase.
Figure 7-10: Powder x-ray diffraction patterns of the Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ and Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$ samples annealed at 1100°C (Co Kα radiation). They are multi-phases To analyzes the phases in these samples, the calculated 1:12, 2:17-H, 1:3 and 1:11 phases are included in the figure.
Table 7-4: The phases and their compositions (EDAX results) in the Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$, Tb$_{8.5}$Fe$_{82}$Ti$_{9.5}$, Tb$_{7.5}$Fe$_{85}$Ti$_{7.5}$ and Tb$_{7.5}$Fe$_{83}$Ti$_{9.5}$ samples annealed at 1100°C for 3 days.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Phase Content</th>
<th>Compositions (EDAX) Tb : Fe : Ti (±0.7 at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$<em>{8.5}$Fe$</em>{84}$Ti$_{7.5}$</td>
<td>P$_{1:12}$</td>
<td>6.7 : 84.9 : 8.4</td>
</tr>
<tr>
<td></td>
<td>2:17-H</td>
<td>8.6 : 85.9 : 5.5</td>
</tr>
<tr>
<td>Tb$<em>{8.5}$Fe$</em>{82}$Ti$_{9.5}$</td>
<td>1:11</td>
<td>8.0 : 80.1 : 11.9</td>
</tr>
<tr>
<td></td>
<td>1:12</td>
<td>7.6 : 83.0 : 9.4</td>
</tr>
<tr>
<td>Tb$<em>{7.5}$Fe$</em>{85}$Ti$_{7.5}$</td>
<td>1:12</td>
<td>6.7 : 86.2 : 7.1</td>
</tr>
<tr>
<td>Tb$<em>{7.5}$Fe$</em>{83}$Ti$_{9.5}$</td>
<td>P$_{1:12}$</td>
<td>6.8 : 84.5 : 8.7</td>
</tr>
</tbody>
</table>

7.2.3. A NEW Tb$_{5}$(Fe$_{1-x}$Ti$_{x}$)$_{29}$ PHASE

As shown above, in contrast to the Nd-Fe-Ti and Gd-Fe-Ti systems, both the hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and tetragonal Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phases can stabilize in a quite broad composition range in the Tb-Fe-Ti system. The hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase which crystallized in the as-cast Tb$_{8.5}$Fe$_{84}$Ti$_{7.5}$ sample has a composition Tb : Fe : Ti = 8.4 : 85.3 : 6.3 which is a even higher Ti content than the tetragonal Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phase formed in the 1100°C annealed Tb$_{7.5}$Fe$_{88}$Ti$_{4.5}$ sample (Tb : Fe : Ti = 7.2 : 88.0 : 4.8) and the P$_{1:12}$ phase formed in the 1100°C annealed Tb$_{7.5}$Fe$_{88}$Ti$_{4.5}$ sample (Tb : Fe : Ti = 7.6 : 86.9 : 5.5). According to these results, it seems that there is a very narrow or no composition gap for any possible intermediate phases between the 2:17 and 1:12 phases in the Tb-Fe-Ti system. However, further study revealed that such intermediate phases do exist in this system.
Figure 7-11 and 7-12 show the SEM photographs and the powder x-ray diffraction patterns of the as-cast, 1000°C and 1100°C annealed Tb$_{10.5}$Fe$_{86.5}$Ti$_{3.0}$ samples, respectively. Although all three samples are multi-phase, the phase contents in them are totally different. The as-cast sample comprises a dominant matrix hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase and some Tb(Fe$_{1-x}$Ti$_x$)$_3$ in the intergranular area. Although annealing at 1000°C for three days did not change the microstructure of the as-cast sample dramatically, the powder x-ray diffraction result shows that the matrix hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase was transformed into the new Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Tb$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase and the impurity Tb(Fe$_{1-x}$Ti$_x$)$_3$ phase in the intergranular area changed to the Tb$_6$(Fe$_{1-x}$Ti$_x$)$_{23}$ phase upon annealing.

(a) as-cast Tb$_{8.5}$Fe$_{88.5}$Ti$_3$

Figure 7-11(1): The SEM photograph of the as-cast Tb$_{8.5}$Fe$_{88.5}$Ti$_3$ sample. It comprises a dominant matrix hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase and a small amount of Tb(Fe$_{1-x}$Ti$_x$)$_3$ in the intergranular area.
Figure 7-11(2): The SEM photographs of the Tb<sub>8.5</sub>Fe<sub>88.5</sub>Ti<sub>3</sub> samples annealed at (b) 1000°C and (c) 1100°C.
Figure 7-12: Powder x-ray diffraction patterns of the (a) as-cast, (b) 1000°C annealed and (c) 1100°C annealed Tb$_{10.5}$Fe$_{86.5}$Ti$_3$ samples with Co Kα radiation. The bars are the calculated diffraction patterns of the 1:3, 2:17-H, 3:29, and 6:23 phases.
The composition of the new $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase determined by EDAX is $\text{Tb} : \text{Fe} : \text{Ti} = 8.7 : 88.0 : 3.3 (\pm 0.6 \text{ at.\%})$, which has a relatively low R content and especially low Ti content compared with the 3:29 phase found in other R-Fe-Ti systems, e.g. $\text{Nd} : \text{Fe} : \text{Ti} = 9.7 : 85.7 : 4.6$ for $\text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$, $\text{Pr} : \text{Fe} : \text{Ti} = 9.2 : 85.9 : 4.9$ for $\text{Pr}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$, and $\text{Gd} : \text{Fe} : \text{Ti} = 9.1 : 85.7 : 5.2$ for $\text{Gd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$. The low Ti content in this $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase is understandable, if one considers the fact that both the rhombohedral $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ and tetragonal $\text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12}$ have relatively low Ti contents (1.5 at.% and 4.8 at.%, respectively). Considering the Ti contents of the rhombohedral $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ and tetragonal $\text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12}$ phases and the relationships between the 3:29 structure and the 2:17-R and 1:12-T structures, the Ti content needed to stabilize $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ should be about $\frac{1}{2} * 1.5 \text{ at.\%} + \frac{1}{2} * 4.8 \text{ at.\%} = 3.15 \text{ at.\%}$, in excellent agreement with the experimental EDAX value of 3.3 at.%. Thus, a relatively low Ti content is required to stabilize the $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase. The lattice parameters of the new $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase derived from our powder x-ray diffraction data are $a=10.6756(7)\text{Å}$, $b=8.5102(6)\text{Å}$, $c=9.6828(3)\text{Å}$ and $\beta=97.4902(6)^°$.

As with the other $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phases reported in chapter 4 and 6, the $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase only forms after a suitable annealing procedure. The formation temperature of the $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase, however, is relatively lower (1000°C) than those of the 3:29 phases found in the other R-Fe-Ti systems. If the annealing temperature reaches 1100°C, the $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phase decomposes. This is shown clearly in the SEM (Figure 7-11(2)) and powder x-ray diffraction (Figure 7-12(c)) results. The SEM result revealed that the matrix phase decomposed to two principal phases after annealing at 1100°C. Although all the characteristic reflections of the rhombohedral and hexagonal $\text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ phases.
phases are evident in the x-ray diffraction pattern, it cannot be indexed as to any combination of known phases formed in the Tb-Fe-Ti system.

The TGA result on the 1100°C annealed sample is shown in Figure 7-13. The TGA trace reveals that the two principal phases in this sample have approximately identical magnetic ordering temperatures, about 450K.

![TGA trace of the 1100°C annealed Tb\textsubscript{10.5}Fe\textsubscript{86.5}Ti\textsubscript{3} sample](image)

*Figure 7-13: TGA trace of the 1100°C annealed Tb\textsubscript{10.5}Fe\textsubscript{86.5}Ti\textsubscript{3} sample.*

According to our SEM, x-ray diffraction and TGA results, it seems that a possible new phase formed in this sample. This phase will be referred to as P\textsubscript{1} hereafter. Unfortunately, there are not enough data available so far for further identification of this possible phase.

As shown in previous chapters, the 3:29 phase is an intermediate phase between the rhombohedral Th\textsubscript{2}Zn\textsubscript{17}-type 2:17 and tetragonal 1:12 phases. In the Tb-Fe-Ti system Tb\textsubscript{2}(Fe\textsubscript{1-x}Ti\textsubscript{x})\textsubscript{17} can crystallize in both the rhombohedral Th\textsubscript{2}Zn\textsubscript{17}-type and hexagonal Th\textsubscript{2}Ni\textsubscript{17}-type structures. In accordance with this, besides the Nd\textsubscript{3}(Fe\textsubscript{1-x}Ti\textsubscript{x})\textsubscript{29}-type Tb\textsubscript{3}(Fe\textsubscript{1-x}Ti\textsubscript{x})\textsubscript{29}-type Tb\textsubscript{3}(Fe...
\( x_{\text{Ti},y} \) phase, our results show a possible existence of another new phase, \( P_i \), in this system. It is likely that this new \( P_i \) phase could be an intermediate phase between the hexagonal \( \text{Th}_2\text{Ni}_{17} \)-type 2:17 and tetragonal 1:12 phases.

The Curie temperatures of the \( \text{Tb}_x(\text{Fe}_{1-x}\text{Ti},y)_{29} \) and new \( P_i \) phases determined by TGA are 448(±10)K and 450(±10)K, respectively.

7.2.4. THE \( \text{Tb}(\text{Fe}_{1-x}\text{Ti},y)_{11} \) PHASE

Figure 7-14a shows the SEM photographs of the as-cast \( \text{Tb}_{85}\text{Fe}_{80.5}\text{Ti}_{11} \) sample. It is nearly single phase with only a very small amount of impurity (less than 5 vol.%) in the intergranular area. The approximately single phase nature of this sample is also apparent from the TGA result (Figure 7-15).

The x-ray diffraction result of the as-cast sample (see Figure 7-1(a)) shows that this sample has the same diffraction pattern as the as-cast \( \text{Gd}_{85}\text{Fe}_{80.5}\text{Ti}_{11} \) sample and is very similar to that of the possible new phase formed in the as-cast \( \text{Tb}_{85}\text{Fe}_{82}\text{Ti}_{9.5} \) sample. The composition of the main matrix phase (the EDAX result) is \( \text{Tb} : \text{Fe} : \text{Ti} = 6.6(±0.4) : 83.9(±0.3) : 9.5(±0.3) \), which has a very high Ti content. Its Curie temperature is 550K (±10K).

This phase, as the matrix phases formed in the as-cast \( \text{Gd}_{85}\text{Fe}_{80.5}\text{Ti}_{11} \) and \( \text{Tb}_{85}\text{Fe}_{82}\text{Ti}_{9.5} \) samples, only stabilizes in the as-cast state. After annealing at 1000°C, it decomposed into two phases (see Figure 7-16), which are identified as the \( \text{Tb}(\text{Fe}_{1-x}\text{Ti},y)_{11} \) and \( \text{Tb}(\text{Fe}_{1-x}\text{Ti},y)_{12} \) phases. The composition (EDAX result) and lattice parameters of \( \text{Tb}(\text{Fe}_{1-x}\text{Ti},y)_{11} \) are \( \text{Tb} : \text{Fe} : \text{Ti} = 9.0 : 79.2 : 11.8 \ (±0.6 \text{ at.%}) \) and \( a=8.2292(5)\text{Å}, c=4.8267(8)\text{Å} \), respectively.
Figure 7-14: SEM photographs of the (a) as-cast and (b) 1000°C annealed Tb$_{8.5}$Fe$_{80.5}$Ti$_{11}$ samples:
Figure 7-15: TGA trace of the as-cast Tb$_{8.5}$Fe$_{80.5}$Ti$_{11}$ sample. It shows that the sample is approximately single phase with only a very small amount of impurity.

Figure 7-16: Powder x-ray diffraction patterns of the as-cast and 1000°C annealed Tb$_{8.5}$Fe$_{80.5}$Ti$_{11}$ samples. (Co Kα radiation). The solid bars are the calculated diffraction pattern of the Tb(Fe$_{1-x}$Ti$_x$)$_{11}$ phase based on indexation of the experimental data.
7.3. CONCLUSIONS

There are at least 7 phases crystallizing at the Fe-rich end of the Tb-Fe-Ti system. They are identified as rhombohedral \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \), hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \), \( \text{Nd}_2(\text{Fe}_{1-\delta}\text{Ti}_\delta)_{29} \)-type \( \text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \), another intermediate phase—\( P_1 \) between 2:17 and 1:12, tetragonal \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \), the new \( P_{1,12} \) phase and \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{11} \).

Unlike the Nd-Fe-Ti and Gd-Fe-Ti systems, the 2:17 phase can crystallize in both the rhombohedral \( \text{Th}_2\text{Zn}_{12} \)-type and the hexagonal \( \text{Th}_2\text{Ni}_{17} \)-type structures in the Tb-Fe-Ti system, depending on both the Tb and Ti contents. The rhombohedral \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase only stabilizes with relatively high Tb and low Ti contents. As Tb content decreases and Ti content increases (\( \geq 2.5 \) at.%), the hexagonal \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) phase will crystallize instead. Besides the composition, the annealing temperature also plays a key role in the structural transition between the two 2:17 phases. Consistent with the fact that two types of the 2:17 phase exist in this system, two intermediate phases between the \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) and \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) phase—the \( \text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) and the \( P_1 \) phases are identified. Although the details of the \( P_1 \) phase are still unknown, it is likely that this phase is an intermediate phase between the hexagonal 2:17 and the tetragonal 1:12 phases.

Another difference between the Tb-Fe-Ti system and the Nd-Fe-Ti or Gd-Fe-Ti systems is that the \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \) phase stabilizes with very low Ti content (4.8 at.%). Consequently, the Ti content required to stabilize the intermediate phases between \( \text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17} \) and \( \text{Tb}(\text{Fe}_{1-x}\text{Ti}_x)_{12} \), the \( \text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) and \( P_1 \) phases, is also relatively low.

The new \( P_{1,12} \) phase, which has been identified in the Gd-Fe-Ti system, also crystallizes in the Tb-Fe-Ti system. Because the compositions and structures of the
Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phases are very similar, it is very hard to separate these two phases exactly. Both Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ stabilize over a quite broad composition range and generally the P$_{1:12}$ phase prefers a higher Ti content and annealing temperature.

Besides the P$_{1:12}$ phase, another new phase closely related to the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ phase was also identified in the as-cast samples with very high Ti contents. This phase has a higher Ti content than the Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ and P$_{1:12}$ phase, but it only stabilizes in the as-cast samples. With such high Ti content the Tb(Fe$_{1-x}$Ti$_x$)$_{11}$ phase crystallizes after annealing.
REFERENCES


Chapter Eight

PHASE FORMATION AND TRANSFORMATION IN
THE Fe CORNER OF THE Dy-Fe-Ti SYSTEM

8.1. INTRODUCTION

The Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase, having an intermediate structure between the rhombohedral 2:17 and tetragonal 1:12, has been generally observed in the ‘light’ rare-earth systems where the 2:17 phase crystallizes in the rhombohedral Th$_2$Zn$_{17}$-type structure$^{17}$. The systematic studies of two ‘heavy’ rare-earth systems, Gd-Fe-Ti and Tb-Fe-Ti, revealed that the rhombohedral Th$_2$Zn$_{17}$-type 2:17 phase crystallizes in both the Gd-Fe-Ti and Tb-Fe-Ti systems and conformably the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Gd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and Tb$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phases were identified in these systems. In the Tb-Fe-Ti system, however, the hexagonal Th$_2$Ni$_{17}$-type 2:17 phase also crystallizes and correspondingly, besides the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Tb$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase, another new phase between 2:17 and 1:12 was identified, which has been deliberately described as an intermediate phase between hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and tetragonal Tb(Fe$_{1-x}$Ti$_x$)$_{12}$.

More interesting result found in these ‘heavy’ rare earth system studies is that although the tetragonal 1:12 phase in both the Gd-Fe-Ti and Tb-Fe-Ti systems can stabilize in a certain composition range, a structural transformation happens in both Gd(Fe$_{1-x}$Ti$_x$)$_{12}$ and Tb(Fe$_{1-x}$Ti$_x$)$_{12}$ if the Ti content exceeds a certain level. This structural transformation changes the tetragonal 1:12 phase to a new phase, P$_{1:12}$, which has a new structure closely related to the tetragonal 1:12 structure. This structural modification has
not been observed in any “light” rare-earth system, such as the Nd-Fe-Ti system where the 1:12 phase has a very defined composition.

Dy is the next neighbor of Gd and Tb. Generally binary Dy$_2$Fe$_{17}$ crystallizes in the hexagonal Th$_2$Ni$_{17}$-type structure. If this remains in the ternary Dy-Fe-Ti system, then the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase should not but the P$_1$ phase shall crystallize in this system. The P$_{1.12}$ may also exit in this system. In this chapter we will report our systematic study on the phase formation in the Fe-rich corner of the Dy-Fe-Ti system.

8.2. RESULTS AND DISCUSSION

Samples with the starting compositions Dy$_{14.8}$Fe$_{80.5}$Ti$_{14.7}$, Dy$_{13.1}$Fe$_{80.1}$Ti$_{6.8}$, Dy$_{11.5}$Fe$_{84}$Ti$_{4.5}$, Dy$_{11.5}$Fe$_{82.5}$Ti$_{6}$, Dy$_{10.5}$Fe$_{84}$Ti$_{4.5}$, Dy$_{7.5}$Fe$_{83.3}$Ti$_{9.2}$, Dy$_{10.5}$Fe$_{73.7}$Ti$_{15.8}$, Dy$_{9.1}$Fe$_{77.3}$Ti$_{13.6}$ and Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ (plus 10 wt.% excess of Dy to compensate the losses during the sample preparation) were prepared for this study. The selected samples were annealed at four different temperatures, 950°C, 1000°C, 1080°C and 1090°C, respectively, for 3 days. The phase characterization was performed by x-ray diffraction, SEM/EDAX, thermal-gravimetric analysis (TGA) and Mössbauer spectroscopy.

There are at least 6 Fe-rich rare-earth compounds crystallizing in the Dy-Fe-Ti system based on our results. Besides the well known hexagonal Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ (2:17-H) and tetragonal Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ (1:12-T) phases, the other 4 phases were identified as the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ (3:29) phase, a novel Dy(Fe$_{1-x}$Ti$_x$)$_{10}$ (1:10) phase, a new orthorhombic 1:12 (1:12-O) phase and the Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ (1:11) phase. Figure 8-1 and 8-2 show the powder x-ray diffraction patterns of these six phases. Their compositions, structures, lattice parameters and magnetic ordering temperatures are listed in Table 8-1.
Figure 8-1: Powder x-ray diffraction patterns of the (a) 1080°C annealed Dy$_{14.8}$Fe$_{80.5}$Ti$_{4.7}$ (2:17-H), (b) as-cast Dy$_{7.5}$Fe$_{83.3}$Ti$_{9.2}$ (1:12-T), (c) 1080°C annealed Dy$_{7.5}$Fe$_{83.3}$Ti$_{9.2}$ (1:12-O), and (d) 1080°C annealed Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ (1:11) (Cu Kα radiation). The bar patterns are the calculated powder x-ray diffraction results.
Figure 8-2: Powder x-ray diffraction patterns of (a) 950°C annealed Dy$_{11.5}$Fe$_{84}$Ti$_{4.5}$ (the new Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase) and (b) 1090°C annealed Dy$_{10.5}$Fe$_{83.5}$Ti$_6$ (the new Dy(Fe$_{1-x}$Ti$_x$)$_{10}$ phase) with Co Kα radiation.

Table 8-1: The compositions (EDAX), structures, lattice parameters and magnetic ordering temperatures of the phases formed in the Fe corner of the Dy-Fe-Ti system.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Structure</th>
<th>Lattice Parameter</th>
<th>T$_c$ (±10K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:17</td>
<td>11.5 : 83.7 : 4.8</td>
<td>Th$<em>2$Ni$</em>{17}$</td>
<td>a (Å) b (Å) c (Å) β (°)</td>
<td>428</td>
</tr>
<tr>
<td>1:10(P$_2$)</td>
<td>9.9 : 84.1 : 6.0</td>
<td>Orthorhombic</td>
<td>8.38 8.55 14.69</td>
<td>*</td>
</tr>
<tr>
<td>3:29</td>
<td>*</td>
<td>Nd$<em>5$(Fe$</em>{1-x}$Ti$<em>x$)$</em>{29}$</td>
<td>10.67 5.51 9.70 97.36</td>
<td>*</td>
</tr>
<tr>
<td>1:12-T</td>
<td>8.9 : 83.7 : 7.4</td>
<td>ThMn$_{12}$</td>
<td>8.51 4.79</td>
<td>508</td>
</tr>
<tr>
<td>1:12-O</td>
<td>8.9 : 81.9 : 9.2</td>
<td>Orthorhombic</td>
<td>8.54 8.51 4.79</td>
<td>535</td>
</tr>
<tr>
<td>1:11</td>
<td>8.8 : 76.4 : 14.8</td>
<td>BaCd$_{11}$</td>
<td>8.22 4.82</td>
<td>&lt;RT</td>
</tr>
</tbody>
</table>

* The results are unavailable so far because the facility problems.
8.2.1. THE Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ PHASE

The approximately single phase Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$, with a very small amount of the Dy(Fe$_{1-x}$Ti$_{x}$)$_{3}$ impurity in the intergranular area, was formed in the 1080°C annealed Dy$_{14.8}$Fe$_{80.5}$Ti$_{4.7}$ sample, see Figure 8-3. The powder x-ray diffraction pattern of this Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase (Figure 8-1(a)) shows the characteristic reflections of the hexagonal Th$_{2}$Ni$_{17}$-type structure. No rhombohedral Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase was observed in the composition range used in the present study.

The composition of this hexagonal Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase, determined by EDAX, is Dy : Fe : Ti = 10.9(±0.6 at.%): 84.5(±0.6 at.%): 4.6(±0.4 at.%) which has a slightly higher rare-earth content than the stoichiometric 2:17 ratio and a specially high Ti content compared with the rhombohedral 2:17 phases formed in the Nd-Fe-Ti, Gd-Fe-Ti and Tb-Fe-Ti systems.

Figure 8-3: SEM photograph of the 1080°C annealed Dy$_{14.8}$Fe$_{80.5}$Ti$_{4.7}$ sample. It contains a dominant matrix hexagonal Dy$_{2}$(Fe$_{1-x}$Ti$_{x}$)$_{17}$ phase with a small amount of Dy(Fe$_{1-x}$Ti$_{x}$)$_{3}$ impurity.
It should note that although the 2:17 phase crystallizes in both the rhombohedral and hexagonal 2:17 structures in the Tb-Fe-Ti system, as reported in Chapter 7, the hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase only stabilizes with relatively higher Ti content than that in the rhombohedral Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase. The fact that the hexagonal 2:17 phase has a comparatively higher Ti content than the rhombohedral 2:17 phase is probably due to their structural difference. In light of the rhombohedral and hexagonal 2:17 structures being stackings of the coordination spheres of particularly large R atoms (CPR), the hexagonal 2:17 structure, differing from the rhombohedral 2:17 structure, is a stacking of $\frac{2}{3}$ the ThMn$_{12}$-type CPRs (Type-I) and $\frac{1}{3}$ the CaCu$_5$-type CPRs. In the discussion of the new Nd$_3$(Fe$_{1-x}$Ti$_{y}$)$_{29}$ structure (Chapter 4) we have discussed that certain amount of the third element atoms (Ti) with a different atomic size from Fe is required in the Type-I CPR to suffice the geometrical requirement. Assuming that each Type-I CPR in the hexagonal 2:17 phase has the same number of Ti atoms as the CPRs in the tetragonal Dy(Fe$_{1-x}$Ti$_{y}$)$_{12}$ phase, the Ti content for the Dy$_2$(Fe$_{1-x}$Ti$_{y}$)$_{17}$ phase would be about $\frac{2}{3}$ * 7.4 at.% = 4.9 at.% , based on the EDAX result that the Ti content for the tetragonal Dy(Fe$_{1-x}$Ti$_{y}$)$_{12}$ phase is 7.4 at%. Comparing with the EDAX result of the hexagonal Dy$_2$(Fe$_{1-x}$Ti$_{y}$)$_{17}$ phase, Ti % = 4.6 at.% , the calculated result is very close to the experimental one and so the observed high Ti content in the hexagonal 2:17 phase is consistent.

The lattice parameters of the Dy$_2$(Fe$_{1-x}$Ti$_{y}$)$_{17}$ phase derived from the refinement of the powder x-ray diffraction results are $a=8.4841(8)$Å and $c=8.3619(7)$Å. Its Curie temperature is 428 (±10)K.
8.2.2. TWO NEW PHASES BETWEEN 2:17 AND 1:12—Dy\(_3(Fe_{1-x}Ti_x)_{29}\) AND Dy\((Fe_{1-x}Ti_x)_{10}\)

Figure 8-4 shows the SEM photographs of the as-cast, 950°C and 1090°C annealed Dy\(_{11.5}Fe_{84}Ti_{4.5}\) and Dy\(_{10.5}Fe_{83.5}Ti_{6}\) samples. All the samples comprise a dominant matrix phase with a small amount of impurities in the intergranular regions. The impurities have been identified as Dy\((Fe_{1-x}Ti_x)_{3}\) in the as-cast samples, the Dy\(_6(Fe_{1-x}Ti_x)_{23}\) in the 950°C annealed samples and both in the 1090°C annealed samples.

Figure 8-5 shows the powder x-ray diffraction patterns of the as-cast, 950°C and 1090°C annealed Dy\(_{10.5}Fe_{83.5}Ti_{6}\) samples. The Dy\(_{11.5}Fe_{84}Ti_{4.5}\) samples annealed at same temperature have the same x-ray diffraction results. The pattern of the 950°C annealed sample can be well indexed by the Nd\(_3(Fe_{1-x}Ti_x)_{29}\)-type structure with a few extra weak peaks from the Dy\(_6(Fe_{1-x}Ti_x)_{23}\) impurity. Therefore, the Nd\(_3(Fe_{1-x}Ti_x)_{29}\)-type 3:29 phase also crystallizes in the Dy-Fe-Ti system. The indexing of the powder x-ray diffraction pattern of the 950°C annealed Dy\(_{10.5}Fe_{83.5}Ti_{6}\) in terms of the Nd\(_3(Fe_{1-x}Ti_x)_{29}\) structure gives the lattice parameters of the new Dy\(_3(Fe_{1-x}Ti_x)_{29}\) phase of \(a=10.674(0)\text{Å}\), \(b=8.505(4)\text{Å}\), \(c=9.697(8)\text{Å}\) and \(\beta=97.360(4)^\circ\).

Although the as-cast and 1090°C annealed samples have the similar microstructures as the 950°C annealed samples, the x-ray diffraction patterns reveal that the matrix phase formed in these samples are totally different. As reported in the previous chapters, the R\(_3(Fe_{1-x}Ti_x)_{29}\) phase only crystallizes after a suitable annealing, but differing from Nd\(_3(Fe_{1-x}Ti_x)_{29}\) and Gd\(_3(Fe_{1-x}Ti_x)_{29}\), Tb\(_3(Fe_{1-x}Ti_x)_{29}\) stabilizes only at relatively lower temperature than those for Nd\(_3(Fe_{1-x}Ti_x)_{29}\) and Gd\(_3(Fe_{1-x}Ti_x)_{29}\). Annealing around 1100°C decomposes Tb\(_3(Fe_{1-x}Ti_x)_{29}\) and forms another new phase, \(P_1\).
Figure 8-4(1): SEM photographs of the as-cast Dy\textsubscript{11.5}Fe\textsubscript{84}Ti\textsubscript{4.5}, and Dy\textsubscript{10.5}Fe\textsubscript{83.5}Ti\textsubscript{6} samples. They comprise a dominant phase with less than 5-8 vol.% impurity phases in the intergranular regions.
Figure 8-4(2): SEM photographs of the \( \text{Dy}_{11.5}\text{Fe}_{84}\text{Ti}_{4.5} \) and \( \text{Dy}_{10.5}\text{Fe}_{83.5}\text{Ti}_{6} \) samples annealed at 950°C. Annealing at this temperature did not obviously change their microstructures.
(e) $\text{Dy}_{11.5}\text{Fe}_{84}\text{Ti}_{4.5}$ annealed at 1090°C

(f) $\text{Dy}_{10.5}\text{Fe}_{83.5}\text{Ti}_{6}$ annealed at 1090°C

Figure 8-4(3): SEM photographs of the $\text{Dy}_{11.5}\text{Fe}_{84}\text{Ti}_{4.5}$ and $\text{Dy}_{10.5}\text{Fe}_{83.5}\text{Ti}_{6}$ samples annealed at 1090°C. Their microstructures are similar to those of the as-cast and 950°C annealed sample. They are composed of a dominant matrix phase with some impurity phases (about 5-8 vol.%) in the intergranular area.
Figure 8-5: Powder x-ray diffraction patterns of the as-cast, 950°C and 1090°C annealed Dy$_{10.5}$Fe$_{83.5}$Ti$_6$ samples (Co Kα radiation). The bar patterns are the calculated powder diffraction patterns based on the 1:3, 6:23, Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and a new proposed Dy(Fe$_{1-x}$Ti$_x$)$_{10}$ structures.
The present study reveals that a suitable annealing is also essential to form the
\( \text{Dy}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) phase. However, as \( \text{Tb}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \), it stabilizes only at relatively low
temperature (950°C). As shown in the x-ray diffraction results (Figure 8-5), the as-cast
and 1090°C annealed samples have the totally different diffraction patterns from that of
the 950°C annealed sample, indicating that a different phase with a different crystal
structure has formed in these samples. Besides the few weak peaks from the \( \text{Dy}(\text{Fe},_x\text{Ti})_3 \) and/or \( \text{Dy}_6(\text{Fe}_1\text{Ti}_x)_23 \) impurities, the patterns cannot be indexed to any known
phases formed in the Dy-Fe-Ti system, indicating that another new phase has formed in
these samples.

Comparing with the P\(_1\) phase identified in the Tb-Fe-Ti system, the new phase
identified in the as-cast and 1090°C annealed \( \text{Dy}_{11.5}\text{Fe}_{84}\text{Ti}_{4.5} \) and \( \text{Dy}_{10.5}\text{Fe}_{83.5}\text{Ti}_6 \) samples
has a very similar powder x-ray diffraction pattern to that of the P\(_1\) phase. However,
several extra superlattice reflections that do not appear in the P\(_1\) phase are evident here,
indicating a structural difference between them. We will refer this new phase as to P\(_2\).

The new P\(_2\) phase can stabilize in a certain composition range. The EDAX
analysis on the 1090°C annealed samples revealed that the P\(_2\) phase has a composition
\( \text{Dy} : \text{Fe} : \text{Ti} = 9.8(\pm 0.9 \text{ at.\%}) : 84.1(\pm 0.7 \text{ at.\%}) : 5.9(\pm 0.9 \text{ at.\%}) \) in the \( \text{Dy}_{10.5}\text{Fe}_{83.5}\text{Ti}_6 \)
sample and a composition \( \text{Dy} : \text{Fe} : \text{Ti} = 10.6(\pm 0.5 \text{ at.\%}) : 84.7(\pm 0.6 \text{ at.\%}) : 4.7(\pm 0.2
\text{ at.\%}) \) in the \( \text{Dy}_{11.5}\text{Fe}_{84}\text{Ti}_{4.5} \) sample. These ratios are very similar to that of the \( \text{Nd}_3(\text{Fe}_1\text{Ti}_x)_29 \) phase but with little higher rare-earth and Ti contents.

As shown in previous chapters, in the systems where the 2:17 phase crystallizes
only in the rhombohedral Th\(_2\)Zn\(_{17}\)-type structure, such as the Nd-Fe-Ti and Gd-Fe-Ti
system, only one intermediate phase between 2:17 and 1:12—\( \text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) (3:29), was
identified. In the Tb-Fe-Ti system where the 2:17 phase can crystallize in both the rhombohedral Th$_2$Zn$_{17}$-type and hexagonal Th$_2$Ni$_{17}$-type structures, two intermediate phases between 2:17 and 1:12—Tb$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and P$_1$, have been observed. R$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ is an intermediate phase between the rhombohedral 2:17 and tetragonal 1:12 phases. The P$_1$ phase, with a different structure from R$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, has been tentatively described as an intermediate phase between the hexagonal 2:17 and tetragonal 1:12 phases.

In the Dy-Fe-Ti system, as mentioned above, only the hexagonal 2:17 phase was identified in the composition range used in this study. Thus, we presumed at the early stage of this study that the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type 3:29 phase would not crystallize in the Dy-Fe-Ti system, but it is possible that the P$_1$ phase will form in this system. However, the results turned out that the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase does crystallize in the Dy-Fe-Ti system and instead of the P$_1$ phase another new intermediate phase between 2:17 and 1:12 was identified.

Although no rhombohedral Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase was observed in the Dy-Fe-Ti system within the present composition range, it is possible that it also crystallizes in the Dy-Fe-Ti system, but only with a relatively lower Ti content than that used in this work (the lowest Ti content in the high Dy samples used in this work is 4.5at.%). This hypothesis can be affirmed by the observation in the Tb-Fe-Ti system. Although both the rhombohedral and hexagonal Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phases were identified in the Tb-Fe-Ti system, the rhombohedral Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ only stabilizes in the sample with a relatively lower Ti content. As the Ti content increases, the structure of the Tb$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase changes from rhombohedral to hexagonal.
So far, besides the \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \)-type 3:29 phase, two other intermediate phases between 2:17 and 1:12, \( P_1 \) and \( P_2 \), have been identified. These two phases form in the Tb-Fe-Ti and Dy-Fe-Ti systems, respectively, where the 2:17 phase can crystallize in the hexagonal \( \text{Th}_2\text{Ni}_{17} \)-type structure. In the x-ray diffraction patterns of both the \( P_1 \) and \( P_2 \) phases, the characteristic (201) and (203) reflections of the hexagonal 2:17 phase are present, indicating a relationship between the new structures and the hexagonal \( \text{Th}_2\text{Ni}_{17} \)-type structure.

Since the 2:17 and 1:12 structures are directly derived from the 1:5 structure by the dumb-bell replacement, it is conceivable that \( P_2 \), as an intermediate phase between 2:17 and 1:12, may have a structure that can also be derived from the 1:5 structure simply by the dumb-bell replacement, just as the \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) structure discussed in Chapter 4.

To resolve the possible structure of the new \( P_2 \) phase, we applied the CPR method introduced in the discussions of the \( \text{R}_3(\text{Fe}_{1-x}\text{Si}_x)_{22} \) and \( \text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29} \) structures in Chapter three and four. This method is based on the fact that the particularly large R atoms in the R-T compounds have an exclusively high coordination number of 20 that is resulted from the geometrical requirement because of the very large atomic size ratio in these compounds. It has been point out long time ago (Kasper, 1956)\(^9\) that a number of the relatively complex structures, particularly of transition metal alloys, may be regarded as determined by the geometrical requirement for sphere packing. A fruitful approach is to consider the coordination polyhedra around particular atoms, which proved to correspond to a certain limited number of types, namely 12, 14, 15 and 16-fold polyhedra. The abundantly observation of these coordination polyhedra in the
transition metal compounds comes from the fact that they have space-filling properties. All these coordination polyhedra have the atomic arrangement that defines a net of triangles on the surfaces of the coordination spheres. Thus, the triads of atoms on the surfaces of the polyhedra together with the central atom form the tetrahedral interstices, a most satisfactory space-filling arrangement.

The coordination number adopted by the specific atoms in the actual compounds depends on the atomic size ratio of the specific and other atoms. In the R-T compounds, the atomic size ratio of R to T is much larger than those of the compounds with only transition metals (see Figure 3-7), so it is expected that the very large R atoms in the R-T compounds should have a high coordination number. Considering a coordination polyhedron possessing the same space-filling properties as the 12, 14, 15 and 16-fold coordination polyhedron, the next coordination number larger than 16 will be 20 and, thus, is abundantly observed in the R-T compounds.

Based on the relationships of the 1:5, 3:22, 2:17 and 1:12 structures in terms of CPR (see Figure 8-6) and the fact that P₂ has some structural similarities with the hexagonal Th₂Ni₁₃-type structure as indicated by the x-ray diffraction result, it is possible that P₂ has an intermediate structure between the hexagonal 2:17 and tetragonal 1:12 structures and, like the hexagonal 2:17 structure, it can be a simply constructed by stacking different proportions of the Type-I and Type-II CPRs in an order that applies. This process can be facilitated by using a variable, η, defined as the ratio of the number of the Type-I CPRs to the number of the Type-II CPR in the structure. Different η value corresponds to a different structure. For example, η = 1/4 and 1/5 correspond to the 3:29 and 1:10 phases, respectively.
The CaCu$_5$, $R_3$(Fe$_{1-x}$Si$_x$)$_{22}$, Th$_2$Ni$_{17}$ and ThMn$_{12}$ structures in terms of the CPRs. The structural relationships among them are apparent. They all are the simple stackings of Type-I and Type-II CPR. The difference between them is only the proportion and sequence of the two CPR types.

The composition of the new P$_2$ phase determined by EDAX is Dy : Fe : Ti = 9.9 : 84.1 : 6.0 that has a Dy : (Fe+Ti) $\approx$ 1 : 9. However, based on the EDAX results of Dy : (Fe+Ti) = 2 : 15.4 for Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Dy : (Fe+Ti) = 1 : 10.2 for Dy(Fe$_{1-x}$Ti$_x$)$_{12}$, it appears that our EDAX compositions always have higher Dy : (Fe+Ti) ratios than the stoichiometric ones. Thus, by making appropriate adjustments catering for inconsistencies inherent to EDAX analysis, the possible $\eta$ value for the new phase could.
be $\frac{1}{4}$ or $\frac{1}{5}$ which corresponds to a 3:29 or 1:10 phase, respectively. From the dumbbell replacement perspective, these two stacking sequences correspond to $\frac{2}{5}$ and $\frac{5}{12}$ of the R atoms being replaced by T-T pairs, respectively.

In Figure 8-7 we show the proposed possible CPR stacking sequences with $\eta=\frac{1}{4}$ and $\frac{1}{5}$ for the new P$_2$ phase. Given these atomic arrangements, the possible structures for the P$_2$ structure are readily apparent. They are monoclinic with a space group Pm (No. 6) for $\eta = \frac{1}{4}$ (a 3:29 phase) and orthorhombic with a space group Pmm2 (No. 47) for $\eta = \frac{1}{5}$ (a 1:10 phase). Figure 8-8 shows the possible crystal structures corresponding to the proposed CPR stacking structures here.

\[\text{Figure 8-7: Proposed CPR stacking sequence for the new P}_2\text{ phase with } \eta=1/4 \text{ and } 1/5, \text{ which correspond to the 3:29 and 1:10 phases, respectively.}\]
Based on these proposed structures, we calculated the theoretical powder x-ray diffraction patterns of the new $P_2$ phase that are shown in Figure 8-9. Comparing with the experimental x-ray diffraction result, the calculated diffraction pattern based on the orthorhombic 1:10 structure ($\eta = \frac{1}{5}$) gives a satisfying agreement with all the reflections of the experimental pattern. Therefore, we conclude that the new $P_2$ phase is a 1:10 phase with a possible orthorhombic structure and the space group Pmm2 (No. 47). The lattice parameters of this 1:10 phase are $a = 8.38(2)$Å, $b = 8.54(8)$Å and $c = 14.69(3)$Å.

![Diagram of crystal structure](image)

Figure 8-8: The possible structures of the new $P_2$ phase and their relationships with the 1:5 structure. For the purpose of clarity, we do not show the $T$ atoms not in the dumb-bells. The dark lines indicate the unit cells.
Figure 8-9: Powder x-ray diffraction pattern of the as-cast Dy_{10.5}Fe_{83.5}Ti_{6.0} sample and the calculated powder x-ray diffraction patterns of the 1:10 (\eta=1/5) and 3:29 (\eta=1/4) phases based on the proposed structures. Since some 1:3 impurity exists in the sample, we also include its calculated diffraction pattern in the figure.

We note that since the calculation is only based on a simple replacement of R atoms with T-T pairs without any atomic adjustment after replacing, the intensities of some peaks do not agree perfectly.

8.2.3. ANOTHER POSSIBLE PHASE BETWEEN THE Dy_{3}(Fe_{1-x}Ti_{x})_{29} AND Dy(Fe_{1-x}Ti_{x})_{13} PHASES

Besides the new Dy_{3}(Fe_{1-x}Ti_{x})_{29} and P_{2} phases, our results also show a trace of another possible new phase between the 2:17 and the 1:12 phases in the Dy-Fe-Ti system.
Figure 8-10: Powder x-ray diffraction pattern of the 1000°C annealed Dy$_9$Fe$_{87.5}$Ti$_{13.5}$ sample with Co Kα radiation. The solid bar patterns are the calculated theoretical diffraction results of the hexagonal Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase and monoclinic Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phases.

Figure 8-10 shows the powder x-ray diffraction pattern of the 1000°C annealed Dy$_9$Fe$_{87.5}$Ti$_{13.5}$ sample. The SEM result shows that this sample comprises two principal phases. In the x-ray diffraction pattern, all the characteristic reflections of the hexagonal Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ phase exist. Besides these peaks, extra peaks are evident. Amongst these extra reflections, the characteristic (122) and (322) reflections of the Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase exist in the pattern. In order to identify the phases in the sample, the calculated diffraction patterns of the hexagonal 2:17 and Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-Type Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phases are included in Figure 8-10. Although the characteristic (122) and (322) reflections of the Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phase appear in the pattern, it is clearly that the experimental data
cannot be explained simply by the Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$ and Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ phases. Therefore, it is possible that another new phase formed in this sample, which we refer to as P$_3$.

This new P$_3$ phase was also observed in the Ho-Fe-Ti and Er-Fe-Ti systems. Figure 8-11 shows the powder x-ray diffraction patterns of the 1000°C annealed Ho$_9$Fe$_{87.5}$Ti$_{3.5}$ and Er$_9$Fe$_{87.5}$Ti$_{3.5}$ samples. These x-ray diffraction patterns have the same characteristic reflections as that of the 1000°C annealed Dy$_9$Fe$_{87.5}$Ti$_{3.5}$ sample. Because no other experimental data on this new phase are available so far, however, the identification of this new phase cannot be completed and further work is needed.

Figure 8-11: Powder x-ray diffraction patterns of the 1000°C annealed (a)Ho$_9$Fe$_{87.5}$Ti$_{3.5}$ and (b)Er$_9$Fe$_{87.5}$Ti$_{3.5}$ samples. (Co Kα radiation)
8.2.4. THE Dy(Fe_{1-x}Ti_x)_{12} (1:12-T) PHASE

Approximately single tetragonal Dy(Fe_{1-x}Ti_x)_{12} phase was formed in the as-cast Dy_{75}Fe_{83}Ti_{9} sample (Figure 8-12(a)). The composition (EDAX result) of this Dy(Fe_{1-x}Ti_x)_{12} phase is Dy : Fe : Ti = 8.8 : 83.6 : 7.4 (±0.5 at.%), which has an \(R:(Fe+Ti)\) ratio of 10.2. Figure 8-1(b) shows the powder x-ray diffraction pattern of this sample. Although the \(R:(Fe+Ti)\) ratio of the main matrix phase deviates from 1:12, the XRD pattern of this sample shows the characteristic reflections of the tetragonal ThMn_{12}-type structure. The lattice parameters calculated from the x-ray diffraction result for this Dy(Fe_{1-x}Ti_x)_{12} are \(a=8.5148(6)\) Å and \(c=4.7948(8)\) Å.

8.2.5. A NEW ORTHORHOMBIC Dy(Fe_{1-x}Ti_x)_{12} (1:12-O) PHASE

After annealing the Dy_{75}Fe_{83}Ti_{9} sample at 1070°C for 3 days, the SEM shows that the sample has a microstructure very similar to that of the as-cast sample, but comprises a small amount of Fe_{2}Ti impurity precipitated from the matrix phase (Figure 8-12(b)). The composition of the main matrix phase in this sample is Dy : Fe : Ti = 8.9 : 81.9 : 9.2. It has approximately the same Dy content as the 1:12-T phase in the as-cast sample, but the ratio of Ti : Fe increased slightly from 0.09 to 0.11.

The powder XRD pattern of this sample revealed that this increase of the Ti : Fe ratio caused a structural transformation from tetragonal 1:12 to a new structure (Figure 8-1(d)). In the x-ray diffraction pattern of the new phase, all the characteristic 1:12-T reflections between \(2\theta = 25^\circ - 65^\circ\) (Cu K\(\alpha\)) exist, but some splitting of the original 1:12 peaks is apparent. A more significant difference between the 1:12-T structure and the new phase is the characteristic superlattice peaks of the new phase around \(2\theta = 38.2^\circ\). The reflection around \(2\theta = 44.4^\circ\) is due to the Fe_{2}Ti impurity.
Figure 8-12: SEM photographs of the (a) as-cast and (b) 1070°C annealed Dy$_{7.5}$Fe$_{83.3}$Ti$_{9.2}$ samples. Both are approximately single phase. After annealing, a very small amount of Fe$_2$Ti impurity precipitated from the main matrix phase.
Disregarding the peak splitting and the superlattice peaks around $2\theta = 38.2^\circ$, the pattern was first indexed in terms of the tetragonal 1:12 structure. Based on this indexation, it was, then, found that the characteristic peaks of the new phase around $2\theta = 38.2^\circ$ can be indexed as a (320) reflection, ignoring the peak splitting. According to the condition limiting the possible reflections for the tetragonal 1:12 structure (space group I4/mmm), however, the (320) reflection should not exist in the 1:12-T structure, since the reflection condition is $h+k=2n$ for the $(h k 0)$ planes in the ThMn$_{12}$-type structure. Considering the similarity of the x-ray diffraction patterns of the new phase and the 1:12-T phase as well as the peak splitting, it is possible that this new phase is a distorted 1:12-T with a new orthorhombic structure. Prior to this consideration, an orthorhombic structure was used to index the x-ray diffraction pattern; the lattice parameters deduced from the XRD pattern are $a=8.5455(5)\text{Å}$, $b=8.5135(7)\text{Å}$ and $c=4.790(6)\text{Å}$. Since this new phase has approximately the same R:T ratio as the Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ phase, in order to distinguish it from the 1:12-T phase, it will be referred to as 1:12-O hereafter.

It is well known that the tetragonal 1:12 phase does not crystallize in any binary R-Fe systems, addition of certain amount of a third element (T) into the R-Fe systems is essential to stabilize the structure$^9$ $^{10}$. The role of the third element is to satisfy the geometrical (or size) requirement. A common observation is that the amount of the third element required to stabilize the 1:12-T structure depends on the atomic size of the third element — the bigger the atomic size of T, the less amount of T is required. These additional T atoms do not occupy the 3 transition metal sites, 8i, 8j and 8f, in the 1:12-T structure randomly, but show a highly preferential site occupation$^{10}$. If the T atom has a smaller atomic size than Fe (such as Si), it prefers the 8f and 8j sites. If T is bigger than
Fe (such as Ti, V), it prefers the 8i sites. Formally, it is this site preferential occupation by T that justifies the general reference to these compounds as ternaries rather than pseudo-binaries.

In the Dy-Fe-Ti system, the tetragonal Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ structure can be stabilized with 7.4 at.% Ti. The new 1:12-O phase, however, has a higher Ti content. If the excess Ti atoms still prefer to occupy some special atomic sites, specially along either the $a$ or $b$ axis of the 1:12 structure, the large Ti atoms will then lengthen this axis and produce a structural transformation from tetragonal to orthorhombic. In this case, using an equation

\[ x(R_{Ti} - R_{Fe}) - (1-x)(R_{Ti} - R_{Fe}) = a - b, \]

where $R_{Ti}$ and $R_{Fe}$ are the radii of Ti and Fe, respectively, and $x$ is the possible occupancy of Ti atoms along the $a$ axis, together with the lattice parameters from the indexation of the powder x-ray diffraction result, the calculated result shows that only 6% more Ti atoms preferentially occupying specific atomic sites along the $a$-axis (or $b$-axis) can cause the structural transformation from tetragonal 1:12 to the new orthorhombic 1:12. Because this preferential occupation changes the symmetry of the structure and therefore the space group of the 1:12-T, the (320) reflection absent in the 1:12-T phase appears in the new 1:12-O phase.

The magnetic ordering temperature ($T_c$) of the new orthorhombic phase is 535 ($\pm$10 K), which is higher than that of the tetragonal Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ phase in the as-cast sample ($T_c$=508 ($\pm$10 K)).

In order to compare the tetragonal 1:12 and novel orthorhombic 1:12 phases, the Mössbauer spectra of the as-cast and annealed Dy$_{7.5}$Fe$_{83.5}$Ti$_{9.2}$ samples were also collected at room temperature. Figure 8-13 shows the results. The solid lines represent the theoretical fits to the experimental data. In analyzing the spectrum of the as-cast
sample, we employed three magnetically-split sextets with variable line-widths. Including extra subspectra in the fitting procedure had little effect on the average hyperfine field value. However, in fitting the spectrum of the annealed sample three subspectra appear not enough and at least four subspectra are required. This indicates that the 1:12-O structure has more complex Fe sites than the 1:12 structure. The average hyperfine field is 23.0(±0.3)T for the Dy(Fe_{1-x}Ti_x)_{12} and 23.1(±0.3)T for the new orthorhombic 1:12 phase.

Figure 8-13: Room temperature $^{57}$Fe Mössbauer spectra of the as-cast and annealed Dy_{7.5}Fe_{83.3}Ti_{9.2} samples. Solid lines are the theoretical fits.
8.2.6. THE HIGH Ti SAMPLES AND THE Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ PHASE

Figure 8-14 shows the SEM photographs of the as-cast Dy$_{77}$Fe$_{76.9}$Ti$_{15.4}$ and Dy$_{9.5}$Fe$_{79.5}$Ti$_{11}$ samples. Both samples comprise a dominant matrix phase with a very small amount of Fe$_2$Ti and an intergranular impurity phase. The compositions of the matrix phase and the intergranular impurity identified by EDAX are Dy : Fe : Ti = 8.5(±0.4 at.%) : 81.2(±0.6 at.%) : 10.3(±0.3 at.%) and 28.0(±1.4 at.%) : 67.2(±1.5 at.%) : 4.8(±0.3 at.%) in the Dy$_{77}$Fe$_{76.9}$Ti$_{15.4}$ sample and Dy : Fe : Ti = 9.0(±0.4 at.%) : 81.8(±0.4 at.%) : 9.2(±0.3 at.%) and 27.4(±1.8 at.%) : 67.4(±1.3 at.%) : 4.8(±0.3 at.%) in the Dy$_{9.5}$Fe$_{79.5}$Ti$_{11}$ sample, respectively. The Dy contents of the matrix phases in these samples are approximately same as that of the Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ and 1:12-O phases. Their Ti contents are higher than that of the Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ phase and similar to that of the 1:12-O phase.

The powder x-ray diffraction patterns of these two samples (Figure 8-15) are the same as those of the as-cast samples with high Ti content in the Gd-Fe-Ti (the Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$ sample, see Figure 6-10) and Tb-Fe-Ti systems (the Tb$_{8.5}$Fe$_{80.5}$Ti$_{11}$ sample, see Figure 7-15). Since the impurity phases in these samples have the compositions close to a 6:23 or 1:3 ratios but the x-ray diffraction patterns resemble a combination of the characteristic reflections of the Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ and Dy(Fe$_{1-x}$Ti$_x$)$_{3}$ phases, the calculated diffraction patterns of Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ and Dy(Fe$_{1-x}$Ti$_x$)$_{3}$ are also shown in Figure 8-15 for phase identification. As in the Gd-Fe-Ti and Tb-Fe-Ti systems, these patterns cannot be indexed as to the Dy(Fe$_{1-x}$Ti$_x$)$_{12}$ and Dy(Fe$_{1-x}$Ti$_x$)$_{3}$ phases. Thus, the matrix phase could be a new phase that was also evidenced in the as-cast Gd$_{8.5}$Fe$_{80.5}$Ti$_{11}$ and Tb$_{8.5}$Fe$_{80.5}$Ti$_{11}$ samples.
Figure 8-14: SEM photographs of the as-cast (a) Dy₇.₇Fe₇₆.₉Ti₁₅.₄ and (b) Dy₉.₅Fe₇₉.₅Ti₁₁ samples. Although they are multi-phase, the amount of the impurity phases is quite small.
Figure 8-15: Powder x-ray diffraction patterns of the as-cast Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ and Dy$_{9.5}$Fe$_{79.5}$Ti$_{11}$ samples (Cu Kα radiation). The bar patterns are the calculated diffraction results of the Dy(Fe$_{1-x}$Ti$_x$)$_2$ and Dy(Fe$_{1-x}$Ti$_x$)$_3$ phases based on the indexation of the experimental diffraction results.

After annealing the Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ and Dy$_{9.5}$Fe$_{79.5}$Ti$_{11}$ samples at 1070°C for 3 days, the tetragonal Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ phase formed in both samples. Figure 8-16 shows the SEM photograph of the annealed Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ sample. It contains approximately single phase Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ with a very small amount of Fe$_2$Ti impurity. Figure 8-1(e) is the powder x-ray diffraction pattern of this Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ phase. It has the characteristic reflections of the BaCd$_{11}$-type structure (space group P4/mmb). The EDAX analysis shows its composition as Dy : Fe : Ti = 8.8 : 76.4 : 14.8 (±0.7 at.%), which has nearly the same Dy content as those of the 1:12-T and new 1:12-O phases, but the Ti content is
twice that of the 1:12-T phase. The lattice parameters of this 1:11 phase deduced from the powder x-ray diffraction pattern in terms of the BaCd$_{11}$ structure are $a=8.2183(7)$Å and $c=4.8160(9)$Å.

Figure 8-16: SEM photograph of the 1070°C annealed Dy$_{7.7}$Fe$_{76.9}$Ti$_{15.4}$ sample. It is approximately single phase with only a small amount of Fe$_2$Ti impurity.

Thus far, the relationship between the CaCu$_5$ and BaCd$_{11}$ structures has not been discussed. From the dumb-bell replacement point of view, it is very difficult to see any relationship between these two structures. However, from the CPR point of view their relationship is readily seen.

Figure 8-14 shows the atomic projections of (a) the 1:5 structure along the [110] direction, (b) the 1:12 structure along the [100] direction and (c) the 1:11 structure along the [100] direction. The coordination polyhedra of the R atoms (CPRs) in these three structures are also shown in the figure.
Figure 8-17: Schematic illustration of the relationships between the 1:5, 1:12 and 1:11 structures in terms of CPRs.
As already mentioned in previous chapters, be viewing the coordination shells of the particularly large R atoms (CPR) in the 1:5 and 1:12-T structures, they can be seen as similar CPR stackings along one direction with the difference mainly in the CPR types. In the 1:5 structure, the CPRs contain two R coordination atoms that stretch the CPRs along the \( c_{1:5} \) direction. In the 1:12-T structure, these two R coordination atoms are replaced by two T atoms (dumb-bell atoms) and consequently transform the elongated CPRs in the CaCu\(_5\) structure to the more symmetric 20-vertex CPRs in the 1:12-T structure.

In the 1:11 structure, all the 20 coordination atoms of the CPRs are transition metal atoms and so these 20-vertex polyhedra are very similar to those in the 1:12-T structure. The difference between the 1:12-T and 1:11 structures is the arrangement of the CPRs (Figure 8-14). In the 1:12-T structure, the CPRs are arranged as a quartet on each layer. This arrangement leaves a large void in the central boundary of the four CPRs, so the next CPR layer must displace along the [110] direction a \( \frac{\sqrt{2}}{2} a_{1:12} \) distance to fill this space in order to form a compact atomic arrangement. In the 1:11 structure, one T atom is inserted between every two adjacent CPRs. This enlarges the space between the four CPRs relative to the 1:12-T structure, allowing enough space for another CPR in the middle of four CPRs on the same CPR layer. However, in order to reach a compacted CPR arrangement so a better space-filling arrangement, all CPRs have to make an adjustment. Because the large space between the CPRs in the 1:12-T structure has been filled by another CPR, there is no need for the next layer of CPRs to be displaced to achieve a compact atomic arrangement.
Hence, to derive the 1:11 structure from the CaCu$_5$ structure, three steps have to be followed, (1) replacing two large R coordination atoms in the CaCu$_5$-type CPRs with two small T atoms (the same dumb-bell replacement as the ThMn$_{12}$-type structure), (2) inserting a T atom between every two adjacent CPRs and (3) adjusting the CPRs appropriately to form a compact atomic arrangement.

From the composition point of view, it is worthwhile noticing that the formation of the 1:11 phase needs more Ti atoms than the 1:12-T phase. Considering the coordination polyhedra around all the atoms in the 1:11 structure, this structure is formed basically with three close-packed coordination polyhedra, namely 12-fold for the 8j, 8k and 2c sites, 15-fold for the 4g sites and 20 fold for the 2a R. If one views the 1:11 and 1:12 structures as the stackings of the 20-fold coordination polyhedra, he can easily note that the 4g sites with 15-fold coordination in the 1:11 structure are exactly corresponds to the 8i sites with 14-fold coordination in the 1:12 structure. It is, then, conceivable to conclude that the site preference occupation of Ti at the 8i sites observed in the 1:12 phase shall stay in the 1:11 phase. Assuming all the 4g sites are occupied by the Ti atoms in the 1:11 phase, the Ti content in the 1:11 phase would be 16.6 at.%.

Based on the EDAX result, the Ti content in the Dy(Fe$_{1-x}$Ti$_x$)$_{11}$ phase is 14.8 at.% that is quite close to the calculated value above. Thus it justifiable to conclude that nearly all the 4g sites are occupied by the relatively large Ti atoms. As we know, only part of the 8i sites is occupied by the Ti atoms in the 1:12 structure. In the 1:11 phase, however, the corresponded 4g sites have a higher coordination number and so are more spacious for large atoms. The consequence of the better space-filling arrangement would be, then, to introduce more large Ti atoms into the 4g sites. Thus, the CPR model explains the
mechanism behind the transformation from the 1:12-T phase to the 1:11 phase as an increase of the Ti content.

8.3. CONCLUSIONS

A systematic study shows that there are at least six phases, namely (1) hexagonal Dy$_2$(Fe$_{1-x}$Ti$_x$)$_{17}$, (2) Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, (3) Dy(Fe$_{1-x}$Ti$_x$)$_{10}$, (4) Dy(Fe$_{1-x}$Ti$_x$)$_{12}$, (5) a novel orthorhombic 1:12 phase and (6) Dy(Fe$_{1-x}$Ti$_x$)$_{11}$, crystallizing in the Fe-rich corner of the Dy-Fe-Ti system. The third element Ti plays a key role in the stabilization of these phases.

The hexagonal 2:17 phase identified in the Dy-Fe-Ti system has a relatively higher Ti content compared with the rhombohedral 2:17 phases formed in other systems. Considering the structural characteristics of the rhombohedral and hexagonal 2:17 phases in terms of the coordination polyhedra around the particularly large R atoms (CPRs), the observed relatively high Ti content in the hexagonal 2:17 phase can be judiciously explained.

Although only hexagonal 2:17 was detected in the Dy-Fe-Ti system in the present work, at least two different intermediate phases between 2:17 and 1:12, the Dy$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$ and Dy(Fe$_{1-x}$Ti$_x$)$_{10}$ phases, have been identified. The former has a monoclinic Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type structure and the latter has a new structure. Considering the structural relationships among the 1:5, 3:22, 2:17-H and 1:12 phases, a possible structure for the Dy(Fe$_{1-x}$Ti$_x$)$_{10}$ phase was proposed which is orthorhombic.

The systematic study of three "heavy" rare earth systems, Gd-Fe-Ti, Tb-Fe-Ti and Dy-Fe-Ti, has shown that the tetragonal R(Fe$_{1-x}$Ti$_x$)$_{12}$ phase undergoes structural
modifications as the Ti content increases, transforming the tetragonal 1:12 structure into new structures. A particularly interesting result here is that corresponding to the observation that the 3:22, 2:17 phases and the intermediate phases between 2:17 and 1:12 undergo the structural changes as R changes from Gd and Tb to Dy, the structural transformation of the 1:12 phase also undergoes a change. In the Dy-Fe-Ti system, the resulted structure differs from those in the Gd-Fe-Ti and Tb-Fe-Ti systems, which is an orthorhombic 1:12 instead of P112. The new orthorhombic 1:12 structure is probably a result of an extremely preferential occupancy of Ti atoms in the tetragonal 1:12 structure.

As the Ti content is very high, the tetragonal 1:11 phase also crystallizes in the Dy-Fe-Ti system. Although the relationship between the 1:5 and 1:11 structures is not apparent from the dumb-bell replacement point of view, it is quite obvious in terms of the CPRs. The 1:11 structure, like the 1:5 and 1:12 structures, is also a simple stacking of the 20-vertex CPRs. The 1:11 phase can be regarded as determined by the geometrical requirement for sphere packing. Consequently, the role of the third element Ti in stabilizing the 1:11 phase can be explained as to satisfy the space-filling.

Besides the six phases discussed above, our results also indicate the possible existence of two other novel phases in this system. One of them is possibly another intermediate phase between the 2:17 and 1:12 phases. The other one has a structure closely related to the tetragonal 1:12 structure.
REFERENCES


9 Ying-Chang Yang, Lin-Shu Kong, Shu-He Sun, Dong-Mei Gu and Ben-Pei Cheng, J. Appl. Phys. 63, 3702 (1988).

Chapter Nine:

PHASE FORMATION IN THE Nd-Fe-Zr SYSTEM

9.1. INTRODUCTION

It is known that the $1:12$ phase does not stabilize in any binary R-Fe systems, a small amount of a third element ($T$), such as Ti, V, Cr, Mn, Mo, W, Al and Si, is essential to stabilize it\textsuperscript{1-4}. The amount of the third element ($T$) required to stabilize the $1:12$ structure is closely related to the atomic size of $T$. The larger the $T$ atom is, the less amount of $T$ is required. In previous chapters we reported the identification of several new phases. These new phases, like the $1:12$ phase, do not crystallize in R-Fe binary systems either and a third element is required. The role of the third element in stabilizing these structures is a size effect. Thus, it is reasonable to predict that these new phases, as the tetragonal $1:12$ phase, should also exist in other R-Fe-$T$ systems, such as $T=V$, Cr, Mn, Mo, W and Al. In fact, the Nd$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$-type $3:29$ phase has been identified in the Nd-Fe-T systems with $T=V$, Cr and Mn\textsuperscript{5,6}. In Figure 3-7, we have shown part of the periodic table, from which it can be seen that Zr is a neighbor of the aforementioned elements, but with a bigger atomic size. In order to investigate the influence of zirconium on phase formation by alloying Zr into the Nd-Fe binary system, we studied the Nd-Fe-Zr system.

9.2. RESULTS AND DISCUSSION

9.2.1. THE AS-CAST SAMPLES

We started this study with samples of starting compositions Nd$_{10}$Fe$_{89.5}$Zr$_{0.5}$, Nd$_9$Fe$_{89.5}$Zr$_{1.0}$, Nd$_9$Fe$_{89.5}$Zr$_{1.5}$, Nd$_{7.5}$Fe$_{89.5}$Zr$_{3}$, Nd$_{7.7}$Fe$_{84.6}$Zr$_{7.7}$, Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$, Nd$_8$Fe$_{75}$Zr$_{17}$.
and Nd₇Fe₇₃₋₁₂Zr₁₉₂ in an attempt to form the 1:12 and 3:29 phases in the Nd-Fe-Zr system. The SEM results show that all the as-cast samples are multi-phase. The SEM microstructure photographs of the as-cast Nd₉Fe₈₉.₅Zr₁₀, Nd₉Fe₈₉.₅Zr₁₅, Nd₇₅Fe₈₉.₅Zr₃, Nd₇₇Fe₇₆.₅Zr₁₅₄ and Nd₈₂Fe₇₂Zr₁₇ samples are shown in Figure 9-1, from which it can be seen that all the samples are composed of two dominant phases with a small amount of a third intergranular impurity phase. The EDAX results indicate a 2:17 matrix phase in all samples. The secondary main phase is either α-Fe (in the samples with low Zr content) or Fe₂Zr(Nd)/Fe₃Zr(Nd) (in the samples with intermediate and high Zr content).

Table 9-1: The phase content and compositions of the matrix 2:17 phase in as-cast Nd₁₀Fe₈₉.₅Zr₀.₅, Nd₉Fe₈₉.₅Zr₁₀, Nd₉Fe₈₉.₅Zr₁₅, Nd₇₅Fe₈₉.₅Zr₃ and Nd₇₇Fe₇₆.₅Zr₁₅₄.

<table>
<thead>
<tr>
<th>Sample (as-cast)</th>
<th>Phases in the sample</th>
<th>Composition (EDAX) Nd : Fe : Zr (±0.6 at.%)</th>
</tr>
</thead>
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<td>NdFe₁₀₅Zr₀.₅</td>
<td>(Nd₁₋αZr₁α)₂Fe₁₇</td>
<td>10.1 : 89.0 : 0.9 /</td>
</tr>
<tr>
<td></td>
<td>α-Fe</td>
<td></td>
</tr>
<tr>
<td>NdFe₁₁ₐZr₁.₀</td>
<td>(Nd₁₋αZr₁α)₂Fe₁₇</td>
<td>10.0 : 88.7 : 1.3 /</td>
</tr>
<tr>
<td></td>
<td>α-Fe</td>
<td></td>
</tr>
<tr>
<td>NdFe₁₀₅Zr₁.₅</td>
<td>(Nd₁₋αZr₁α)₂Fe₁₇</td>
<td>9.6 : 89.3 : 1.1 /</td>
</tr>
<tr>
<td></td>
<td>Fe₃Zr(Nd), Fe₂Zr(Nd)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe₂Zr(Nd), Fe₃Zr(Nd)</td>
<td></td>
</tr>
<tr>
<td>NdFe₉₆Zr₃.₀</td>
<td>(Nd₁₋αZr₁α)₂Fe₁₇</td>
<td>9.6 : 88.8 : 1.6 /</td>
</tr>
<tr>
<td></td>
<td>Fe₂Zr(Nd), Fe₃Zr(Nd)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe₂Zr(Nd)</td>
<td></td>
</tr>
<tr>
<td>Nd₇₇Fe₇₆.₅Zr₁₇</td>
<td>(Nd₁₋αZr₁α)₂Fe₁₇</td>
<td>9.0 : 87.2 : 3.8 /</td>
</tr>
<tr>
<td></td>
<td>Fe₂Zr(Nd)</td>
<td></td>
</tr>
</tbody>
</table>

The phase formed in the as-cast Nd₁₀Fe₈₉.₅Zr₀.₅, Nd₉Fe₈₉.₅Zr₁₀, Nd₉Fe₈₉.₅Zr₁₅, Nd₇₇Fe₇₆.₅Zr₁₅₄ and Nd₇₇Fe₇₆.₅Zr₁₇ samples and the compositions (EDAX data) of the 2:17
Matrix phases in these samples are listed in Table 9-1. The results indicate that the solubility of Zr in the Nd$_2$Fe$_{17}$ phase is very low. More importantly as the Zr content increases, the Nd content decreases in a related manner indicating that Zr replaced Nd instead of Fe in the 2:17 phase. Hence, the behavior of the Zr atoms is different from other transition metal atoms, such as Ti and Si that prefer to occupy the R sites rather than the Fe sites. If we compare the atomic size of Zr (2.16Å) with those of Nd (2.64Å) and Fe (1.72Å), we can see that the atomic size of Zr is marginally closer to that of Nd rather than that of Fe. Thus, in terms of the atomic size it is feasible that Zr atoms may occupy Nd sites instead of Fe sites in the (Nd$_{1-x}$Zrx)$_2$Fe$_{17}$ phase. This result is consistent with the argument of size factor in the R-T compounds discussed in the previous chapters. In the rhombohedral R$_2$T$_7$ structure, there are 3 different coordinations, 20-fold coordination for the particularly large R atoms and 12, 14-fold coordinations for the small T atoms. Considering the large size of the Zr atoms, it is understandable that preferred sites for the Zr atoms are the R sites instead of T sites.

\[ \text{Nd}_{9.3}\text{Fe}_{89.5}\text{Zr}_{1.0} \]

*Figure 9-1(1): SEM photograph of the as-cast Nd$_{9.5}$Fe$_{89.5}$Zr$_{1.0}$ sample.*
Figure 9-1(2): SEM photographs of the as-cast \(\text{Nd}_9\text{Fe}_{89.5}\text{Zr}_{1.5}\) and \(\text{Nd}_{7.5}\text{Fe}_{89.5}\text{Zr}_3\) samples.
Figure 9-1(3): SEM photographs of the as-cast $Nd_{7.7}Fe_{76.9}Zr_{15.4}$ and $Nd_{8}Fe_{75}Zr_{17}$ samples.
Figure 9-2: Powder x-ray diffraction patterns of as-cast $\text{Nd}_{10}\text{Fe}_{89.5}\text{Zr}_{0.5}$, $\text{Nd}_{9}\text{Fe}_{89.5}\text{Zr}_{1.5}$, $\text{Nd}_{7.5}\text{Fe}_{89.5}\text{Zr}_{3}$, $\text{Nd}_{7.7}\text{Fe}_{76.9}\text{Zr}_{15.4}$ and $\text{Nd}_{7.7}\text{Fe}_{73.1}\text{Zr}_{19.2}$ (Cu Ka radiation). The bars are calculated x-ray diffraction patterns of rhombohedral 2:17 and $\text{Fe}_2\text{Zr}$. 
Figure 9-2 shows the powder x-ray diffraction patterns of the as-cast Nd$_{10}$Fe$_{89.5}$Zr$_{0.5}$, Nd$_9$Fe$_{89.5}$Zr$_{1.5}$, Nd$_7$Fe$_{89.5}$Zr$_{5.0}$, Nd$_7$Fe$_{76.9}$Zr$_{15.4}$ and Nd$_7$Fe$_{73.1}$Zr$_{19.2}$ samples. Except for the Nd$_7$Fe$_{73.1}$Zr$_{19.2}$ sample, all the patterns show the characteristic reflections of the rhombohedral 2:17 phase with several extra peaks from Fe$_2$Zr(Nd). The diffraction pattern of Nd$_7$Fe$_{73.1}$Zr$_{19.2}$ shows the characteristic reflections of the Fe$_2$Zr structure with several weak peaks of the 2:17 phase, indicating that Fe$_2$Zr becomes the dominant phase in the high Zr content samples.

Considering that the R$_3$(Fe$_{1-x}$Ti$_x$)$_{29}$, R(Fe$_{1-x}$Ti$_x$)$_{12}$ and R(Fe$_{1-x}$Ti$_x$)$_{11}$ phases only crystallize after annealing, we annealed selected samples at 720°C, 850°C and 1100°C for 3 days.

9.2.2. THE 1000°C ANNEALED SAMPLES

After annealing at 1100°C for 3 days, the SEM/EDAX results show that this annealing procedure did not have dramatic effects on the microstructure and the phase content (see Figure 9-3). All samples have similar phase content and microstructure to their as-cast counterpart. Apart from the (Nd$_{1-x}$Zr$_x$)$_2$Fe$_{17}$ phase and α-Fe (low Zr content samples) or Fe$_2$Zr(Nd) and Fe$_3$Zr(Nd) (intermediate and high Zr content samples), no 3:29 or 1:12 phases were found in these annealed samples. In the samples with low Zr content the (Nd$_{1-x}$Zr$_x$)$_2$Fe$_{17}$ phase is the dominant phase with some α-Fe/Fe$_2$Zr(Nd) impurity and as the Zr content increases the Fe$_2$Zr(Nd) phase becomes the principal phase with some (Nd$_{1-x}$Zr$_x$)$_2$Fe$_{17}$ and Fe$_3$Zr(Nd) impurities. The fact that no 3:29 and 1:12 phases exist in the Nd-Fe-Zr system is probably because of the fact that the Zr atoms prefer occupying the R sites instead of the T sites in the compounds formed in the Nd-Fe-Zr system due to its large atomic size.
Figure 9-3(1): SEM photographs of the 1100°C annealed (a) Nd$_9$Fe$_{89.5}$Zr$_{1.5}$ and (b) Nd$_{7.5}$Fe$_{89.5}$Zr$_3$, samples. They are multi-phase with a main matrix ($Nd_{1-x}Zr_x$)$_2$Fe$_{17}$ phase and some α-Fe/Fe$_2$Zr(Nd).
9.2.3. THE SAMPLES ANNEALED AT 720°C AND 850°C—A NEW (Nd\(_{1/3}\)Zr\(_{2/3}\))Fe\(_{3}\) PHASE

After annealing at 720°C and 850°C for 3 days, the samples with low Zr content are also identical to the as-cast samples. The annealing process did not have an apparent effect on these low Zr samples (see Figure 9-4(a) and (b)). In the samples with high Zr content, however, SEM clearly indicates that although large amounts of the Fe\(_2\)Zr(Nd) and (Nd\(_{1-x}\)Zr\(_x\))\(_2\)Fe\(_{17}\) phases still exist, a new phase is formed. Figure 9-4(c) and (d) show the SEM microstructure photograph of the Nd\(_{77}\)Fe\(_{76.9}\)Zr\(_{15.4}\) and Nd\(_{8}\)Fe\(_{75}\)Zr\(_{17}\) samples annealed at 850°C for 3 days. From these photographs it can be seen clearly that a new phase (the light gray phase) formed from the Fe\(_2\)Zr(Nd) phase in these samples. The stoichiometric composition of this new phase, identified by EDAX, is Nd : Zr : Fe = 8.2 : 17.3 : 74.5 (±0.5 at.%), a precisely defined 1 : 2 : 9 ratio.
Figure 9-4(1): SEM photographs of the Nd$_{9.5}$Fe$_{89.5}$Zr$_{1.0}$ and Nd$_{7.5}$Fe$_{89.5}$Zr$_{3.0}$ samples annealed at 850°C for 3 days. They have the same phase contents and microstructures as the as-cast and 1100°C annealed samples.
Figure 9-4(2): SEM photographs of the Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$ and Nd$_8$Fe$_{75}$Zr$_{17}$ samples annealed at 850°C for 3 days. A new phase (the light gray phase) formed upon annealing.
Figure 9-5: Powder x-ray diffraction patterns of the as-cast, 720°C, 850°C and 1100°C annealed (for 3 days) Nd7.7Fe76.9Zr15.4 sample. The bars are calculated diffraction patterns of Fe2Zr and Fe3Zr.
The powder x-ray diffraction results are consistent with the SEM/EDAX results. Figure 9-5 shows the as-cast, 720°C, 850°C and 1100°C annealed Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$ samples. The x-ray diffraction patterns of the as-cast and 1100°C annealed Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$ samples are typical Fe$_2$Zr diffraction pattern with some extra weak peaks from (Nd$_{1-x}$Zr$_x$)$_2$Fe$_{17}$. However the patterns of the 720°C and 850°C annealed samples show several new reflections indicating the formation of the new phase.

In order to identify this new phase, the Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$, Nd$_{7.7}$Fe$_{76.9}$Zr$_{15.4}$ and Nd$_{7.7}$Fe$_{73.1}$Zr$_{19.2}$ samples were annealed at 720°C and 800°C for 13 and 25 days in an attempt to make a single-phase sample. Figure 9-6 shows the SEM photographs of the Nd$_{7.7}$Fe$_{73.1}$Zr$_{19.2}$ samples annealed at 800°C for 3, 13 and 25 days. From these SEM results it can be seen that as the annealing time increased, the amounts of (Nd$_{1-x}$Zr$_x$)$_2$Fe$_{17}$ (the phase in the intergranular regions) and Fe$_2$Zr(Nd) (the dark gray phase) decreased.

![SEM photograph of the Nd$_{7.7}$Fe$_{73.1}$Zr$_{19.2}$ sample after annealing at 800°C for 3 days](a) 3 days

*Figure 9-6(1): SEM photograph of the Nd$_{7.7}$Fe$_{73.1}$Zr$_{19.2}$ sample after annealing at 800°C for 3 days*
Figure 9-6(2): SEM photographs of Nd$_{7.7}$Fe$_{73.1}$Zr$_{19.2}$ after annealing at 800°C for 13 and 25 days. The amount of the new phase (the light gray phase) increases with the annealing time.

and the amount of the new phase (the light gray phase) increased. After 25 days annealing, a nearly single phase sample was obtained. Clearly, this new phase has a very
low formation kinetics. Even after 25 days annealing some \((\text{Nd}_{1-x}\text{Zr}_x)\text{Fe}_{17}\) and 
\(\text{Fe}_2\text{Zr(Nd)}\) phases still exist in the sample. The EDAX analysis shows that the new phase in all the samples has a well defined composition \(\text{Nd} : \text{Zr} : \text{Fe} = 8.1 (\pm 0.5 \text{ at.\%}) : 17.6 (\pm 0.6 \text{ at.\%}) : 74.3 (\pm 0.6 \text{ at.\%})\) (at.\%) which corresponds to a \(1 : 2 : 9\) ratio.

Figure 9-7 shows the x-ray diffraction pattern of the 25 day annealed sample. This XRD pattern can be well indexed by the rhombohedral \(\text{PuNi}_3\) structure (space group \(\text{R} \overline{3} \text{m}\)). Refinement of the powder x-ray diffraction data gives the lattice parameters of this new \((\text{Nd}_{1/3}\text{Zr}_{2/3})\text{Fe}_3\) phase as \(a = 5.038(2)\text{Å}\) and \(c=24.311(2)\text{Å}\).

![Figure 9-7: Powder x-ray diffraction pattern of the new \((\text{Nd}_{1/3}\text{Zr}_{2/3})\text{Fe}_3\) phase (\(\text{Nd}_{7.7}\text{Fe}_{73.1}\text{Zr}_{19.2}\) annealed at 850°C for 25 days). The solid bars are the calculated diffraction pattern based on a \(\text{PuNi}_3\)-type structure.]

It is well known that although the \(\text{RFe}_3\) phase with the \(\text{PuNi}_3\)-type structure crystallizes in most of the binary \(\text{R-Fe}\) systems, this phase does not stabilize in the
binary Nd-Fe system. In the composition range around NdFe₂ two other phases with structures different from the PuNi₃, namely A₁ and A₂, have been identified in the long-time annealed samples at about 800°C. The A₂ phase has a composition of Nd₂₂₈Fe₇₇₂ with a hexagonal structure. This A₂ phase was also formed in rapidly quenched Sm₂Fe₁₇Ti alloys and has a very high c-axis anisotropy. In all the samples used in the present study, however, neither A₁ nor A₂ were identified.

In 1989, starting from YFe₃, Itoh et al. investigated the influence of zirconium substituted for yttrium in the series of Y₁₋ₓZrₓFe₂₉. They found that the rhombohedral PuNi₃ structure can remain unchanged at low Zr content range (x≤0.3). However, when the Zr content is increased, the structure transformed from the rhombohedral PuNi₃ structure to an orthorhombic type structure in the range 0.3<x<0.7, then to a C14-like hexagonal type structure in the range of 0.7<x<0.85 and finally to a C15 type structure in the range of 0.85<x<0.95. The easy magnetization direction is directed along the b-axis for the PuNi₃ structure phase (x≤0.3) and is parallel to the c-axis for all the other phases (0.4≤x≤0.95). The Curie temperature increases from 257°C for YFe₂₉ to 337°C for Y₀.₈Zr₀.₄Fe₂₉. Following this work, M. Katter et al. studied the (Y₁₋ₓSmₓ)Zr₀.₄Fe₂₉ system and found that Sm₀.₆Zr₀.₄Fe₂₉ has the PuNi₃-type structure. Their results show that the Curie temperature increases from 355°C for x=0 to 385°C for x=1 and, contrary to the results of Itoh and coworkers, the easy magnetization direction lies in the basal plane for x≤0.2 and change to the c-axis for x≥0.4 in this system. The anisotropy field of Sm₀.₆Zr₀.₄Fe₂₉ is 10.5T at room temperature, which is even larger than that of Nd₁₂Fe₁₄B (about 6.5T). Thus they believed that if one could find a way to prepare anisotropic magnets, this material would be interesting for practical permanent magnet applications.
Although the rhombohedral 1:3 phase does not exist in the binary Nd-Fe system, by introducing a third element Zr into Nd-Fe alloy this phase can be stabilized. However our results are different from those obtained by Itoh et al.\textsuperscript{10} and M. Katter et al.\textsuperscript{11}. In the Nd-Fe-Zr system the \((\text{Nd}_{1-x}\text{Zr}_{x})\text{Fe}_3\) phase has a well-defined Nd : Zr : Fe ratio, 1 : 2 : 9, that is, a fixed stoichiometric composition \((\text{Nd}_{1/3}\text{Zr}_{2/3})\text{Fe}_3\). Changing the composition in the samples only introduces impurities and the Nd : Fe : Zr ratio of the new phase remains unchanged.

As mentioned in previous chapters, many structures formed between rare earths and transition metals, such as the \(\text{R}_3(\text{Fe}_{1-x}\text{Si}_x)_{22}\), rhombohedral 2:17, hexagonal 2:17, \(\text{Nd}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}\), \(\text{Dy}(\text{Fe}_{1-x}\text{Ti}_x)_{10}\) and \(\text{R}(\text{Fe}_{1-x}\text{Ta}_x)_{12}\), can be directly derived from the \(\text{CaCu}_5\) structure by replacing a fraction of the R (Ca) atoms with two transition metal atom T (Cu) (dumb-bells). The \(\text{PuNi}_3\) structure can also be derived from the \(\text{CaCu}_5\) structure in this manner. However, unlike the structures mentioned above, in order to obtain the \(\text{PuNi}_3\) structure one has to replace \(\frac{1}{10}\) of the T(Cu) atoms with R(Ca) atoms in the \(\text{CaCu}_5\) structure. This process is illustrated in Figure 9-8. There are two types of atomic layers in the \(\text{CaCu}_5\) structure, in the lowest layer both R (Ca) and T (Cu) atoms are found whereas in the next layer only T (Cu) atoms are found. To form the \(\text{PuNi}_3\) structure, in the top or basal plane of every second \(\text{CaCu}_5\) unit cell one out of two T(Cu) atoms is replaced by a R(Ca) atom followed by a layer shift and a minor rearrangement of the atoms. This leads to a \(\text{PuNi}_3\) unit cell that has the same unit cell edge in the \(a\) direction but a \(c\) axis four times as long as that of the \(\text{CaCu}_5\) structure. After replacement, all the R (Ca) atoms in the basal planes in which the replacement occurs form the 6\(c\) site of the \(\text{PuNi}_3\) structure and the remaining R(Ca) atoms on the basal planes where no replacement occurs form the 3\(a\) site of the \(\text{PuNi}_3\) structure.
Figure 9-8: The PuNi$_3$ and CaCu$_5$ structures and their relationship. The former structure can be derived by replacing 1/10 of the $T$($Cu$) atoms by $R$($Ca$) atoms in the latter structure following a layer shift and some minor atomic adjustment.

In the new (Nd$_{1/3}$Zr$_{1/3}$)Fe$_3$ phase, the Nd : Zr : Fe = 1 : 2 : 9 ratio infers that all the $6c$ rare earth sites are occupied by Zr atoms and all the $3a$ sites are occupied by Nd atoms. Considering the structural transformation between CaCu$_5$ and PuNi$_3$, this extreme preferential site occupancy by Nd and Zr atoms is quite obvious. One out of two smaller $T$ atoms on every other basal plane of CaCu$_5$ must be replaced by larger $R$ atoms ($6c$), thus favoring the occupancy by smaller Zr atoms instead of the larger Nd atoms. As we have discussed in the previous chapters, in accordance with the consideration due to the Kasper and Frank$^{13, 14}$, most of the R-$T$ compounds can be
regarded as determined by the size factor or space-filling factor. If we look at the PuNi$_3$ structure from the CPR point of view that we introduced in Chapters 3 and 4, we see that the R atoms in this structure, as in most of other structures of rare earth-transition metal compounds, have

![Figure 9-9: The stacking sequences of coordination polyhedra of R atoms (CPRs) in the CaCu$_5$ and (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ (PuNi$_3$) structures and their structural relationship.](image)

20 coordination atoms. In Figure 9-9 we show the CaCu$_5$ and (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ (PuNi$_3$) structures in the form of CPRs stackings. From this figure we see that the PuNi$_3$ structure is also a simple stacking of 20-vertex CPRs. The structure of the CPR in the PuNi$_3$ structure is close to that in the CaCu$_5$ structure. The CPRs in both the CaCu$_5$ and
PuNi$_3$ structures are composed of 18 T atoms and two R atoms. In the CaCu$_3$ structure these two R coordination atoms are quite distant and sometimes they are not regarded as the coordinate atoms of R. As in the CaCu$_3$ structure, the CPR of the 3a site R atoms in the PuNi$_3$ structure also has two R coordination atoms (6c atoms). However, those two R coordination atoms are much closer to the central R atoms than those in the CaCu$_3$ structure, making the CPRs in PuNi$_3$ structure more symmetric and like an intermediate between the CPRs in the CaCu$_3$ and ThMn$_12$ structures. In the case of the (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ phase, since the two R coordination atoms of the CPRs (6c atoms) are accommodated by two Zr atoms, the R atoms in the (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ structure, as in the 1:12 structure, have 20 transition metal atoms as coordination atoms.

![Figure 9-10: Powder x-ray diffraction pattern of a magnetically aligned (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ phase. The pattern shows clearly that this phase has easy-plane anisotropy. The solid bars are the calculated powder diffraction pattern of the PuNi$_3$ structure.](image)

The magnetic ordering temperature ($T_c$) of the new (Nd$_{1/3}$Zr$_{2/3}$)Fe$_3$ phase derived from our TGA measurements show that this new phase, like Sm$_{0.6}$Zr$_{0.4}$Fe$_{2.9}$, has a high
magnetic ordering temperature ~658 (±10)K. However, unlike Sm_{0.6}Zr_{0.4}Fe_{2.9}, the magnetically aligned x-ray diffraction pattern (see Figure 9-10) of (Nd_{1/3}Zr_{2/3})Fe reveals that this phase has easy-plane anisotropy.

9.3. CONCLUSIONS

In contrast to the other transition metals, because the atomic size of Zr is closer to that of Nd than that of Fe, the Zr atoms prefer to occupy the R sites rather than the Fe sites in the (Nd_{1-x}Zr_{x})_{2}Fe_{17} phase. However, only a small amount of Nd atoms can be replaced by Zr atoms because of their large size disparity. The tendency of Zr atoms to occupy the R sites in R-M compounds can be seen clearly in the new (Nd_{1/3}Zr_{2/3})Fe_{3} phase. Although the rhombohedral 1:3 phase does not exist in the binary Nd-Fe system, addition of the third element Zr into the binary Nd-Fe system stabilizes the 1:3 phase in this system. This new pseudo-binary phase has a well-defined stoichiometric composition (Nd_{1/3}Zr_{2/3})Fe_{3}, which suggests that Zr atoms occupy all the 6c R sites and all the 3a R sites are occupied by Nd atoms. Considering the atomic arrangement in the 1:3 structure, we see that the role of the Zr atoms in stabilizing the 1:3 structure, like the role of the third element in the 1:12 and 3:29 structures, is also a size effect.
REFERENCES


Chapter Ten

SUGGESTIONS FOR FURTHER WORKS

Our results have shown that in addition to the well known 2:17 and 1:12 phases, several other novel Fe-rich phases, namely $\text{R}_3(\text{Fe}_{1-x}\text{Si}_x)_{22}$, $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$, $\text{P}_{1}$, $\text{Dy}(\text{Fe}_{1-x}\text{Ti}_x)_{10}$, $\text{P}_{112}$ and 1:12-O, also crystallize in the R-Fe-T systems.

$\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ is an intermediate phase between the rhombohedral 2:17 and tetragonal 1:12 phases and has been generally observed in the “light” rare earth (LR) systems where the 2:17 phase crystallizes in the rhombohedral structure. The study on three “heavy” rare earth (HR) systems, Gd-Fe-Ti, Tb-Fe-Ti and Dy-Fe-Ti, shows that $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ also crystallizes in these systems. In the Gd-Fe-Ti, Tb-Fe-Ti systems, the rhombohedral 2:17 phase has been identified, thus we expect to observe $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ in these systems. However, no rhombohedral $\text{Dy}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ has been found in the present study. A possible explanation for this is that the rhombohedral 2:17 phase also crystallizes in the Dy-Fe-Ti system, but only stabilizes with a lower Ti content than those used in our study. This conjecture is supported by the observation in the Tb-Fe-Ti system that although both rhombohedral and hexagonal $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ crystallize, rhombohedral $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$ only stabilizes in a relatively lower Ti content range than that of hexagonal $\text{Tb}_2(\text{Fe}_{1-x}\text{Ti}_x)_{17}$. To verify this suggestion, further work on the Dy-Fe-Ti system in the low Ti content range is required. This suggestion also leads to the possibility that both the rhombohedral and hexagonal 2:17 phases may crystallize in other ternary “heavy” rare earth HR-Fe-Ti systems with $\text{H}=\text{Er}$, $\text{Ho}$, $\text{Tm}$ and $\text{Lu}$. Consequently the $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$ may also exist in these HR-Fe-Ti systems.
We know that the $\text{R}_2\text{T}_7$ phase adopts two different structures depending on the $\text{R}$ atoms. In the composition range with lower $\text{R} : \text{T}$ ratio than 2:17, an intermediate phase between the 1:5 and 2:17 phases, $\text{R}_3(\text{Fe}_{1-x}\text{Si}_x)_{22}$, has been identified, which also crystallizes in two different structures correlated with those of the 2:17 phases. In the composition range with larger $\text{R} : \text{T}$ ratio than 2:17, however, things appeared more complicated. Besides $\text{R}_3(\text{Fe}_{1-x}\text{Ti}_x)_{29}$, two other new intermediate phases between 2:17 and 1:12, $\text{P}_1$ and $\text{Dy}(\text{Fe}_{1-x}\text{Ti}_x)_{10}$ (1:10), have been observed in the Tb-Fe-Ti and Dy-Fe-Ti systems, respectively, where the 2:17 phase can crystallize in the hexagonal structure. $\text{Dy}(\text{Fe}_{1-x}\text{Ti}_x)_{10}$ was identified as an intermediate phase between the hexagonal 2:17 and tetragonal 1:12 phases, but it is still unclear what $\text{P}_1$ is and whether the $\text{P}_1$ and 1:10 phases crystallize in other "heavy rare earth systems."

Furthermore, the two structural modifications in the tetragonal 1:12 phase were observed in the "heavy" rare earth systems, depending on $\text{R}$, which results in two new phases, $\text{P}_{1:12}$ and 1:12-O. $\text{P}_{1:12}$ formed in the Gd-Fe-Ti and Tb-Fe-Ti systems and 1:12-O in the Dy-Fe-Ti system. Although our results have shown that the third element Ti plays a key role in these two structural modifications, how the structural modification happens, what structures the $\text{P}_{1:12}$ and 1:12-O have and what happens in other "heavy" rare earth systems are still unknown.

Besides the phases mentioned above, traces of some other new phases were also observed in present work, such as the $\text{P}_3$ phase formed in the 1000°C annealed Dy$_9$Fe$_{87.5}$Ti$_{3.5}$, Er$_9$Fe$_{87.5}$Ti$_{3.5}$ and Ho$_9$Fe$_{87.5}$Ti$_{3.5}$ samples and another tetragonal 1:12 related phase observed in the as-cast samples with high Ti content in the Gd-Fe-Ti, Tb-Fe-Ti and Dy-Fe-Ti systems. The identification of these phases requires further work.
Thus, the whole picture of the phase formation and transition in the composition range with larger R:T ratio than 2:17 is still very unspecific so far. Much work is needed.

Furthermore, it is very worthwhile to perform the magnetic property investigation on these new phases.