Effect of titanium additions to low carbon, low manganese steels on sulphide precipitation

Sima Aminorroaya-Yamini
University of Wollongong


This paper is posted at Research Online.
http://ro.uow.edu.au/theses/403
NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
5-1 Introduction

New finishing processes such as hot direct-rolling and near-net-shape processing routes require more intimate knowledge of precipitates that form in cast steel [113]. Conventional controlled rolling of steels requires the reheating of slabs and soaking at 1200-1250°C. Therefore, the homogeneity of austenite increases and its grain size is controlled by precipitates which are stable at the soaking temperature. However, even in thick slabs that are reheated, it is necessary to study the evolution of precipitates during finishing processes (reheating and rolling).

In previous chapters, the main focus was on the analysis of centreline precipitates (Type II sulphide) which form as a result of macrosegregation during continuous casting of steel slabs. Previous studies [4, 12] suggested that titanium can be dissolved in manganese sulphide precipitates and that it is even possible that TiS can replace MnS in high manganese steels. However, in the present study, it was found that titanium replaces iron in
iron sulphide but does not dissolve in manganese sulphides. In the current chapter, the nature of precipitates, which form in the solid state immediately following solidification and transformation and during micro-segregation are evaluated by the use of TEM analysis and atom probe tomography.

5-2 Experimental method

Two steels (Table (5-1)), supplied in the form of as-cast, 230-mm-thick continuously cast slab, were used to investigate the effect of titanium on the chemical composition of precipitates formed in cast slabs as a result of microsegregation and/or precipitation during cooling and solid state transformations.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Al</th>
<th>Ti</th>
<th>Si</th>
<th>N</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel A</td>
<td>0.095</td>
<td>0.29</td>
<td>0.009</td>
<td>0.03</td>
<td>0.024</td>
<td>0.005</td>
<td>0.0037</td>
<td>0.018</td>
<td>0.024</td>
<td>0.022</td>
<td>0.026</td>
</tr>
<tr>
<td>Steel B</td>
<td>0.090</td>
<td>0.30</td>
<td>0.01</td>
<td>0.03</td>
<td>0.008</td>
<td>0.005</td>
<td>0.0036</td>
<td>0.015</td>
<td>0.024</td>
<td>0.021</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Specimens were selected from the centreline and edge of the slabs perpendicular to the casting direction as shown in Figure (5-1). Due to macrosegregation of elements to the centreline of the slab, the chemical composition at the centre would be different from that at the edge. Scanning electron microscopy was conducted on mirror polished surfaces (1 μm). Precipitates were characterised and subsequently analysed using a Zeiss, Supra 55 VP High-Resolution Scanning Electron Microscope (HR-SEM), equipped with energy dispersive spectroscopy (EDS). Carbon replica techniques have been employed to study the precipitates. The techniques have been described in detail in Chapter (3-4-1). These precipitates were further analyzed in a JEOL JEM 2011 Transmission Electron Microscope operating at 200 kV.

Nano-particles have been analyzed in Steel A by using a Three Dimensional Local Electrode Atom Probe. Samples were prepared from the edge and centre of the slab,
perpendicular to the casting direction in order to compare the effect of macrosegregation on the formation, nature and morphology of nano-precipitates.

Figure (5-1): Schematic illustration of samples positions in slab

The effects of titanium and sulphur additions on pseudo binary Fe-C phase diagrams are shown in Figure (5-2). All diagrams have been calculated for the iron rich corner by using Thermo-Calc software package [28] and employing the TCFE4 thermodynamic database [29]. Figures (5-2-a to c) show the effect of titanium addition on a 0.3 wt% manganese, 0.01 wt% sulphur steel with 0, 0.008 wt% and 0.024 wt% titanium respectively. Thermo-Calc predicts that the addition of titanium results in the formation of Ti_4C_2S_2 at high temperature and that the austenite-Ti_4C_2S_2 phase field will be extended to lower temperatures to quite low carbon contents. Generally, the Ti_4C_2S_2 phase is more likely to form than manganese sulphide even in the delta phase field at higher titanium concentrations. By reducing the sulphur content to 0.006 wt% (Figure (5-2-d), the temperature at which manganese sulphide precipitates in austenite is decreased from 1500 K to 1200 K for a steel with 0.1 wt% carbon. Figure (5-3) shows more clearly the effect of sulphur addition to steels containing 0.1 wt% C, 0.3 wt% Mn and 0.024 wt% Ti. The addition of sulphur which can be caused by microsegregation during solidification increases the temperature at which manganese sulphide is stable. Consequently, it is likely that finely distributed manganese sulphide precipitates form in steels with a low sulphur content.
Figure (5-2): Pseudo-binary Fe-C phase diagrams predicted by Thermo-Calc: (a) Fe-C- 0.3% Mn-0.01% S phase diagram, (b) Fe-C- 0.3% Mn-0.01% S-0.008% Ti phase diagram, (c) Fe-C- 0.3% Mn-0.01% S-0.024% Ti phase diagram, (d) Fe-C- 0.3% Mn-0.006% S-0.024% Ti phase diagram
In the current chapter, an account is given of TEM and Atom Probe Tomography studies that have been employed to investigate the chemical compositions, size and distribution of precipitates in steels with 0.008 and 0.024wt% titanium respectively. The precipitations at the edge and at the centre of the slabs are compared.

5-3 TEM analyses of precipitates formed at the edge of Slab A

In addition to the SEM analyses, the precipitates which formed in columnar area of slabs and are not large enough to be evaluated by SEM techniques were further explored by using TEM technique. Carbon replica extraction techniques have been employed to study these precipitates.

Figures (5-4-a to d) demonstrate bright field TEM images of precipitates extracted from the edge of Slab A. Energy Dispersive Spectroscopy (EDS) analysis of large particles revealed the presence of sulphur and copper. The appearance of the particles suggests shell formation and/or partial dissolution of precipitates during extraction by Nital. Copper sulphide shell formation accompanied by iron sulphide precipitation has been reported previously [7]. The sizes of the cubic and rectangular particles that formed close to
sulphides are 2 to 3 times larger than other precipitates observed on the carbon layer and it seems that sulphide precipitates act as nucleation sites for these larger particles. Figure (5-4-e) shows a typical EDS analysis of rectangular particles. Titanium and nitrogen are present and therefore these particles are most likely titanium nitrides.

Figure (5-4): (a-d) Bright field images of precipitates extracted from the edge of Slab A by carbon replica extraction, e) EDS analysis of rectangular precipitates
Another group of cubic precipitates, most likely titanium nitrides has been observed at the edge of Slab A. A bright field TEM image of this group of particles as well as EDS analysis are shown in Figure (5-5). A bright field TEM image of similar particles extracted from a different area, with corresponding Selected Area Diffraction Pattern are shown in Figure (5-6). Patterns analyses revealed a FCC structure with an Fm3m space group. It is worth noting that TiC and TiN have the same crystal structure and space group and even similar lattice parameters (TiC: a= 0.432 nm, TiN: a= 0.424 nm (even reported as high as 0.44 nm)) [104]. Consequently, is not possible to distinguish between TiC and TiN by SADP analysis. Although the presence of Ti(C,N) precipitates has frequently been reported [43, 66, 113, 114], SADP analysis alone cannot discriminate between these Ti-containing precipitates. Moreover, nitrogen is a light element and the K$_\alpha$ peak of nitrogen overlaps the L$_\alpha$ peak of titanium and hence, it is very difficult to confirm the presence of nitrogen by EDS analysis. Hence, the chemical formula of the precipitates extracted from Steel A can be TiN, TiC or Ti(C, N). The convention adopted in the present study is that, when nitrogen is noticeably picked up by EDS analysis, the particle will be referred to as TiN, otherwise as Ti(C,N).

Figure (5-5): (a) A bright field TEM image of precipitates and (b) corresponding EDS analysis
Chapter 5- Characterisation of precipitates in low carbon, low manganese, titanium added continuously cast steel slabs

Figure (5-6): A bright field TEM image and corresponding Selected Area Diffraction Pattern (SADP) of a precipitate formed at the edge of Slab A

Figure (5-7) shows a bright field TEM image taken from a thin foil prepared from the edge of Slab A in the same area where previously carbon replicas were extracted. It seems as if cubic titanium nitrides precipitate on grain boundaries where diffusion and nucleation is faster.

Figure (5-7): A bright field TEM image of a thin foil prepared from the edge of Slab A

Figure (5-8) demonstrates that rod like and round-shaped copper sulphides are attached to a TiN particle and hence, it seems as if TiN act as nucleation sites for copper sulphides.
Another group of small cubic precipitates mostly 10-20 nm or smaller in size, were observed at the edge of Steel A. EDS analysis of this group of particles revealed the presence of titanium and carbon. Carbon might be picked up from the carbon layer or from the particle. Hence, the chemical formula of these precipitates might be TiN, TiC or Ti(C,N).

![Figure (5-8): Bright field TEM images of precipitates formed at the edge of Slab A](image)

5-4 TEM analyses of precipitates formed at the edge of Slab B

The morphology of precipitates formed at the edge of Slab B is slightly different from those of Slab A. A few micrometers thin, rod-like particles are dominant in addition to round particles as shown in Figure (5-9). Figure (5-10) shows one of these rod-like precipitates at higher magnification together with its EDS analysis. EDS analysis close to the particle reveals that the particle contains copper. The similarity of this particle to the rod-like
precipitates observed in Slab A strengthens the notion that these particles are manganese sulphides with a copper shell around the particle as shown in Figure (5-10-b). Titanium nitrides with cubic and irregular shapes are attached to the sulphide particles.

Figure (5-9): Bright field TEM images of precipitates formed at the edge of Slab B

Figure (5-10): (a) Bright field TEM images of rod-like precipitates formed at the edge of Slab B, (b) Bright field TEM images of precipitate in Figure (5-10-a) at higher magnification, (c) EDS analysis
Figure (5-11) shows bright field TEM images of several sulphide precipitates which are attached to TiN.

![Figure (5-11): Bright field TEM images of sulphides extracted from the edge of Slab B attached to TiN](image)

A group of small cubic precipitates, smaller than 10 nm, were also observed at the edge of Steel B but they were fewer in number than in Slab A.

### 5-5 TEM analysis of precipitates formed at the centreline of Slab A

High-Resolution SEM analysis of precipitates formed inside of equiaxed grains at the centreline of Slab A reveals images of particles, a few hundreds nanometer in diameter as shown in Figure (5-12). Figure (5-12-a) reveals that ferrite formed around the particle and this observation indicates that the particle formed in the austenite phase and acted as a nucleation site for α-ferrite. This is not the case for the particle shown in Figure (5-12-b).

EDS analysis revealed that both precipitates contain only titanium and they are believed to be titanium rich nitrides. SEM evaluation revealed a fine ferrite microstructure.

TEM analyses were carried out on carbon extraction replicas. Cubic particles, 40-50 nm in size as well as very small spherical precipitates (< 10 nm), which could be barely distinguished from the replica background, were distributed throughout the microstructure as shown in (5-13). EDS analysis revealed that they contained titanium and carbon and therefore, they might be TiC, TiN or Ti(C,N). Rows of cubic precipitates (Figure (5-13-b)) indicate precipitation on grain boundaries of very small grains (< 500 nm). Previous SEM
studies revealed a fine microstructure of α-ferrite inside large prior austenite grains as shown as an example in Figure (5-12). It can be concluded that small cubic particles formed on α-ferrite grain boundaries and that they might have precipitated during or subsequent to the γ to α transformation.

Several large particles were observed that were associated with other precipitates. Figure (5-14) illustrates an example of these types of particles. EDS analyses on different areas of the particles marked in Figure (5-14-a), are shown in Figures (5-14-b to d). Areas 1 and 3 contain titanium and with regard to their appearance, are believed to be titanium nitrides.
Area 2 contains copper, titanium and sulphur. Titanium may be picked up from the attached particle and it is likely that copper sulphide grew on the titanium nitride.

![Image](image1.png)

**Figure (5-14):** (a) Bright field TEM images of precipitates formed at the centreline of Slab A, (b) EDS analysis of particle 1, (c) EDS analysis of particle 2, (d) EDS analysis of particle 3

Figures (5-15-a and b) show large (200-400 nm) cubic and rectangular titanium nitrides which are attached to copper sulphide and titanium nitride respectively. There is the possibility that large particles can attach to small particles during the carbon extraction procedure. A bright field TEM image of similar particles as well as Selected Area Diffraction Patterns are shown in Figure (5-16). The patterns confirm a FCC structure with an Fm3m space group and it is interpreted that the particles are most likely TiN.

Copper sulphides were observed as Rod-like and spherical particles in Slab A. A spherical type copper sulphide, attached to titanium nitride is shown in Figure (5-17). Copper sulphides formed as a thin layer and probably on the surface of another particle which was
dissolved in the solution during carbon extraction. Copper sulphides which formed a shell around manganese sulphide precipitates were also observed in the samples prepared from the edge of Slab B.

Figure (5-15): Bright field TEM images of precipitates formed at the centreline Slab A

Figure (5-16): Bright field TEM image of TiN formed at the centreline Slab A together with corresponding Selected Area Diffraction Pattern (SADP)
Chapter 5- Characterisation of precipitates in low carbon, low manganese, titanium added continuously cast steel slabs

**Figure (5-17):** Bright field TEM images of copper sulphide attached to TiN at the centreline of Slab A at different magnifications

5-6 TEM analyses of precipitates formed in the centre of Slab B

High resolution SEM analysis of precipitates at the centreline of Slab B revealed the presence of particles that formed within austenite grains, similar to those observed at the centre of Slab A but they were larger in size. Nucleation of α-ferrite on such a precipitate is shown in Figure (5-18-a). Carbon extraction techniques were employed for further evaluation of these types of particle.

**Figure (5-18):** HR-SEM image of precipitates formed at the centreline of Slab B

A bright field TEM image of particle similar to that shown in Figure (5-18) as well as a Selected Area Diffraction Pattern and EDS analysis are shown in Figure (5-19). The pattern confirms FCC titanium nitride with an Fm3m space group. Figure (5-20) shows precipitates
observed at the centreline of Slab B which formed within austenite grains. Copper sulphide shells are covered by a few hundred nanometers thick titanium nitrides. The particles are similar to precipitates formed at the centreline of Slab A but larger in size.

Figure (5-19): (a) Bright field TEM image of a precipitate formed in centre of slab in Steel B, (b) Selected area diffraction pattern of the precipitate, (c) EDS analysis of the precipitate

Figure (5-20): Bright field TEM image of precipitates formed at the centre of Slab B

Figure (5-21) illustrates another group of cubic TiN particles together with a Selected Area Diffraction Pattern of the particle marked in Figure (5-21-a). It confirms a FCC structure with an Fm3m space group. Titanium content of Steel B is less than the required stochiometric amount for reaction with nitrogen. Hence, it is believed that only TiN and not TiC or Ti(C, N) will form in this steel.
Chapter 5- Characterisation of precipitates in low carbon, low manganese, titanium added continuously cast steel slabs

5-7 Comparison of precipitation in different steels

The calculated phase diagram in Figure (5-2) predicted the formation of Ti₄C₂S₂ but current experimental results has not revealed any trace of titanium carbosulphide while manganese sulphides and copper sulphides are the dominant sulphide precipitates. Table (2-2) shows the compositions of steels in which Ti₄C₂S₂ was observed. These steels contain more titanium and sulphur and/or less carbon and manganese than the steels studied in this investigation. Therefore, the Thermo-Calc prediction are not valid for the steels under investigation in this study. Yang et al. [18] determined experimentally the solubility products of TiS and Ti₄C₂S₂ and compared then to earlier findings as shown in Figure (5-22). There are considerable differences between the reported equations. In these solubility products analyses, it was assumed that the activity coefficients of the microalloying elements as well as that of carbon, nitrogen and sulphur are equal to unity. Moreover, the micro-additions were treated as dilute solutions and interactions between solutes in the system were neglected. Consequently, the individual solubility equations apply only to a particular steel composition. Ti₄C₂S₂ precipitate is not observed in the current study and therefore the equations summarized in Figure (5-22) cannot be used to predict the solubility in the steels where the solute interactions may be significant.
Chapter 5- Characterisation of precipitates in low carbon, low manganese, titanium added continuously cast steel slabs

The size and appearance of sulphide precipitates indicate that manganese sulphides formed in the austenite phase as observed by Yuki et al. [76] who employed Laser-Scanning Confocal Microscopy. It is most likely that copper sulphides nucleated on manganese sulphides and formed a shell around rod-like and globular manganese sulphides. EDS analyses of manganese sulphides extracted by carbon replicas show that there is negligible dissolution of iron atoms in MnS and therefore the melting point of manganese sulphides which formed in the solid state is much higher than sulphides precipitated on prior austenite grain boundaries at the centreline of slabs. It is contended that these sulphides remained intact for a longer period of time during solution treatment of the slabs.

Following cooling of the slabs, when the nitrogen solubility decreases, titanium nitrides precipitate on sulphides as a separate phase but smaller in size. Table (5-2) summarises the morphology, size and chemical compositions of precipitates observed at the centre and the edge of the two steels studied, containing 0.008 and 0.024 wt% titanium respectively. Rectangular titanium nitrides, a few hundreds nanometers in size formed on the surface of sulphide particles. These particles are larger than other titanium nitrides because they nucleated on sulphides and therefore precipitated at higher temperature. More of these large TiN particles were observed in Steel B than in Steel A. Moreover, automated inclusion
analysis revealed that TiN, a few micrometers in size formed in Steel A (0.024 wt % Ti) but were not, or very seldom observed in Steel B (0.008 wt % Ti). (The inclusion analysis were described in Chapter 4).

TiN will form according to equation (5-1) [18].

\[
\log[\text{Ti}][\text{N}] = -15020/T + 3.82
\]  \hspace{1cm} (5-1)

<table>
<thead>
<tr>
<th>Position in Steel</th>
<th>Morphology</th>
<th>Size (nm)</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge of Steel A</td>
<td>Rod-like</td>
<td>500-1000</td>
<td>MnS/CuS shell</td>
</tr>
<tr>
<td></td>
<td>Round</td>
<td>100-200</td>
<td>MnS, CuS shell</td>
</tr>
<tr>
<td></td>
<td>Rectangular</td>
<td>Mostly 200-400</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td>Cubic (majority)</td>
<td>70-80</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Around 100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spherical</td>
<td>&lt;20 (mostly 10-20)</td>
<td></td>
</tr>
<tr>
<td>Edge of Steel B</td>
<td>Rod-like</td>
<td>1000-5000</td>
<td>MnS/CuS shell</td>
</tr>
<tr>
<td></td>
<td>Round</td>
<td>100-500</td>
<td>MnS, CuS shell</td>
</tr>
<tr>
<td></td>
<td>Rectangular</td>
<td>100-200</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td>Spherical</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Centre of Steel A</td>
<td>Rectangular</td>
<td>Mostly 100-300</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td>Cubic (majority)</td>
<td>30-40</td>
<td>TiN or Ti(C, N)</td>
</tr>
<tr>
<td></td>
<td>Cubic</td>
<td>Around 60</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td>Spherical (distributed)</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Centre of Steel B</td>
<td>Rectangular</td>
<td>Mostly 200-400</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td>Cubic (majority)</td>
<td>40-60</td>
<td>TiN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Around 100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spherical</td>
<td>&lt;10</td>
<td></td>
</tr>
</tbody>
</table>

The higher concentration of titanium in Steel A increases the temperature at which TiN will precipitate. Consequently TiN in Steel A precipitates at higher temperature and grows faster than in Steel B due to the higher diffusivity of elements at higher temperatures. Titanium nitrides in Steel B are smaller in size and higher in number than in Steel A because of the reduced diffusion distances at lower temperature. Following cooling, when
the solubility of titanium and nitrogen in the matrix is decreased, titanium and nitrogen will
diffuse towards the existing titanium nitrides but there is a competition between long range
diffusion to grow existing TiN and to nucleate new TiN particles. The presence of a large
number of small cubic (70-100 nm) titanium nitrides in Steel A indicates that nucleation
might be dominant in this steel. On the other hand, much larger and fewer TiN particles
were observed in Steel B, indicating that existing TiN particles may have grown.

5-8 Three dimensional Atom probe analysis

Several attempts [19, 87-90] have been made to characterise the clusters and ultrafine
precipitates in steels by using Local Electrode Atom Probe Tomography (LEAPT)
techniques. In this study, a group of precipitates less than 10 nm in size, was observed in
extraction carbon replicas but could not be uniquely identified by TEM techniques. In order
to further explore the composition of these precipitates, Atom probe tomography was
conducted on samples selected from Steel A.

The principles of Atom Probe Tomography, the standard two-stage electropolishing
procedure and data analyses were described in Chapter (3-6). The needles were prepared
perpendicular to the casting direction. The atomic characterisation of particles were
performed at the University of Sydney using a 3D Local Electrode Atom Probe with a
sample temperature of 45K, pulse repetition rate of 200 kHz and 15% pulse fraction.
A few samples have been examined from each position of the slab. Samples prepared from
the centreline fractured frequently during fine polishing due to the presence of large
particles on grain boundaries. Figure (5-23) illustrates the atom maps and 1.5% C iso-
concentration surface of a sample prepared from the edge of Slab A. The atomic map of
carbon clearly shows the presence of plate-like precipitates in the specimen.
In order to measure the concentration profile of different elements within the precipitates, several small ‘boxes’ were selected perpendicular to the surface of the precipitates. Different positions were selected to evaluate compositional variations within the particles. Concentration profiles across the particle revealed a carbon content of about 6 at% and 1 at% titanium at the centre of the particle as shown in Figure (5-24). The compositional analysis revealed that this particle is carbide.
Specimens prepared from the centreline of Slab A revealed several small particles as illustrated in the atom maps shown in Figure (5-25). The atom maps clarify the difference in chemical compositions of the particles. One of the precipitates contains the elements Ti, C, S and N but the others only Ti, C and S. Figure (5-26) illustrates the 2% C isoconcentration surface in the specimen. The appearances of these particles are very similar to that of the precipitates extracted from the centreline of Slab A by carbon replication (described in Chapter (5-5)).

In order to measure the concentration profile of different elements within the precipitates, small ‘boxes’ were selected perpendicular to the surface of the precipitates (1 and 2 in Figure (5-26)). The ‘box’ position and distribution of elements in precipitate 1 are illustrated in Figure (5-27). It is shown that elements are homogenously distributed in the particle. The concentration profile across the particle revealed that the carbon, titanium, nitrogen and sulphur contents ranged between (5-30 at.%), (4-12 at.%), (0-12 at.%) and (3-22 at.%) respectively as shown in Figure (5-28).
Figure (5-25): Titanium, sulphur, nitrogen and carbon atom map of a specimen which was prepared from the centreline of Slab A
The formation of TiN, Ti(C, N), and Ti₄C₂S₂ in steels has frequently been reported but the current results show the presence of Ti, C, N and S in a single precipitate. IVAS software was employed to repeat the analysis in order to compare the results and check the accuracy of these findings. Figure (5-29) shows the atom map of the precipitate prepared by IVAS and the concentration profiles of elements through the particle. The high percentage of carbon, sulphur and nitrogen in both analyses confirm that Ti, C, S and N are contained in a single particle.

Similar analysis has been conducted on particle 2 in Figure (5-26). The concentration profile across the particle is shown in Figure (5-30). The particle has a thickness of less than 2 nm and therefore the errors in estimating the concentrations are significant. However, the particle contains titanium, carbon and sulphur but the stochiometric ratios do not indicate that the particle could be Ti₄C₂S₂.
Due to the large distance between this group of precipitates in the slab, the possibility of detection by atom probe analysis is decreased considerably. Therefore, more efforts are required to further explore the composition of these precipitates.

Figure (5-27): The position of selected ‘box’ perpendicular to precipitate 1 as well as distribution of elements within the precipitate shown in Figure (5-26)

Figure (5-28): Concentration profile of elements across the precipitate 1 in Figure (5-26)
Figure (5-29): Atomic map and concentration profile of elements across the precipitate prepared by IVAS

Figure (5-30): Concentration profile of elements across the precipitate 2 in Figure (6-23)
Chapter 5- Characterisation of precipitates in low carbon, low manganese, titanium added continuously cast steel slabs

5-9- Summary

Formation of iron-manganese sulphides a few micrometer in size, in close proximity to iron-titanium sulphide has been confirmed at the centreline of Slabs A and B in Chapter 4. It was concluded that when there is not enough manganese to combine with sulphur, FeS can form instead of MnS and addition of titanium results in the formation of an iron-titanium solid solution. Automated Inclusion Analysis revealed that the number of sulphides at the centreline of Steel A (0.024 wt% Ti) is significantly higher than the Steel B. Iron-titanium sulphide precipitates were dominant in Slab A. However, the melting point of both groups of sulphides ((Mn,Fe)S and iron-titanium sulphide) in Slab A is higher than Slab B (with reference to the FeS-MnS and FeS-TiS phase diagrams). Therefore, addition of titanium results in the formation of less deformable sulphide inclusions at the centreline of slabs. However, further investigation is required to fully understand the behaviour of these newly identified iron-titanium sulphides during deformation of steel.

Further TEM investigation had been done by carbon replica technique at the edge and centre of both slabs in order to explore the nature and composition of smaller precipitates that were also present in the structure. Thermo-Calc software was employed to predict the composition of precipitates at thermodynamically equilibrated conditions. Formation of titanium carbosulphides was predicted in the steels but this prediction was not in agreement with TEM observation. Therefore, there is a need to develop the currently available thermodynamic databases to take into account the steel compositions of current study. That was beyond the scope of current study.

TEM analysis of titanium nitride precipitates has revealed a large number of small cubic TiN precipitate in Steel B whilst Steel A contains large TiN particles. However, a vast number of nanometer size TiN formed in Steel A at lower temperatures. At lower temperatures, when the solubility of titanium and nitrogen is decreased in the matrix, there is a competition between nucleation of new TiN precipitates was dominant to growth of existed titanium nitrides. Further study is required to clarify the effect of the size of titanium nitrides on microstructure and rolling behaviour of studied steels.
Atom probe investigations of nanometer size precipitates at the centreline of slabs have indicated that a single particle contains Ti, C, S as well as N. This observation requires further study.