The effects of cooling rate and alloying elements on the solidification behaviour of continuously cast super-austenitic and duplex stainless steels

Tong Wang

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The effects of cooling rate and alloying elements on the solidification behaviour of continuously cast super-austenitic and duplex stainless steels

This thesis is presented as part of the requirement of the conferral of the degree

Master of Philosophy, Master of Material Engineering

from

University of Wollongong

by

Tong Wang

School of Mechanical, Materials, Mechatronics and Biomedical Engineering

Faculty of Engineering and Information Sciences

January, 2019

Principal Supervisor: Prof. Huijun Li

Co-Supervisor: Dr David Wexler

Assoc/Supervisor: Dr Dominic Phelan
ABSTRACT

Super-austenitic and duplex stainless steels are advanced alloys used for demanding applications in the oil and gas, desalination and hydrometallurgical industries. To date, crack formation in Super-austenitic and gas pore formation in duplex stainless steels have a substantial negative impact on production output. The present research leveraged a unique combination of experimental and computational facilities to elucidate the underlying cause of these defects.

Based on a study of the literature, the root cause of gas pores and secondary phase cracking defects in continuously cast stainless steels is tied to the solidification microstructure. As elements including nickel, molybdenum, chromium and nitrogen are less soluble in the solid than in the liquid, these elements are rejected from the growing solid into residual liquid phase. It is this segregation that drives changes in thermodynamic phase stability, which in turn, lead to the defects of nitrogen gas pores and secondary phase cracking.

In present work, High Temperature Confocal Microscopy combined with Differential Thermal Analysis was used to study the segregation behaviour of duplex stainless steel and super-austenitic stainless steel under different cooling rates. According to the experimental results, the cooling rate can affect the microstructure morphology of these two alloys. The solidification process was simulation by Thermo-Calc software using ‘Scheil solidification’ function. By using ‘property diagram’ function in Thermo-Calc software, the amount of all phases under particular temperature can be calculated. This ‘property diagram’ function can calculate the phase transformation and gas phase commencement temperatures of S32101 duplex stainless steel and the amounts and formation temperatures of secondary phases of S31254 super-austenitic stainless steel. The effects of alloying elements such as nickel, chromium, molybdenum and nitrogen on super-austenitic and duplex stainless steels were simulated by Thermo-Calc through ‘phase diagram’ function.

For S32101 duplex stainless steel, the solidification mode is liquid $\rightarrow \delta$-ferrite $\rightarrow \gamma$. Higher cooling rates represent larger undercooling, and increasing undercooling leads to finer microstructure. Differential Scanning Calorimetry revealed that $\delta$-ferrite to $\gamma$ phase transformation commenced at higher temperatures under enhanced cooling rates. Based on the Thermo-Calc calculation and HTCM experiments, it was concluded that the gas phase forms after the steel fully solidified and before the commencement of phase transformation. As the cooling rate increases, the solid’s size will be smaller and finer, and the solidification behaviour in the body of the liquid pool will commerce faster.
For S31254 super-austenitic stainless steel, the solidification mode is liquid + δ-ferrite → γ. SEM-EDS mapping shows that regions subject to cracking have more Mo and Cr elements and less Ni element. The steel solidifies via a peritectic transformation and the cooling rate will affect the nucleation and microstructure of δ-ferrite. Along with the increasing of cooling rate, the nucleation temperature decreases, and the microstructure becomes finer. Through the calculation of Thermo-Calc, the precipitation temperatures of σ phase, Cr2N nitrides and Laves phase are estimated to be 1105.93°C, 1025.50°C and 799.60°C, respectively. The amount of σ phase is the largest, then is Laves phase, followed by Cr2N nitrides. According to DTA output, larger cooling rates lead to a sharper exothermic peak, smaller solidification interval and more energy release. The formation of σ phase in austenite was found to be related to the grain size and shape in austenitic stainless steels. Small grain size can provide more grain boundaries for σ phase to form.
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UOW, Jan 2019
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STATEMENT OF ORIGINALITY

I, Tong Wang, declare that this thesis, submitted as part of the requirements for the award of Master of Engineering, in the School of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of Wollongong, is my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications or assessment at any other academic institution.

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Student ID Number: 5657003

Signature:

Print Name: Tong Wang

Date: 20/01/2019

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<tr>
<td>DSS</td>
<td>Duplex Stainless Steel</td>
</tr>
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<td>SASS</td>
<td>Super-Austenite Stainless steel</td>
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<tr>
<td>Fe</td>
<td>Iron</td>
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<td>Cr</td>
<td>Chromium</td>
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<td>Ni</td>
<td>Nickel</td>
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<td>Molybdenum</td>
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<td>δ-ferrite</td>
<td>Delta-ferrite</td>
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<td>γ</td>
<td>Austenite</td>
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<td>L</td>
<td>Liquid</td>
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<td>σ</td>
<td>Sigma phase</td>
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<td>χ</td>
<td>Chi phase</td>
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<tr>
<td>PREN</td>
<td>Pitting Resistance Equivalent Number</td>
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<tr>
<td>PESR</td>
<td>Pressurized-Electro-Slag-Remelting</td>
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<tr>
<td>CPT</td>
<td>Critical Pitting Temperature</td>
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<tr>
<td>CCT</td>
<td>Crevice Corrosion Temperature</td>
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<tr>
<td>BCC</td>
<td>Body Centred Cubic</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centred Cubic</td>
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<tr>
<td>SDAS</td>
<td>Secondary Dendrite Arm Spacing</td>
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<tr>
<td>HTCM</td>
<td>High Temperature Confocal Microscopy</td>
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<td>DTA</td>
<td>Differential Thermal Analysis</td>
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<tr>
<td>LSCM</td>
<td>Laser Scanning Confocal Microscopy</td>
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<td>MICRESS</td>
<td>MICRostructure Evolution Simulation Software</td>
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<td>X-Ray Diffraction</td>
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<td>Electron Probe Microanalysis</td>
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<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
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Chapter 1

Introduction

The process of continuous casting is the most commonly used technology to produce solid steels from the liquid. The process of the liquid-to-solid phase transformation is called solidification. For casting and welding, the process of solidification will basically contribute to the properties, mechanical performance and lifetime of products. Hence, the study of solidification is critical to improve and control the properties of steels.

Solidification generally proceeds by the nucleation and then the growth of solid. Casting parameters such as temperature, cooling rate, as well as steel composition play important roles in determining the mode; e.g. planar, cellular or dendritic, as well as the rate of growth. These solidification conditions will affect the surface and subsurface quality of final products[1]. It is the complex interplay between thermodynamics and kinetics in this liquid-to-solid phase transformation that defines the nature of the dendritic growth and hence the quality of cast products such as stainless steels.

Duplex and super-austenitic stainless steels are two important types in Fe-Ni-Cr alloys. Both of these two stainless steels are highly alloyed and found in a range of different corrosive environments, for example within-, the chemical industry, especially in the production of organic and inorganic acids, and for the protection of oil products and in seawater cooling.

Although these two types of stainless steels were invented a long time ago, for the industrial production of high molybdenum super-austenitic and high nitrogen duplex stainless steels, cracking and gas pore defects respectively, are often encountered. These defects arise during continuous casting solidification. Currently, it is still a challenge to decrease the defect ratios of precipitated gas holes and cracks in Fe-Ni-Cr alloys to a very low level.

The purpose of this research is to conduct a combined Physical and Numerical simulation study to investigate crack formation in super-austenite stainless steel and gas pore formation in duplex stainless steels in continuous casting. The aim will be to develop an understanding of the thermodynamics of the relevant alloy systems using both computational and experimental approaches. We will undertake advanced in-situ experimental studies to investigate the solidification of these stainless steels and to quantify the role of solidification pathway on segregation profiles. We will also utilize the thermodynamic and in-situ study results to benchmark
a microstructural model of solidification during continuous casting of the steel grades to elucidate the root cause defect analysis. A combination of Physical Simulation (Confocal Microscopy and Confocal-DTA) and Numerical Simulation (Thermodynamics –ThermoCalc) techniques can be combined to tackle these issues. The specific aims of this research include:

1) Conduct HTCM-DTA experiments to establish transformation temperatures for the steels being investigated
2) Conduct HTCM Concentric Solidification experiments to assess role of cooling rate on solute segregation
3) Undertake a thermodynamic assessment of the steels under investigation using ThermoCalc
4) Benchmark the Thermodynamic model outcomes to the experimental results
5) Conduct DSC experiments to analyse the energy change of secondary phase formation and phase transformation aspects of the two steels grades investigated.
Chapter 2

Literature Review

Fe-Ni-Cr alloy is a very important material for strategic equipment. In this project, there are two steel grades including high elements of Mo and N in Fe-Ni-Cr alloy, such as N08367 and S32101. Additionally, N08367 and S32101 are classified as super-austenite and duplex stainless steel, respectively. The main compositions of the above alloys are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>N08367</td>
<td>&lt;0.03</td>
<td>&lt;2</td>
<td>21.0</td>
<td>24.5</td>
<td>6.5</td>
<td>&lt;0.75</td>
<td>0.21</td>
<td>&lt;0.04</td>
<td>&lt;1</td>
</tr>
<tr>
<td>S32101</td>
<td>&lt;0.04</td>
<td>5</td>
<td>21.5</td>
<td>1.5</td>
<td>0.4</td>
<td>0.40</td>
<td>0.22</td>
<td>&lt;0.04</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

It can be seen that the presence of approximately 0.2%wt N are the main characteristics of these grades of Fe-Ni-Cr alloys, while N08367 is also characterised by its containing 6.4wt% Mo. In the continuous casting process, precipitated gas holes in continuous casting slab is the main problem of S32101, while the cracking is main defect in N08367 slab.

Based on previous investigation, it can be concluded that the above two problems are derived from solidification processes during continuous casting. However, effective measures to solve the problems haven’t been found.

Fig 2.1 Micress simulation of dendritic solidification. Colour scale showing solute segregation ahead of the growing dendrite, with Delta-ferrite transforming to Austenite.
CHAPTER 2 LITERATURE REVIEW

In continuous casting liquid steel is poured into a water-cooled copper mold, with the high rate of heat extraction chilling a solid shell of steel that contains the yet to be solidified liquid in the centre. As shown in Figure 2.1 (personal communication with Dr Dominic Phelan), the phase transformation from liquid to solid proceeds with a dendritic structure with solutes such as carbon, chromium and importantly for the steels in question Molybdenum and Nitrogen being rejected into the liquid. The interplay of casting, thermodynamic and kinetic parameters of individual grades of steel on the rate and mechanism of solidification needs to be better understood if product quality is to be ensured. In the current proposal, an array of computational and experimental approaches broadly grouped as Thermodynamic and Microstructural, will be employed in a bid to understand and remediate defects.

The review will be conducted in two aspects according to different types of alloys: duplex stainless steel and super-austenitic stainless steel.

2.1 Duplex Stainless Steels

2.1.1 Background

The first type of duplex stainless steels (DSSs) were invented in 1930. DSS was firstly used in sulphite paper industry. In 2002, Swedish company Aveata Polarit (Outokumpu) invented LDX 2101 DSSs with high N content witch also named S32101[2]. DSSs are dual phases steels come with $\delta$ (ferrite) and $\gamma$ (austenite) microstructures. S. Mazumdar and S. Kary[3] pointed that the $\delta$ and $\gamma$ formed during and subsequent to solidification predominantly and the relative proportions them decide the solidification structure, micro-segregation, and the high-temperature strength & ductility. Hence, the proportion ratio of $\delta$ and $\gamma$ closer to 1, the properties of DSS are better. Because of this mixed microstructure, DSSs have excellent chloride corrosion resistance, good fabricability and high strength[4]. Their strength is about twice of traditional austenitic steels and the PREN (Pitting Resistance Equivalent Number = wt%Cr + 3.3wt%Mo +1.65wt%W +16wt%N) is around 29~36. These steels are mostly used in some industries such as chemical, nuclear and petroleum. Meantime, they also are needed in offshore and marine application[5]. However, it is important to point that below the temperature of 250°C, DSSs are less suitable than austenitic steels since the ferrite becomes brittle below this temperature. The excellent properties of DSS contributed to wide applications and the different alloying elements play important roles.
2.1.2 Role of Alloying Elements

Different alloying elements will have different influences on the mechanical and corrosion properties of DSS[4]. The following parts make a brief review of some essential elements of DSS.

**Chromium:** At least 20% of Cr is necessary in DSSs and it can enhance corrosion resistance and increase oxidation resistance at high temperature. Cr is ferrite stabilizer, it will increasing the tendency to form BCC structure of iron[6]. Young Hwan Jang & Jinil Son[7] reported that as the content of chromium increased from 23 to 28wt% pct, the volume fraction of ferrite phase in DSS increased from 48 to 63 pct. Meantime, the Cr element can form a stable Cr₂O₃ film and it provide a good protection for DSS in chloride environment[8]. Hence, element chromium can improve the corrosion resistance of DSS.

**Molybdenum:** As the content of Mo increases, the pitting corrosion resistance of stainless steels is enhanced. Mo content. Molybdenum is also a ferrite former and promotes the forming of detrimental intermetallic phases. Hence, the content of Mo should be restricted. Y. Jang & S, Kim[9] concluded that when the Mo content was less than 2wt% in DSS, it was detrimental to the corrosion properties due to the significant increase in the volume fraction of ferrite phase. The secondary phase sigma phase contains large percentage of Mo, hence, high Mo in DSS could increases the possibility of secondary phase formation.

**Nickel:** Nickel equivalent and chromium equivalent can determine the crystal structure of the alloy as shown in Figure 2.2. Nickel is an austenite stabilizer and can promote BCC (ferrite) crystal structure to FCC (austenite) structure as shown in Figure 2.3 and Figure 2.4. In DSS, nickel normally replaced by nitrogen in order to reduce the cost.

Fig 2.2 Crystal structure of commercial stainless steels as a function of the nickel equivalent and the chromium equivalent[10].
Manganese: Mn has a partitioning effect of nitrogen, it is the reason of adding Mn into stainless steels[11]. The addition of Mn, which stabilized austenite[12], has complicated influences on the microstructure of DSS, and microstructure variation leads to different properties of products such as tensile and corrosion behaviours. Y.H. Jang & S.S. Kim[13] investigated how different Mn contents influenced the tensile and corrosion behaviour of DSSs. Their study shows that the Mn content affects the primary and secondary austenitic phase in aspects of grain size, volume fraction and microstructural morphology.

Nitrogen: Nitrogen presented in steels and alloys can at times be considered as a detrimental impurity and at other times, as an alloying element which improves the properties[10]. Nitrogen
CHAPTER 2 LITERATURE REVIEW

was introduced into DSS as alloying element. It is an austenite stabilizer and has similar influences with Ni, hence, it was taken as a replacement of Ni[14]. The properties of intercrystalline corrosion resistance, pitting corrosion resistance and crevice corrosion resistance can be enhanced by adding nitrogen element[15]. Particularly, the pitting corrosion resistance of N equals to 16 times that of Cr. The austenite-stabilizing effect of it equals to 30 times that of Ni. Furthermore, the N can improve the strength of DSSs as it is the most effective solid solution strengthening element. Hence, nitrogen can replace nickel and reduce the cost of the production of DSS[16]. Many theoretical and experimental studies have been conducted about the specific features of the interaction between nitrogen dissolved in the steel and the alloying elements.

![Fig 2.5 CCT and CPT for austenitic stainless steels (left side) and DSSs (right side)[4]](image)

S. Girija et al[17] studied the link between the corrosion behaviour and nitrogen content in nitric acid and chloride environment. They found that as nitrogen content increased form 0.132wt% to 0.193wt%, the pitting corrosion resistance was enhanced. As nitrogen content increased to 0.406wt%, it was found to be detrimental because that along the grain boundaries, chromium nitride and manganese-rich precipitates formed. The improved toughness of nitrogen-bearing DSSs is due to their greater austenite content and reduced intermetallic content[18]. And also, nitrogen can promote the prevention or retardation of grain-boundary precipitate formation[19]. Girija Suresh et al[20] reported that a high nitrogen 304LN stainless steel showed a better pitting corrosion resistance comparing with lower nitrogen contained steels in chloride medium. A comparison of pitting and crevice corrosion resistance for a number of stainless steels in the solution annealed condition has shown in Figure 2.5 in which CPT represents Critical Pitting Temperature and CCT means Crevice Corrosion Temperature [21]. DSSs have excellent pitting corrosion resistance, and H. Vannevik et al[22] concluded that to estimate the pitting corrosion resistance of DSSs, the calculation of overall chemical composition PRE-value is not an adequate parameter because the DSS has strong partitioning between ferrite and austenite. The partitioning effect in DSS could
cause an unbalance between several crucial alloying elements such as chromium, molybdenum and nitrogen, and all these elements have contributions to pitting corrosion resistance.

Nitrogen has the positive effect of strongly subduing the formation of intermetallic phases. However, the nitrogen content should be limited strictly. The lower amount is limited by structural stability and austenite stability issues, while the upper content is limited by the solubility of nitrogen in the melt and at casting. High nitrogen content is the main cause of the gas pores, and the mechanism of gas formation will also be elucidated.

2.1.3 The Formation of Nitrogen Gas Pores

O.A. Bannykh[23] discussed three complex problems of high nitrogen steels that puzzle metallurgists and metallographers. The first one is the search for the methods to introduce the necessary quantity of nitrogen into steel. Fortunately, we have already solve this problem with a whole series of technological processes of the nitrogen introduction both into molten and into solid steels[24]. The second problem is of special importance for dual phase austenitic-ferrite steels, is to establish the regularities of the nitrogen distribution in the lattice of each phase. This distribution affects the mechanism and kinetics of the phase transformations under the thermal actions during solidification. There are several ways to introduce N into DSSs, pressurized-electro-slag-remelting (PESR), powder metallurgy, thermos-chemical treatment, melting and ingot process in pressurized atmosphere, etc.[25]. The last difficult task, which should be solved for the processing of high-nitrogen steels by ingot technology, is the formation of gas pores upon the ingot solidification.

2.1.3.1 Mechanism

The most significant research for the mechanism of gas pore formation is focused on the nucleation and growth of nitrogen bubbles in DSS during solidification process. Kaiju Dai et al [26] conducted a calculation based on the classic nucleation theory during solidification process. They calculated the critical sizes of the bubble under the condition of homogeneous nucleation and heterogeneous nucleation at the solid-liquid interface. The critical nucleation radius of gas bubbles at the interface of solid and liquid increases and the gas bubble growth rate decreases as the initial nitrogen content and cooling rate decreases.

Hong-chun Zhu et al [27] conducted a research based on the segregation and solubility of nitrogen and concluded the mechanism of nitrogen gas pore formation. They also discussed the phase transformation of DSS, and mainly focused on the influence of various factors for the formation of
gas pores. However, in their research, no solid proves was stressed to show that the bubbles are exactly nitrogen gas pores.

Based on the classical solidification nucleation theory, Young-Hwan Park [28]analysed the precipitation conditions of bubbles. However, the effect of the bubble radius on the pressure hasn’t been taken into consideration, which was a common simplification so far in classical nucleus theory during solidification.

There are 4 kinds of solidification modes for Fe-Cr-Ni alloys: L→γ, L→δ, L→γ→δ, L→δ→γ (L: liquid, δ: ferrite, γ: austenite), and the solidification mode of S32101 is L→δ→γ. The δ-Fe phase forms at the front stage of solidification and then, γ phases nucleate and grow on the surface of the δ dendrite arms via heterogeneous nucleation and due to the dramatic low solubility of N in δ phases, the nitrogen will segregate into liquid phase and nitrogen gas pores form in this period.

Nitrogen gas pores nucleate between dendrites when the segregated nitrogen reaches the critical content in the residual melt. The formation of nitrogen gas pores is closely related to the δ-ferrite formation, in which nitrogen has lower solubility than austenite.

![Diagram of gas pore formation during solidification](image)

Fig 2.6 Formation of gas pores during solidification: (a) segregation of nitrogen, (b) nucleation, and (c) growth of pore[27]

Seong-ho Yang & Zin-hyoung Lee [29]calculated the critical nitrogen partial pressure and proposed a way to predict the critical nitrogen content. The nitrogen gas pore forms between δ-
ferrite in the residual melt when the segregated N reaches this critical content. However, the calculation did not take the effect of the additional pressure generated by surface tension on the external pressure of the bubble surface into consideration which makes it can only be applied in the molten steel bubble nucleation. In fact, this additional pressure has a greater influence on the nucleation of bubbles.

The formation of gas pores during the solidification of DSSs is schematically presented in Figure 2.6. As shown in Frame (a), $N_{liq}$ accumulated at the front of the ferrite and increases rapidly because nitrogen solubility in the ferrite phase is much lower than it in austenite phase, and the mass-transfer rate of nitrogen is very low. When $N_{liq}$ reaches the critical nitrogen content necessary for the formation of nitrogen gas pores nitrogen gas pores can form, as shown in Figure 2.6(b). Subsequently, the austenite phase nucleates and grows on the surface of the ferrite dendrite arms via heterogeneous nucleation; this is accompanied by the decrease in the growth rate of $N_{liq}$. The austenite phase gradually covers the ferrite dendrite arms, and then captures the nitrogen gas pores. As solidification progresses, nitrogen gas pores grow on the surface of the austenite phase and are elongated along the direction of solidification (Figure 2.6(c)).

The nitrogen gas pores form and grow at relative later stage of solidification and surrounded by dendrites, that leads to irregular shapes.

2.1.3.2 Influence of Solute Segregation on Gas Pore Formation

M. R. Ridolfi & O. Tassa[30] investigated how the chemical and process parameters influence the nitrogen bubble formation during mould solidification of austenitic stainless steels with nitrogen content above 0.2% and found that the nitrogen bubbles caused by the segregation and supersaturation phenomena of nitrogen. Segregation and liberation occur easily in high nitrogen stainless steels, which can result in the formation of pores and the discarding of the steels[31]. In the aspect of chemical parameters, steel composition can affect the gas bubbles formation. It has been shown that nitrogen solubility in liquid steel is increased by some elements, such as Cr, Mn and Mo. From another point of view, nitrogen segregation from the solid into the liquid is favoured by ferritic solidification. In the aspect of process parameters, the dendritic arm spacing is also an important factor contributes to the formation of bubbles. The smaller the SDAS measure, the higher the $N_2$ pressure requested for pore formation where the SDAS is the value of the local secondary dendrite arm spacing, defined as the distance between two adjacent secondary branches developed during the dendrite growth. However, the steel composition between high nitrogen austenitic stainless steel and DSS is different, the influence of chemical parameter should be verified in DSS.
Kangwei Li & Jianghua Liu [32] analysed the bubble nucleation in molten steel supersaturated with nitrogen based on the theory of classical solidification nucleation. They derived mathematical models of critical radii for homogeneous and heterogeneous nucleation processes and the results show that these critical radii are identical. Upon low supersaturation of steels with nitrogen, nitrogen bubbles have small sizes and rounded shape and, upon high supersaturation, they are analogous to cellular bubbles in rimmed steels in shape and arrangement over the cross section of the ingot [33, 34]. The amount of bubbles is determined by the rate of nitrogen precipitation into the gas phase that is controlled by the rate of the chemical reaction of nitrogen desorption from the molten-metal surface into bubbles. In this period, the degree of supersaturation of the molten metal with nitrogen during solidification is determined by the total pressure in the system rather than the partial pressure of nitrogen [35].

Seong-ho Yang & Zin-hyoung Lee [36] reported that the nitrogen content, cooling rate and melt pressure will influence the formation of gas pores. As the increasing of nitrogen content and cooling rate, more gas pores will form. Increasing solidification pressure is effective to suppress the formation of gas pores. Marcus V. A. Bianchi & Raymond Viskanta [37] reported that porosity of bubble increases with enhanced cooling rate due to large segregation caused by fast cooling.

Young-Hwan Park et al [28] studied some factors related to the formation of gas bubbles. The nitrogen solubility was the most significant factor of the gas pore formation. Other factors include partial pressure, initial nitrogen content and cooling rate.

For some other alloying elements, the contribution to gas pores formation is also significant. Element Cr can improve the nitrogen solubility, as well as segregation, in the residual liquid. The influences of Cr on the gas pore formation is complex. Mn is austenite stabilizer and suppress the formation of Cr$_2$N. Mn can increase the tendency of the nitrogen-rich phase formation and nitrogen solubility in the residual liquid surrounding the dendrites. Hence, addition of Mn can reduce suppress the formation of nitrogen gas pores.

In addition, comparing to increasing cooling rate, a more effective way to suppress nitrogen gas pore formation is to increase melt height and solidification pressure. The formation of irregular gas pores at centreline can be promoted by solidification shrinkage.

In conclusion, nitrogen gas pores mainly form during the time interval between the nucleation of δ-Fe and γ-Fe. Hence, reducing this period can decrease nitrogen gas pores. Nitrogen gas pores
mainly form in the region of dendrite arms, and if the arms could be broken, and the nitrogen gas then macrosegregation could be reduced.

### 2.2 Super-Austenitic Stainless Steel

#### 2.2.1 General Background

Super-austenitic stainless steels (SASS) with special composition of high Mo content can meet the high requirements on a combination of high corrosion resistance, especially in inorganic and organic acids and mixtures thereof, good general corrosion resistance, good structure stability as well as improved mechanical properties in combination with good workability, in particular in tubes, especially seamless tubes and seam welded tubes for application in these environments[38-41].

#### 2.2.2 Secondary Phase Formation

Generally, inappropriate heat treatment or prolonged exposure at elevated temperatures could embrittle austenitic stainless steels due to the formation of secondary phases such as carbides, nitrides and intermetallic phases[42]. It is well known that austenitic stainless steels exposed to elevated temperature could cause decomposition of the austenite matrix into various carbides and intermetallic phases. M7C3, M23C6, M6C, MC carbides and sigma (σ), chi (χ), Laves intermetallic phases, and Cr2N nitride frequently were reported to form on isothermal aging treatment [42-44]. Moreover, when nitrogen is alloyed to Cr-Ni or Cr-Mn austenitic stainless steels, cellular precipitation of M23C6 or Cr2N takes place quite often [45].

The control of formation of precipitates σ, χ and Laves phases is a critical aspect of crack mitigation in N08367, and is intimately tied to solidification and the δ-ferrite to austenite phase transformation. In this instance, the balance between Cr/Ni, the level of Mo additions and segregation during solidification, combined with overall balance between ferrite and austenite stabilisers are all critical. To study this interplay three steel grades are selected (N08367, N08904, S31254) that offer a range of Cr/Ni ratios and levels, influence of Nitrogen as an austenite stabiliser, two levels of Mo addition as a ferrite stabiliser, two levels of copper addition as an austenite stabiliser. Grade N08904 is specifically included to provide a baseline low Mo grade for the experimental studies only. Composition for these steel grades is shown in Table 2.2.
According to existing literatures, alloys that containing transition elements A, such as Fe, Ni, Mn, Co etc., together with transition elements B, of type Cr, Ti, V etc., can form intermetallic phases with formula ranging from A₄B to AB₄[46-49]. The intermetallic compounds could be σ, χ or Laves phases[50]. The precipitation took place initially on grain boundaries and proceeded intragranularly[46]. The mechanical and corrosion resistance could be affected by intermetallic phases and finally caused secondary phase induced cracking[51]. Along the grain boundaries, coarse sigma phase is observed and within the grains, some small rod shape M₂₃C₆ carbide particles are detected[49]. AA. Popov et al [52] analysed two grades of austenitic steels with different concentrations of austenite and ferrite stabilizing elements. They found that the dominant intermetallic phase in these two grades of steel is σ phase. J. Anburaj et al [53] studied the precipitate phases of SASS with 7.5wt% Mo and found that χ forms from low temperature up to 800°C and σ at temperatures above 900°C. Comparing with χ, σ phase contains more molybdenum. Toughness decreased along with increasing the amount of these two precipitated phases and this is attributed to the presence of incoherent σ in austenitic matrix. High solubility of interstitial elements in austenite matrix tends to promote the formation of χ and Laves phases. Molybdenum helps to form the precipitation of intermetallic phases at elevated temperatures. Nitrogen can suppress the formation of χ phase and the Laves phase formation is delayed with addition nitrogen[54].

### 2.2.3 Influence of Solute Segregation on cracking susceptibility

It was pointed by several papers that the temperature interval of solidification and amount/distribution of solute element rich liquid remains at the terminal stage of solidification affects the secondary phase induced cracking formation of austenitic stainless steels[55-57]. J. N. Dupont et al [56] studied the relation between alloy composition, solidification behaviour, microstructural development and solidification cracking susceptibility. They pointed cracks can
form during the terminal stages of solidification when a liquid film is distributed along grain boundaries and interdendritic regions and the strains cannot be accommodated, and the boundaries separate to form a crack. In this process, the solidification temperature range and morphology of the interfacial liquid that exists at the terminal stages of solidification are primary factors that control solidification cracking susceptibility. And also, solidification temperature range and the amount of terminal liquid influenced by solute redistribution.

Mo segregates to liquid in solidification process because of low solubility of Mo in the austenite phase[55] and low diffusion rate of Mo in austenite, it cannot diffuse back toward the dendrite cores to eliminate the concentration gradient.

2.3 Conclusion

According to the literature review, the gas pores and secondary phase cracking defects are related to the segregation of alloying elements such as Mo, Cr, Ni and N during continuous casting process. The pertinent features of microstructural development during solidification can be illustrated with reference to Figure 2.1, dendritic solidification of a stainless steel. Under continuous casting conditions the solid phase grows with a dendritic or branched structure. Since elements such as Cr, Ni, Mo etc. are less soluble in the solid than in the liquid, they will be rejected from the growing solid into the remaining liquid phase. It is this segregation that drives changes in thermodynamic phase stability, which in turn, lead to the defects of nitrogen gas pores and secondary phase cracking. The influence of alloying elements on the phase formation of duplex stainless steel and super-austenitic stainless steel has been studied by lots of researches. The mechanism of gas pores formation has also been reported. The formation of gas pores is highly related to the nitrogen content and its solubility difference between liquid and solid metal. The gas pores defects normally form during the nucleation of δ-ferrite. Hence, reducing the δ-ferrite nucleation time could lock the nitrogen in the steel. The gas pores tend to form between the dendritic arms, so the method of ultrasonic vibration which aims to break the secondary dendritic arms is doable theoretically. For super-austenitic stainless steel, the secondary phase induced cracking is detrimental. In SASS, secondary phases and intermetallics such as σ phase, χ phase, Laves phase and nitrides are brittle and can cracking. The segregation of Mo is the root cause of secondary phase formation.

In previous studies, a lot of research approaches and different techniques were used or designed to study the gas pores and cracking in stainless steels. Some are based on thermodynamic calculation
or simulation. More of them just used optical microscopy or electrical microscopy such as SEM and EBSD to analyse the microstructure of tested samples under different conditions. It only concluded how the cooling rate or alloying elements’ content affects the microstructure and amount of phases ($\gamma$, $\delta$-ferrite, $\sigma$, $\chi$, Laves phase and nitrides).

In present research, the High Temperature Confocal Microscopy will be used as main research equipment. In-situ observation combining with Differential Thermal Analysis can tell us how the cooling rate will affect the solidification process. The growth of dendrites, phase transformation and formation of secondary phase can be revealed. Through Differential Scanning Calorimetry (DSC) experiment, the phase formation temperatures can be detected accurately by the changing of energy. The revolution of microstructure during the melting and solidification processes will be studied using techniques mentioned above. Thermodynamic calculation is used to predict the phase transformation and secondary phase formation temperatures and the amount of them. The prediction will provide a guide for the following experiments.
Chapter 3

Research Approach and Methodology

This proposal is to conduct research about the gas pores formation in high nitrogen DSS and crack formation in high molybdenum SASS by combining physical and numerical simulation and aim to develop an intimate understanding of the thermodynamics of the relevant alloy systems using both experimental and computational methods. A High Temperature Confocal Microscopy (HTMC) is used for in-situ observation of the phase transformation during solidification and to quantify the role of solidification pathway on segregation profiles. The experiments data including thermodynamic and in-situ results will be utilized to benchmark a microstructure model of solidification during continuous casting of S32101 DSS and S31254 SASS with a view to elucidate the root cause defect analysis. A combination of Physical Simulation (HTCM and HTCM-DTA) and Numerical Simulation (Thermodynamics –ThermoCalc) techniques to tackle these issues.

3.1 Experiments and Instruments

In order to observe the phase transformation of DSS and SASS during solidification, HTCM was used in this research and this technique can provide a so-called ‘in-situ’ observation.

Many researchers have applied LSCM (Laser Scanning Confocal Microscopy) to the study of phase transformation of iron based alloys in specific heating or cooling rate since 1990’s such as Yin[58, 59], Dominic Phelan, R. Dippenaar [60, 61], Kimura[62] and Liu[63]. However, most of the research has been mainly concerned with low carbon steel and this technique has rarely been applied to the study of DSS and SASS. Yong Zhao & Yanhui Sun[64] applied LSCM in their research of DSS. They observed the transformation of $\gamma \rightarrow \delta$-ferrite and $\delta$-ferrite $\rightarrow \gamma$ with different nitrogen contents. With different nitrogen contents, this rate and start temperature of $\gamma \rightarrow \delta$-ferrite phase transformation is different. However, they didn’t try to find the links between cooling rates and phase transformation rate and, their main focus is about how different nitrogen contents affect the emerging and disappearing of $\delta/\gamma$ interphase boundaries and $\delta/\delta$ grain boundaries.

In the present work, a HTCM has been used to observe in-situ and in real-time the planar to cellular to dendritic transition of the progressing solid/liquid interface in high nitrogen duplex stainless steel and high molybdenum super austenitic stainless steel. The methodology is based on the design of
Rain Dippenaar et al[65]. The HTCM facility is shown in Figure 3.1. It was made by Lasertec Corporation, based on Yokohama, Japan. A 1.0 Kw halogen lamp, located at one focal point of a gold-plated ellipsoidal cavity in the bottom half of the infra-red furnace chamber. The sample were heated by radiation in this chamber. The heat was been concentrated by gold-coated ellipsoidal chamber onto the surface of the sample. It is located at the other focal point of the furnace chamber. Figure 3.2 schematically illustrated the furnace chamber.

Fig 3.1 High Temperature Confocal Microscopy equipment (HTCM-DTA)

Fig 3.2 Schematic representation of the HTCM chamber[65]
3.1.1 Concentric HTCM

To improve the quality of in-situ observation at different cooling rates, Reid et al [65, 66] developed and described the concentric solidification technique. As shown schematically in Figure 3.3, a thin slice of DSS sample is melted partially around the centre of the slice and form a liquid pool surrounded by solid rim in concentric HTCM. Samples are placed in a cylindrical alumina crucible with an inner diameter of around 9.2mm. A platinum specimen holder, to which a B-type thermocouple is attached, holds the crucible in position as shown in Figure 3.4. Because the in-situ observation of HTCM is restricted to the surface of the sample, the thickness of the sample is an importance parameter and it varies with different method of HTCM. By many attempts using different sample thickness, it was determined that ~250μm is the minimum thickness for carrying out the concentric solidification experiments. On one hand, if the thickness is less than 250μm, the liquid pool will rupture easily. If the thickness is more than 300μm, the output power that required to melt the sample will be too high to reach.

![Solid Rim](image1)

Fig 3.3 Concentric solidification technique, showing the liquid pool and solid rim in a DSS sample[66]

![Crucible](image2)

Fig 3.4 Schematic representation of the concentric HTCM sample holder and crucible[66]
CHAPTER 3 RESEARCH APPROACH AND METHODOLOGY

The sample and the holder are then inserted into the top half of the furnace chamber. This section is atmosphere controlled to avoid oxidation of the specimen at elevated temperatures. The top half of the microscope chamber is filled with ultra-high purity argon gas. To ensure a high integrity inert gas, the purified gas is passed through a stainless steel tube filled with titanium turnings, held at a temperature of 1173K, before entering the furnace chamber. The purity of the resulting carrier gas before entering the furnace chamber is better than $1 \times 10^{-13}$ ppm $O_2$.

The main advantage for using the concentric HTCM is the temperature gradient between the liquid pool and solid rim. In another word, the temperature that been measured is actually the temperature of the edge of the solid rim instead of the real-time temperature of liquid pool.

An inherent limitation of this technique in the study of opaque metallic systems is that observations can only be made of the free surface and information on the commencement and completion time of a phase transformation within the bulk of the material cannot be categorically determined. This has raised the question of what, if any, effects the free surface may be imparting to the observed phase transformations. Calorimetry is a standard technique for the study of phase transformation, of which differential thermal analysis (DTA) is one type[67].

3.1.2 HTCM-DTA

In this study, a unique High Temperature Confocal Microscopy combined with Differential Thermal Analysis (HTCM-DTA) will be used. This new technique, developed by Dominic Phelan et al [66], enables in-situ observations of phase transformations on the surface of a sample while thermodynamic data from the bulk of the sample is determined at the same time. It will be the first time that his new technique be used to study solidification and subsequent phase transformations in stainless steels.

In DTA two holders, the sample and the reference are placed in a furnace with a thermocouple attached to each. The reference holder is used as the control thermocouple for the furnace. On heating/cooling through a phase transformation, the temperature of the thermocouple measuring the sample will show a divergence from the control thermocouple as enthalpy changes occur (positive or negative). A limitation of this technique is that no observations of events occurring locally within the sample can be made; only the average response of the entire sample is possible. When interpreting measurements, phenomena such as the relative velocity of interphase boundaries cannot be directly observed, but must be assessed using some pre-assumed nucleation rate. In the study reported here, in-situ observations have been made using high temperature confocal microscopy.
combined synchronically with differential thermal analysis. A specially designed apparatus developed by Dominic Phelan and Rain Dippenaar, combines both techniques in one unit, solving inherent limitations of each. In-situ observations can be referenced to events in the bulk and observed events on the surface can be used to refine our understanding of bulk events. In this project the technique of measuring data on the enthalpy released by phase transformations whilst at the same time observing the transformation in-situ will be used for the first time to study solidification of stainless steels.

S. Niknafs et al [65] has had prior success on controlling the gas atmosphere in HTCM to study various phenomena. The HTCM at UOW has a controlled gas train that enables the mixing of different gases to control the atmosphere in the sample furnace. The nitrogen partial pressure can be controlled through mixing a high purity nitrogen source with high purity Argon. By controlling the partial pressure of nitrogen, the composition of nitrogen in a sample can also be controlled as it is cycled through solidification. The DTA capability enables accurate measurement of phase transformations throughout the bulk of the sample.

For HTCM-DTA experiment, the diameter of the sample is 4.2mm and it need to be cut into 3mm height. The crucible size and sample holder is shown in Figure 3.5.

![Fig 3.5 Schematic representation of the DTA-HTCM sample holder and crucible](image)

3.2 Simulation

**Develop Model Framework for Microstructure and Segregation in Continuous Casting**
In present work, the simulation software Thermo-Calc will be benchmarked against experimental and modelled thermodynamic data, and a modelling framework developed specifically for simulating solidification of selected typical duplex stainless steels as pertains to the vertical caster.

The evolution of material microstructures is essentially governed by thermodynamic equilibria, alloy element diffusion, stress and strain in the solid state and phase boundary curvatures. Phase field simulations of solidification microstructure as a function of thermal conditions as pertains to continuous casting will be conducted using Thermo-Calc. Thermo-Calc is used worldwide as a research tool in academia and industry, in particular the steel industry. As phase formation simulations give the spatial and temporal evolution of microstructures together with integral thermodynamic quantities like enthalpy release, they are an ideal virtual counterpart to the experimental techniques described above. Phelan[68] and Dippenaar[65] have applied this phase field modelling technique to solidification under continuous casting and strip casting conditions to understand phenomena including segregation, peritectic reaction and cracking in continuous casting. 2D simulations of dendritic solidification fully linked to ThermoCalc and benchmarked with experimental quantification of solute profiles in as cast and confocal experiments will enable multiple scenarios to be tested.

Defining thermodynamic phase stability in the steel grades under investigation is central to developing a benchmarked microstructure modelling capability. Differential Scanning Calorimetry (DSC) is the experimental technique that will be used to quantify phase transformations including precipitation of secondary phases. Experimental data obtained with DSC will then be used to benchmark modelling of phase stability using the software ThermoCalc. As microstructural development is driven by kinetics it is important to assess thermodynamics under non-equilibrium conditions.

3.3 Innovation and Strategic Alignment

The most important innovation in the proposed project is the combination of in-situ observations of microstructural development in the course of solidification with bulk analysis of the pertaining phase transitions. Moreover, the experimental data will be integrated into predictive models that should provide operators guidance towards reducing the incidence of casting defects. With respect to phase equilibria, we will use experimental thermodynamic analysis (Netsch DSC and HTCM-DTA) of the two steel grades of interest, along with an assessment of segregation and phase
CHAPTER 3 RESEARCH APPROACH AND METHODOLOGY

stability issues. The research will be focussed on applying the phase field methodology to model dendritic solidification in the continuous casting of these steels including the quantification of segregation of all solutes of interest.

3.4 Experiment Procedure

3.4.1 Materials

The samples used in the present research were provided by Baosteel which were obtained in wrought bar forms with two different diameters, 9.7mm and 4.3mm as shown in Figure 3.6. In this stage, two grades of alloys will be tested, S32010 as duplex stainless steel and S31254 as super-austenitic stainless steel. Table 3.1 shows the composition of these two alloys.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>S31254</td>
<td>&lt;0.03</td>
<td>&lt;2</td>
<td>20</td>
<td>18</td>
<td>6</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>S32101</td>
<td>&lt;0.04</td>
<td>5</td>
<td>21.5</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.1 The main compositions of S32101 and S31254 (wt%)

![Fig 3.6 Samples bars of S32101 and S31254](image)

3.4.2 Sample Preparation

To prepare samples, using TechCut 5™ Precision High Speed Saw (Figure 3.7) to cut the sample into 0.25mm thick slices and ground on 800, 1200, 2400 and 4000 SiC papers. Then polish the sample by standard metallographic techniques with 6-micron diamond paste and 1-micron diamond paste. Five group samples of S32101 DSS will be prepared for different cooling rates: 5°C/min,
10°C/min, 20°C/min, 50°C/min, 80°C/min and 100°C/min to study the influence of cooling rate on the phase transformation during solidification. The cooling rates can be changes through Omron ES100P digital PID controller.

All the samples were cleaned carefully to avoid contact with any particulate other than the diamond polishing paste and the cleaning solvents (acetone, isopropyl alcohol and DI water). At the end of each polishing step, the samples were degreased with acetone, rinsed with isopropyl alcohol and rinsed with DI water (in that order). The samples were then dried with high purity compressed air.

The concentric solidification HTCM experiment can conduct as soon as the 0.250mm thick discs are prepared, the procedure of conducting the concentric solidification has been elucidated above.

After the experiment done, the discs can be mounted with StruersCitopress 20 hot mounting equipment and polished by Metprep 4™ Grinder/Polisher semi-automatic. The surface morphology of tested samples can be observed by Nikon Eclipse LV100NDA optical microscope. All the facilities used above shown in Figure 3.8.
3.4.3 Thermodynamic Assessment of the Fe-Cr-Ni-Mo-(N) Alloy System.

Numerical approach using ThermoCalc benchmarked with DSC characterization of plant materials supplied by Baosteel. DSC will enable identification of secondary phases that may form. This stage of the project will use both experimental and computational techniques to assess the phase stability in the two steel grades as a function of temperature and solidification. The modelling package ThermoCalc will be used to assess phase stability of the two grades as a function of both equilibrium and Scheil conditions. Equilibrium assessment will focus on phase stability as a function of composition, whilst Scheil simulations will enable an initial assessment of the impact of segregation on phase stability to be undertaken. This computational approach will be backed up with experimental assessment using a Netsch 404 DSC (as shown in Fig 3.9) to measure transition temperatures and specific heat capacity of the different steels.

The experimental investigation provides a benchmark for the modelled thermodynamic parameters. This ensures the accuracy of the modelled parameters for the specific steels being investigated. This is important as the thermodynamic assessment will play an integral role in the kinetic modelling of dendritic solidification to be conducted using Micress software. The thermodynamic assessment using ThermoCalc can commence at the start of the project as there are existing databases available to conduct the initial investigation.
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3.4.4 Microstructure Analysis

Characterisation of the microsegregation in cast products supplied by Baosteel. It is essential that the cast microstructures of product from Baosteel are analysed to quantify microstructure and segregation as a function of casting parameters. Samples provided by Baosteel will be examined using optical microscopical techniques, segregation of solutes will be analysed using Scanning Electron Microscopy plus Energy Dispersive Spectroscopy (SEM-EDS), X-Ray Diffraction (XRD), Electron Probe Microanalysis (EPMA). Additionally, Transmission Electron Microscopy (TEM) examination of the secondary phases in the cast and/or rolled form for S32154 will need to be undertaken to characterise the defect causing sigma/chi/laves phases. In present research, the microstructural characterizations including size, morphology, and crystallography of ferrite, austenite grains and secondary phases conducted by Optical Microscopy (OM), SEM-EDS and TEM.

Fig 3.10 SEM JEOL JSM-7001F equipped with EBSD

3.5 Conclusions

The ultimate aim of the project is to establish a kinetic modelling framework that will allow us to define optimum casting parameters on the plant. The first step is to define segregation behaviour during solidification under controlled conditions to establish benchmarking for the kinetic modelling. High temperature confocal microscopy (HTCM) has found widespread application to the in-situ study of phase transformations under conditions both close to equilibrium and far from
equilibrium. Experimental studies conducted with this technique include solidification [58, 66, 69], the peritectic reaction and transformation [70-72], and austenite decomposition.
4.1 Introduction

Duplex stainless steel is an important strategic alloy. The development of DSS in China is far behind the average level of western world. This history of Duplex Stainless Steel can be traced back to last century. In 1927, Bain and Griffiths[73] reported an iron-chromium-nickel with ferrite an austenite duel phases. Several years later, England, France, Germany and USA also developed this grade alloys. In 1929, Avesta Jernverk released a commercial product of DSS named 453E with 25%Cr and 5%Ni. Three years later, a new grade of DSS added with 1%Mo was put into market. Germany and Sweden developed 22%Cr duplex steel grades, i.e. DIN 1.4462 or UNS S31803 in the early 1970s. In 1982, the first international conference for DSS was held in St Louis, Missouri, USA. Figure 4.1.1 shows the development of modern DSS for year 1970-1991. Nitrogen was introduced as an alloy element into the steel since 1980. To endure more aggressive environments, more and more elements were added into DSSs.

![Fig 4.1.1 The development of hot rolled grades in terms of nitrogen against chromium and molybdenum content][12]

Each alloying additions in DSS plays an important role. The Cr in DSS can stabilize ferrite phase and form a passive Cr-rich oxy-hydroxide film to enhance the localised corrosion resistance[74]. However, the formation of intermetallic phase, σ phase for instance, limits the amount of Cr[75]. Equation 4.1 quantifies the ferrite stabilization effects of ferrite stabilizers and named as chromium
equivalents. In counter to ferrite stabilizers, there are austenite stabilizers in DSS. Equation 4.2 is the nickel equivalent which quantifies the austenite stabilization effects in DSS. The nitrogen can improve the pitting corrosion resistance, increase γ content and enhance strength of DSS.

\[
\text{Cr}_{eq} = \%\text{Cr} + \%\text{Mo} + 0.7 \times \%\text{Nb} \quad \text{Equation 4.1}
\]

\[
\text{Ni}_{eq} = \%\text{Ni} + 35 \times \%\text{C} + 20 \times \%\text{N} + 0.25 \times \%\text{Cu} \quad \text{Equation 4.2}
\]

The molybdenum in DSS can improve the pitting and crevice corrosion resistance, especially in high temperature environments[76]. The appearance of other elements such as nitrogen[77, 78], tungsten[79] can also increase pitting and crevice corrosion resistance. The combination of these alloy elements contributes to the special microstructure of DSS.

Fig 4.1.2 Typical microstructures of DSS: (a) hot rolled plaste, × 200; (b) casting × 50 [2]

Fig 4.1.3 Optical microscopy of S32101 DSS cast without etching
Duplex stainless steel has a so-called dual-phase structure which, for S32101, contains around 50% volume Face Centred Cubic $\gamma$ islands and 50% volume Body Centred Cubic $\delta$-ferrite matrix (as shown in Figure 4.1.2). After grinding and final polishing of the sample with the 0.04 µm grain size silica cloth, Optical Microscopy was used to observe the surfaces of S32101 DSS and S31254 Super-Austenitic Stainless Steels. For S32101 DSS, as shown in Figure 4.1.3, even without etching, we can easily tell the dual-phase structure, and the proportion of each phase is observed to be nearly equal. In Figure 4.1.3, the austenite shows an island structure and appears located within the $\delta$-ferrite based matrix. On further in-situ observation using HTCM experiments, the island structures disappear as the temperature rises. This phenomenon is consistent with the analysis of previous literature review[40] and is consistent with the premise that the island structures are austenite.

### 4.2 Experiments details

#### 4.2.1 Materials

As shown in Figure 4.2.1, the samples were cut from S32101 DSS cast without hot rolling. In continuous casting, different positions of cast products have different segregation behaviour. During the solidification of continuous casting, segregation in centreline is worse than bulk. Sample 1, two types of rods with 4.3mm and 9.7mm diameter used for HTCM-DTA and Concentric HTCM experiments respectively, were centred on the location of gas pore defect in S32101, which is located in 10mm beneath the surface. Sample 2 should be as close to the centreline as possible. Sample 3 is along the longitude direction of the cast. Length of the rod is 200mm.

![Fig 4.2.1 Schematic representation of sample location for S32101 DSS](image)
4.2.2 High Temperature Confocal Microscopy

Two different techniques were used in present research, HTCM-DTA technique and Concentric HTCM technique. They were detailed in Chapter 3.

All the samples were cut into two sizes. For concentric HTCM experiments, the diameter of the sample is 9.7mm and the thickness is 0.25mm. For HTCM-DTA experiments, the diameter of the sample is 4.3mm and the thickness is 1.5mm. All the slices were polished and grounded on 800, 1200, 2400 and 4000 SiC papers. Then polish the sample by standard metallographic techniques with 6 micron diamond paste and 1 micron diamond paste. Five group samples of S32101 DSS were be prepared for different cooling rates: 5℃/min, 10℃/min, 20℃/min, 50℃/min, 80℃/min and 100℃/min to study the influence of cooling rate on the phase transformation during solidification. The cooling rates were varied using an Omron ES100P digital PID controller. The program of temperature controller is set as Figure 4.2.2 and the cooling stage time varying to satisfying different cooling rates. All HTCM experiments including HTCM-DTA experiments are based on this program to change the cooling rate. The HTCM was the dominant method to investigate the solidification process and phase transformation behaviour.

![Fig 4.2.2 Program set up of temperature controller](image)

4.2.3 DSC

Dedicated DSC analysis was also used to measure melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition
temperature and energy, precipitation energy and temperature, denaturization temperatures, oxidation induction times, and specific heat or heat capacity.

Differential Scanning Calorimetry was conducted using a Netzsch 404 instrument to do the thermal analyse of S32101 DSS to generate more accurate data comparing with DTA. Since the amount of heat which required to heat up the sample and reference is different, and the reference sample has a specific well-known capacity over the range of temperatures to be scanned, the curve plotted by computer will give us a lot of information about phase transformation during heating and cooling process. In present research, the sample was heated up to 1500°C to make sure it was fully melted in Ar gas atmosphere. The sample weight 22mg. The sensitivity of the instrument is 0.001°C. Temperature accuracy of +/- 1°C based on metal melting standards Heat flow accuracy better than +/- 2% based on metal melting standards.

4.2.4 Lv-6490LA SEM

Scanning electron microscopy (SEM) was performed using a JEOL JSM-6490LA operating at 30 kV with conventional tungsten filament. The instrument is equipped with an Oxford Instruments X-MAX large area Energy Dispersive Spectroscopy (EDS) detector and is located in Electron Microscopy Centre in the University of Wollongong. The maximum resolution of JEOL JSM-6490LA SEM can reach 3.5 nm at 30 kV. EDS spot and mapping features were employed for both qualitative and semi-quantitative (standardless) micro-analysis.

The virtue of the Oxford instruments SDD energy dispersive detector will collect the EDX signal and the integrated AZtecSynergy software suite is used for the post EDX analysis. In present
research, the SEM was used to analyse the distribution of different alloying elements regards to different solidification conditions, for instance, cooling rate.

Fig 4.2.4 JEOL JSM-6490LA SEM

4.2.5 Thermo-Calc software

The original software, Thermo-Calc, was released over 30 years and has now became the most popular worldwide software package for thermodynamic calculations. All the calculations of Thermo-Calc are based on thermodynamic data which is supplied in a database. The simulation of Thermo-Calc can improve the design during manufacture process and help to choose the temperature of heat treatment. Through the calculation, the experiments results can be predicted so that the amount of experiments can be minimized. Sometimes, the results of calculation even more reliable. In this thesis, Thermo-Calc was used to calculate the amounts of phases and their compositions, transformation temperatures and phase diagrams based on ‘TCFE9: Steels/Fe-Alloys version 9.0’ database.

4.3 Experiment Results

In the present work, a HTCM has been used to observe in-situ and in real-time the planar to cellular to dendritic transition of the progressing solid/liquid interface in DSS. DSC experiments can provide information about the energy change of melting and solidification processes of DSS. By
thermodynamic calculation of ThermoCalc, the experiment results of phase transformations can be compared to verify the correction of hypothesis.

4.3.1 HTCM-DTA Experiments

The combination of two different techniques, DTA and HTCM, enabled in-situ observations of phase transformations on the surface of a sample while thermodynamic data from the bulk of the sample is determined at the same time.

For S32101, the melting point is around 1470°C, based on the DSC and DTA output (Figure 4.3.2). DSS solidifies completely in δ-ferrite field and followed by solid state transformation to γ. This process is reversible. Figure 4.3.1 shows that the microstructures of S32101 DSS under different cooling rates are totally different. In frame (a), small cooling rate leads to large dendritic microstructure. In frame (b), the dendrites are longer and slimmer than frame (a). The microstructure is also finer. In frame (c), no more secondary arms stretched from primary dendritic arm. In frame (d), since the cooling rate is very fast, no enough time for the liquid to form dendrites. Lager cooling rates left no time for dendrites to grow secondary dendritic arms and as cooling rate increasing, even no time to form dendrites.

(a)

(b)
Differential Thermal Analysis (DTA) is a thermoanalytic technique. In HTCM-DTA experiments, two crucibles were tested in chamber, one of them was used to hold sample and another was used as reference. Both sample and reference underwent identical thermal cycles. The temperature difference between the sample and reference were recorded and plotted against time or temperature.
Different cooling rates, 20°C/min, 100°C/min, 200°C/min and 300°C/min respectively, were applied for the solidification process of S32101 DSS using the HTCM-DTA, as shown in the DTA output of Figure 4.3.2. The heating rate is fixed. Each experiment was divided into 3 stages, heating stage, holding stage and cooling stage. To melt the sample, the holding temperature was set as 1470°C. In this Figure, the black line represents reference temperature, the red line represents sample temperature and the blue line represents temperature difference (dT = Sample Temperature – Reference Temperature). At the beginning of heating stage, the black line and red line are overlapped, at the temperature around 800°C, they start diverging. The temperature difference dT is negative which is consistent with the expected phase transformation of the sample from γ to δ-ferrite is an endothermic process. Since the heating rate is fixed for these four experiments, the temperatures of γ to δ-ferrite phase transformation are roughly the same. During the melting process, part of the input heat was absorbed by the sample to melt and the rest of the heat was used to rising the temperature. This is the reason why the temperature of the sample is lower than the reference’s. During the cooling stage, the sample solidifies in the same temperature regardless of different cooling rates. However, the cooling rates affect the transformation temperature; as the cooling rate increasing, the nucleation commences at higher temperatures. DTA can be used to determine the temperature associated with these reactions and therefore can be used to determine the relationships between compositions, solidification temperature range.
4.3.2 Thermodynamic calculation

Thermo-Calc was employed to calculate the amount of all phases as a function of temperature. The phase equilibria were calculated with a temperature range from 500°C to 1500°C.

As shown in Figure 4.3.3, the green line is gas phase. The black line is BCC_A2 which represents δ-ferrite and the purple line is FCC_A1#2 which means γ. The pink line is liquid phase. FCC_A1 could be some face centred cubic precipitates. Around 1420°C, the steel starts melting and about 1470°C, the steel fully melt. As temperature decreases, the liquid phase first solidifies into δ-ferrite and after solidification finished, δ-ferrite will remain for a while and then partially transit into γ. As temperature decreasing, meanwhile, under equilibrium solidification conditions, the precipitation of secondary phases, such as chromium nitrides, σ phase and χ phase, will proceed. The calculations of Thermo-Calc are consistence with the observation of HTCM experiments.

According the thermodynamic calculation of S32101 DSS, the δ-ferrite to γ phase transformation occurs around 1280°C. The calculated volume fraction of equilibrium phases at 1100°C are 50% of
CHAPTER 4 RESEARCH OF S32101 DUPLEX STAINLESS STEEL

δ-ferrite and 50% of γ. The gas phase forms after the steel fully solidified and before the commencement of phase transformation. Approximately at the range of 1280°C-1430°C.

4.3.3 DSC

For DSC experiments, the sample size is 10-50 mg, alumina lined Pt crucibles were used to hold the samples. Temperature is below 1500°C, heating rate set as 20 °C/min, cooling rate is 20°C/min and below around 400-500°C the cooling is likely to be slower. In this research, the DSC was employed to study the phase transformation during solidification process and provide more sensitive information comparing to DTA-HTCM experiments.

![DSC output of S32101 with 20°C/min heating rate and 20°C/min cooling rate](image)

Fig 4.3.4 DSC output of S32101 with 20°C/min heating rate and 20°C/min cooling rate

The sample was heated up to 1500°C to make sure it was fully melted and enable monitoring of its solidification behaviour while cooling down. As shown in Figure 4.3.4, this typical DSC melting curve contains 3 stages, a heating stage, a holding stage and a cooling stage. An endothermic peak commences at the temperature of 547.9°C during the heating stage represents the dissolving of chromium-rich α'-phase[80]. In contrast, an exothermic peak at the temperature of 545.1°C in cooling stage represents the formation of α'-phase. By comparing the DSC results with thermodynamic calculations, some phenomena can be explained.

Heating stage:
At the temperature of 1171.1°C, the endothermic peak is related to the solid-state transformation of secondary austenite ($\gamma_2$) into $\delta$-ferrite[80]. The following several endothermic peaks with lower intensities at the temperatures of 1171.1°C, 1241.7°C, 1281.4°C and 1318.0°C can be ascribed to the phase transformation of $\gamma$ to $\delta$-ferrite and the dissolving of secondary phases. The major endothermic peak starts at the temperature of 1436.5°C, and is related to the melting of the steel, comparing to the thermodynamic calculation result (Figure 4.3.3), and it ends at the temperature of 1494.9°C.

**Cooling stage:**

During the solidification process, the major exothermic peak starts at the temperature of 1459.2°C which represents the formation of $\delta$-ferrite from the melt. According to thermodynamic calculation, the exothermic peak at the temperature of 948.2°C related to the formation of secondary phase Cr2N. An exothermic peak in the temperature range of 823.5°C-803.5°C can be detailed as the transformation of $\delta$-ferrite into tertiary austenite ($\gamma_3$) and the formation of precipitate such as nitrides, $\chi$ phase and $\sigma$ phase[80, 81].

### 4.3.4 Concentric HTCM Experiments

To improve the quality of in-situ observation at different cooling rates, the concentric solidification technique was developed[66]. In Concentric HTCM, a thin slice of specimen is partially melted around the centre of the disc and form a liquid pool surrounded by solid rim. The invention of this experimental method has been proven to be better than conventional LSCM. The curvature caused by meniscus effect has been minimised by using concentric HTCM.

In continuous casting processes, the quality of products is highly related to the grain structure during solidification, including grain size, morphology and orientation[68]. It is essential to study the microstructure for improving product quality under different cooling rates.
Fig 4.3.5 HTCM revealing the solidification process of S32101 under 5°C/min cooling rate

During the solidification process, cooling rate can influence the solidification behaviour and the solids’ shapes. For the 5°C/min cooling rate, the sample starts solidifying from outside of the liquid pool and to inside gradually, with a columnar solidification structure (Figure 4.3.5). No nucleation emerges under this cooling rate. The grain boundaries is easy to observe and grain size is large. The columnar structure can be taken as dendrites without secondary arms. Because of the very slow cooling rate, the growth of primary arms is even towards the centre of the liquid pool, no space for secondary arms to grow.

The columnar structure is compact, the content of alloy elements and gas precipitates is low, hence, it is unlikely to form gas pores in this area. The columnar structure is another form of dendritic solidification in which there are no secondary arms. The temperature gradients in the liquid promote the growth of columnar grains. The cooling rate also plays an important role in the growth of a columnar structure. As the cooling rate increases, the length of columnar structure will decrease.
As shown in Figure 4.3.6, under a 10°C/min cooling rate, the solidification starts in the liquid/solid interface and the nucleation will happen from outside of the liquid pool to inside with a few minutes delay. In the second and third frame, the growth of primary and secondary dendritic arms is clearly observed. The growth of a primary dendrite is followed by the appearance of secondary dendrite arms and the growth of secondary arms is orientated. The direction of the arrows in second frame pointed the preferred growth direction of primary and secondary dendritic arms. The microstructure under 10°C/min cooling rate shows large graininess and large dendritic shapes.
For the sample cooled at 20°C/min, as shown in Figure 4.3.7, solidification starts in the liquid/solid interface and the nucleation will happen from outside of the liquid pool to the inside within 1 minute. The microstructure comprises cellular structure domains with a small part of needle shape particles, and no more dendritic microstructure.
For the sample cooled at 50℃/min, as shown in Figure 4.3.8, solidification starts in the liquid/solid interface and the nucleation happens both the centre and the edge of the liquid pool. In the second frame, the dendrites grow in the centre of the liquid pool. The grain size is still large.

Fig 4.3.9 HTCM revealing the solidification process of S32101 under 80℃/min cooling rate

For the sample cooled at 80℃/min, as shown in Figure 4.3.9, solidification starts and grows in the liquid/solid interface and the nucleation will happen in the liquid pool. The dendrites became more needle-like, and the primary arms are prolonged.
Fig 4.3.10 HTCM revealing the solidification process of S32101 under 100°C/min cooling rate

For a 100°C/min cooling rate, the sample starts solidifying both outside and inside at the same time and the dendritic structure is much finer (Figure 4.3.10).

Fig 4.3.11 HTCM revealing the solidification process of S32101 under 150°C/min cooling rate
For a 100°C/min cooling rate, as shown in Figure 4.3.11, solidification starts in the liquid/solid interface and the nucleation happens both the centre of the liquid pool and edge of the liquid/solid interface at same time. The morphology comprises grains of finer cellular shape without evidence of a dendritic microstructure. The grain size became finer and smaller than outside of the liquid pool.

In conclusion, as the cooling rate increases, the solid’s size will be finer, the morphology comprises smaller grains and the solidification behaviour in the body of the liquid pool will commerce faster.

### 4.4 Discussion

**4.4.1 Thermo-etching**

During the heating stage, when the temperature reaches 850–900°C, the colour of δ-ferrite will get darker and it’s very easy to distinguish γ and δ-ferrite in this period (Figure 4.4.1(a)). As the temperature increasing, γ transform to δ-ferrite. The grain boundaries enlarge and slip before melting and thermal etching appears, as shown in Figure 4.4.1(b). After these phenomena, the steel will melt soon.

![Figure 4.4.1 HTCM images revealing (a) δ-ferrite getting darker when the temperature rising, (b) the slipping of grain boundaries (c) and the groves remain intact after cooling down](image_url)

Fig 4.4.1 HTCM images revealing (a) δ-ferrite getting darker when the temperature rising, (b) the slipping of grain boundaries (c) and the groves remain intact after cooling down
When polished samples were heated to high temperature and exposed in an inert atmosphere, argon gas in present experiments for example, the grain boundaries will slip. Figure 4.4.2 (a) and Figure 4.4.2 (b) shows the thermal etching in solid rim of concentric experiments. The grooves as indicted on Figure 4.4.1 (b) will form in elevated temperature and remain intact after cooling down. Figure 4.4.2 illustrates the theories the formation of mobile and stationary grain boundaries. Figure 4.4.2 (b) also reveals mobile grain boundaries and stationary grain boundaries.

Fig 4.4.2 (a) Groove formed at the intersection of a free surface with a grain boundary (b) Characteristic steady-state profile of a thermal groove formed at a free surface by a moving grain boundary. θc is the critical grain boundary angle[82]

It could be a tough task to reveal austenite grain boundaries by normal chemical etching, especially for those steels which are not sensitive to chemical etching, such as medium carbon microalloyed steels[83, 84]. Concentric HTCM can provide a very effective method to study the grain boundaries. A novel method of thermal etching had been proposed by C. G. de Andrés et al[82], however, their method cannot provide in-situ observation of thermal etching. In concentric HTCM, the process of the thermal etching can be observed, and the velocity of grain boundary slipping can be detected and calculated in the solid rim of the tested sample.

4.4.2 Precipitates Commencement

The transformation of δ-ferrite to γ is revealed to commence after the “dark points” and “dark marks” form, as shown in Figure 4.4.3. Along with the time passing, the “dark points” and “dark marks” will spread all over the surface of δ-ferrite, after that, the γ will "grow" on the surface of δ-
ferrite and this means the phase transformation starts. The cooling rate will affect the proportion of transformed phases.

The transformation of δ-ferrite to γ is revealed to commence after the “dark points” and “dark marks” form, as shown in Figure 4.4.3. Along with the time passing, the “dark points” and “dark marks” will spread all over the surface of δ-ferrite, after that, the γ will “grow” on the surface of δ-ferrite and this means the phase transformation starts. The cooling rate will affect the proportion of transformed phases. As cooling rate increases, the proportion of transformed γ phases from δ-ferrite decrease.
4.4.3 Phase Transformation

The phase transformation of δ-ferrite to γ in S32101 DSS is observed by HTCM, as shown in the sequence of frames presented in Figure 4.4.4. In Frame (a), the structure at 915°C following cooling from 1400°C is fully δ-ferrite and precipitates commence to form above this temperature. In the next Frame (b), soon after the commencement of precipitation, the phase transformation starts randomly. Frame (c) shows the growth of austenite. In Frame (d), the phase transformation completed above the temperature of 769°C and the phase transformation happened in on side of the grain boundary (will be illustrated in Figure 4.4.10).

![Fig 4.4.4 HTCM images revealing phase transformation of S32101 under 10°C/min cooling rate. In the sequence of the frame shows the growth of austenite](image)

For different cooling rates, the temperature of phase transformation commencement is different. As shown in Figure 4.4.5, for cooling rates of 5°C/min, 20°C/min, 50°C/min, 80°C/min, 100°C/min and 150°C/min, the phase transformation temperatures are 895°C, 1005°C, 1165°C, 1168°C, 1174°C...
and 1226°C, respectively. As the cooling rate increases, the phase transformation starts earlier and occurs at a higher temperature.

Fig 4.4.5 HTCM revealing the commencement of phase transformation of S32101 under the cooling rate of (a) 5°C/min (b) 20°C/min (c) 50°C/min (d) 80°C/min (e) 100°C/min (f) 150°C/min
As shown in Figure 4.4.6 (a), there are 6 grains, and the phase transformation happened mainly in Grain 1 and 6. Grain 2, 3, 4 and 5 still remain as δ-ferrite. The red lines highlight the grain boundaries. Frame (b) shows the phase formation is orientated and Frame (c) shows the phase transformation can occur across grain boundaries. That means the transformation not strictly happens inside a specific grain. The last Frame (d) shows the morphology of transformed phases. This figure also provides evidence to prove the orientation of phase transformation. The ‘dendrites’ grow towards the right direction preferably.

In order to find the relationship between observations on the surface and solidification behaviour occurring in the bulk, optical microscopy was used. As shown in Figure 4.4.7 (a), a sample was mounted in Bakelite following cooling from 1400°C at a rate of 20°C/min and was half polished to determine if the solidification behaviour observed using HTCM and presented in Figure 4.4.3 and Figure 4.4.6, was only a surface effect or whether it represented solidification behaviour in the bulk. The transformed clusters disappeared after polishing. The grain boundaries are still continuous with the surface. In Frame (b), a sample was mounted in Bakelite following cooling from 1420°C at a rate of 5°C/min and fully polished. The figure focused on the centre of the sample which was liquid pool during HTCM experiment. The austenite clusters still remain and concentrate in the centre of the sample. Hence, even though the pattern of the phase transformation remain in the surface instead of the bulk, the behaviour of phase transformation is continuous both on the surface and in the bulk.
As soon as the tested samples were polished, it was easy to observe the island structure in the bulk. To ensure that the island structures are austenite, EDS mapping and spectrum analyses were conducted. As shown in Figure 4.4.8, the island particles are depleted in Cr and Si and rich in Ni and Mn. Since Cr and Si are ferrite stabilizers, and Ni and Mn are austenite stabilizers, the island particles are more likely to be austenite and the matrix is ferrite.
Fig 4.4.8 EDS mapping of HTCM tested sample revealing the distribution of alloying elements

In Figure 4.4.8, from the observation of optical microscopy, after polishing, we can find the austenite in the bulk of the sample is mainly located in the centre of the slice, which was liquid pool during the HTCM experiments. In another words, the austenite accumulated in the liquid pool after solidification. The rim of the sample shows a lower fraction of austenitic product. That means even
though the rim of the sample did not melt during the HTCM experiments, the composition of the solid rim changed. When the sample was heated up, even though the temperature of the solid rim cannot reach the melting point of the DSS, the free energy increased and this lead to the diffusion of some elements, such as Ni and Mn, into the liquid pool.

![Fig 4.4.9 Optical microscope images of five groups of tested samples with different cooling rates, for each group, left is unpolished, and right is polished. (a) 5°C/min (b) 20°C/min (c) 50°C/min (d) 80°C/min (e) 100°C/min](image)
CHAPTER 4 RESEARCH OF S32101 DUPLEX STAINLESS STEEL

Following HTCM experiments, all specimens were examined with OM for a preliminary evaluation of the microstructures. Comparing the five unpolished samples, large undercooling leads to smaller and finer solidifying structures. In the images of the polished samples, the $\gamma$ phases spread on the base of $\delta$-ferrite. In Figure 4.4.9 (a), low cooling rate gives $\gamma$ stabilizers enough time to transit into centre of the liquid pool and promote the formation of $\gamma$. The cooling rate will influence the segregation of alloying elements and finally determine the formation of $\gamma$. For different cooling rates, the segregation behaviour of different elements is complex.

![Figure 4.4.9](image)

Fig 4.4.10 Optical microscopy revealing austenite growth along the grain boundaries

As shown in Figure 4.4.10, the sample was tested under a concentric HTCM experiment under 150°C/min. After the HTCM experiment, the sample was polished with 1$\mu$m diamond paste and electrolytic etched in a 10 wt% oxalic acid solution (2.7 V for 10 seconds). The austenite grows along the grain boundaries preferably, except in the very centre of the sample, where a small amount of austenite grows inside the grains of the DSS.

4.4.4 Gas Pores Defects

The production of S32101 DSS in Baosteel suffers from the formation of nitrogen gas pores which leads to nearly 20% disqualification ratio. At present, gas pore defects are hindering the commercialisation S32101 DSS of Baosteel. Hence, the study of nitrogen gas pore formation is important for this project.

Although homogeneous nucleation of gas pores is possible, it is more likely that heterogeneous nucleation on the crystal surface is the main mechanism for gas pore formation[37]. As shown in
Figure 4.4.11, the nitrogen gas pores nucleate in the spaces between the primary dendritic arms. Figure 4.4.12 is an HTCM observation of nitrogen gas pores. It also shows up in the space between dendrite arms. As shown in the HTCM, the gas pores form between 1300°C and 1400°C. These results are highly consistency with the calculated outputs of Thermo-Calc. In figure 4.3.16, the blue solid line represents nitrogen gas phase and the nitrogen gas formation between 1420°C and 1290°C.

Fig 4.4.11 Formation of gas pores during solidification: (a) segregation of nitrogen, (b) nucleation, and (c) growth of pore[27]

Fig 4.4.12 HTCM revealing the gas pore formation of S32101 during solidification
The output of Table 4.1 was calculated by Thermo-Calc which can be used to estimate the mole, mass and the volume fraction of all phases and even can calculate the mole and mass fraction of every component for each specific phase. For example, at the temperature of 1300°C, there are two stable phases of S32101 DSS, one is gas and another is δ-ferrite. The component of gas phase is 100% N, hence, nitrogen gas pores more likely to form at this stage. The volume fraction of gas phase is 0.0369. BCC_A2 represents δ-ferrite in this software and the volume fraction of it is 0.9631.

### Table 4.1 Composition of stable phase of S32101 DSS at 1300°C calculated by Thermo-Calc

<table>
<thead>
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<th>Component</th>
<th>Mole Fraction</th>
<th>Mass Fraction</th>
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<td>1.0000</td>
</tr>
<tr>
<td>N</td>
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<td>0.0014</td>
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<tr>
<td>BCC_A2#1</td>
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<td>54.7149</td>
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Table 4.2 shows the amount of all phases as a function of temperature from 1270°C to 1424°C based on ‘property diagram’ function. This function can predict the solidification process of S32101.
DSS and provide a specific temperature range to focus during HTCM experiments. In the range of 1270℃ and 1424℃, the amount of nitrogen gas phase decreases along with the temperature’s decrease. Since the N solubility in liquid steel is much larger than in the solid state, a large amount of N will be rejected and form gas phase through heterogeneous nucleation. The δ-ferrite remains for a while, in this period, and the nitrogen diffuses back to the solids and δ-ferrite nucleation completes as soon as γ forms.

Table 4.2 The amount of all phases of S32101 DSS in the temperature range of 1270℃ and 1424.34℃ calculated by Thermo-Calc software

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4.4.5 Influence of alloying elements based on Thermo-Calc calculation

Thermo-Calc can calculate different phase diagrams for different alloying elements. As shown in Figure 4.4.13, by changing the mass percent of alloying elements, each phase will form at different temperatures. In frame (a), during the process of solidification, as the mass percentage of Cr increases, the austenite will form earlier, in another word, at higher temperature. That means that the element Cr is an austenite stabiliser. When the mass percentage of Cr is 21.5, the phase transformation point is 837°C and the melting point is 1467°C. In frame (b), as mass percentage of Mo increases, the austenite formation temperature increases slightly. Same effects of element Cu as shown in frame (c). In frame (d), even Ni is a ferrite stabilizer, and a small amount of Ni won’t affect the austenite formation temperature dramatically. The transformation temperature decreases slightly along with the increasing of Ni mass percentage. When the mass percentage of Ni is 1.5, the phase transformation temperature is 837°C and the melting point is 1467°C which is consistent with HTCM experimental result and Thermo-Calc calculations. In frame (f), when N content is greater than 0.135 mass percent, the gas phase will form.
4.5 Conclusions

The duplex stainless steel investigated contains around 50% FCC γ islands and 50% BCC δ-ferrite matrix. For S32101 DSS, the solidification mode is liquid → δ-ferrite → γ.

The solubility of nitrogen in austenite is the critical limitation of nitrogen content in DSSs, so the nitrogen content cannot exceed the solubility of nitrogen in austenite. Some nitrogen stabilizing elements can be added into the steel to promote the nitrogen remaining in the austenite or to increase its solubility in austenite. Since the N solubility in liquid steel is much larger than in solid state, a large amount of N will be rejected and form gas phase through heterogeneous nucleation of solid. The δ-ferrite will remain for a while, in this period, and the nitrogen will diffuse back into the solids as soon as γ forms.

HTCM-DTA and Concentric HTCM experiments results shows that cooling rate can influence the phase transformation through segregation of elements. DTA can be used to determine the temperature associated with these reactions and therefore can be used to determine the relationships between compositions and solidification temperature range. Higher cooling rates leads to larger undercooling. And increased undercooling leads to finer microstructures. As the cooling rate increases, the solid’s microstructure is finer, and the solidification behaviour in the body of the liquid pool will commerce more rapidly. During the heating stage, when the temperature reaches
850~900°C, the grain boundaries of S32101 DSS will slip, this is called thermal etching. As the cooling rate increases, the phase transformation starts earlier and at a higher temperature. The austenite grows along the grain boundaries preferably.

DSC is a more sensitive technique than DTA, and the results generated from DSC can provide a lot of useful information. The temperature difference $dT$ is negative which means that the phase transformation of the sample from $\gamma$ to $\delta$-ferrite is an endothermic process. The $\delta$-ferrite to $\gamma$ phase transformation is an exothermic process. The cooling rate can affect the phase transformation temperature during the solidification process. As the cooling rate increases, the phase transformations commence at higher temperatures. For S32101, the DSS solidifies under 20°C/min cooling rate, an endothermic peak commencing at the temperature of 547.9°C in the heating stage represents the dissolving of chromium-rich $\alpha'$-phase. In contrast, an exothermic peak at the temperature of 545.1°C in the cooling stage represents the formation of $\alpha'$-phase. During the melting process, at the temperature of 1171.1°C, the endothermic peak is related to the solid-state transformation of secondary austenite ($\gamma_2$) into $\delta$-ferrite. The endothermic peaks with lower intensities at the temperatures of 1171.1°C, 1241.7°C, 1281.4°C and 1318.0°C could be the phase transformation of $\gamma$ to $\delta$-ferrite and the dissolution of secondary phases. The major endothermic peak starts at the temperature of 1436.5°C and ends at the temperature of 1494.9°C. Based on the results of thermodynamic calculations, this endothermic peak is related to the melting of the steel. During the solidification process, the major exothermic peak starts at the temperature of 1459.2°C which represents the formation of $\delta$-ferrite from the melt. According to thermodynamic calculation, the exothermic peak at the temperature of 948.2°C is related to the formation of the secondary phase, Cr$_2$N. An exothermic peak in the temperature range of 823.5°C-803.5°C can be described as the transformation of $\delta$-ferrite into tertiary austenite ($\gamma_3$) and the formation of precipitates such as nitrides, $\chi$ phase and $\sigma$ phase[80, 81].

According to the thermodynamic calculations and HTCM experiments for S32101 DSS, the $\delta$-ferrite to $\gamma$ phase transformation occurs around 1280°C. The calculated volume fraction of equilibrium phases at 1100°C are 50% of $\delta$-ferrite and 50% of $\gamma$. The gas phase forms after the steel is fully solidified and before the commencement of phase transformation, approximately within the range of 1280°C-1430°C. For S32101, the melting point is around 1470°C. This DSS solidifies completely in the $\delta$-ferrite field and is followed by a solid state transformation to $\gamma$. This process is reversible. Around 1420°C, the steel starts melting and about at 1470°C, the steel fully melted. As the temperature decreases, the liquid phase first solidifies into $\delta$-ferrite and after solidification is
complete, the δ-ferrite will remain for a while and then partially transform into γ. The calculations of Thermo-Calc are consistent with the observation of HTCM experiments.

Different alloying elements have different influences on the solidification behaviours of S32101 DSS. As the Cr content increased, the austenite will form earlier and at a higher temperature. Cr is an austenite stabilizer. As the amount of Mo increase, the austenite formation temperature will increase slightly. The same trend is observed for the element Cu. Ni is a ferrite stabilizer, small amount of Ni won’t affect the austenite formation temperature dramatically, yet the transformation temperature will decrease slightly along with the increasing of Ni mass percentage. When the N content is greater than 0.135 mass percent, the gas phase will form.
Chapter 5

Research of S31254 Super-Austenite Stainless Steel

5.1 General Introduction

S31254 SASS was wildly used in paper, pulp, chemical, gas, oil industries, as well as marine and offshore application due to its high pitting corrosion resistance. It also can be used as structure material for desalination, piping and heat exchangers [25, 85-87]. Other excellent properties of S31254 SASS including enhanced mechanical properties, good formability and weldability, superior impact toughness. However, this type of stainless steels has been suffering of various kinds of precipitates. The mostly reported secondary phase is \( \sigma \) phase, others including \( \text{M}_2\text{C}_6 \) and \( \text{M}_6\text{C} \) carbides, Cr2N and AlN nitrides, \( \chi \) and Laves intermetallic. All mentioned secondary phases are detrimental to the properties of S31254 SASS and could lead to product failure.

![Image](image1.png)

Fig 5.1.1 Optical microscopy revealing secondary phase induced crackings of S31254 SASS

For S31254 SASS, the defect of secondary phases induced cracking is the most serious problem that encountered during plantial production (Figure 5.1.1). To realize industrial production of S31254 SASS, the secondary phase induced cracking must be eliminated. This chapter mainly focused on
CHAPTER 5 RESEARCH OF S31254 SUPER-AUSTENITIC STAINLESS STEEL

generating a deep understanding of secondary phases formation during solidification processes under different cooling rates.

5.2 Experiments Details

5.2.1 Materials

For HTCM experiments, the samples were cut into two different sizes. The diameter of samples used for concentric HTCM is 9.7mm and the thickness is 0.25mm. The diameter of samples used for DTA-HTCM is 4.3mm and the thickness is 1.5mm. For concentric HTCM, the samples need to be polished very fine to generate high quality images. The procedure of preparing well-polished sample has been discussed in Chapter 3.

5.2.2 JEOL JSM-7001F SEM

The facility of JEOL JSM-7001F SEM (Figure 5.2.1) is located in the Electron Microscope Centre, University of Wollongong. This instrument can provide a resolution of 1.2nm, which can guarantee an observation at magnifications of ×100,000. Fine surface structures can be observed with a low electron beam energy. JSM-7001F has high power optics which can produce a small electron probe, and make it easy to characterize nanostructures. The JSM-7001F can produce large probe current while maintaining a small diameter probe. Figure 5.2.2 is the cracking defect of S31254 SASS taken by JEOL JSM-7001F SEM.

Fig 5.2.1 JEOL JSM-7001F SEM equipped with EBSD
5.2.3 HTCM experiments

All the samples were cut into two size which was detailed above. All the slices need to be polished and grounded on 800, 1200, 2400 and 4000 SiC papers. Then polish the sample by standard metallographic techniques with 6 micron diamond paste and 1 micron diamond paste. Samples of S31254 SASS were prepared to conduct HTCM experiments under different cooling rates to study the influences of cooling rate on the secondary phases formation during solidification processes.

5.2.4 Thermodynamic calculation

The introduction of Thermo-Calc software has been detailed in Chapter 4. In this chapter, the Thermo-Calc software will be used to calculation the formation temperature of secondary phases and intermetallic during the solidification process of S31254 SASS, including the amount of these precipitations. The influence of different alloying elements on the formation of secondary phases and intermetallic will also be studied in this chapter through thermodynamic calculation.

5.3 Experiments Results

The fundamental of tackleing the cracking defect of S31254 SASS is to comprehend the secondary phases and intermetallic formation process during the solidification process. Thermo-Calc software can calculate the amount of all phases as a function of temperature by using ‘property diagram’
function. The result generated by Thermo-Calc can be used as a comparison of experimental results when analysing the DTA output. The HTCM results can provide more direct information of solidification behaviour.

5.3.1 Thermodynamic calculation

Thermo-Calc was employed to calculate the amount of all phases as a function of temperature. The phase equilibria were calculated with a temperature range from 500°C to 1500°C through ‘property diagram’ function in Thermo-Calc.

![Figure 5.3.1: The amount of all phases as a function of temperature calculated by Thermo-Calc](image)

Figure 5.3.1 is calculated by Thermo-Calc, it shows the amount of all phases. In the plot, the steel starts melting in 1370°C, this is consistent with the DTA output in Figure 5.3.4. The red line represents austenite (FCC_A1) and the green line represents SIGMA phase. Below the temperature of 1110°C, SIGMA phase separates out and the amount increases with the decreasing of
temperature till 800°C. Another secondary phase Cr$_2$N (HCP_A3#2) precipitates around 1020°C and Laves phase precipitates at 800°C. All these phases have a detrimental effect on the material properties.

### 5.3.2 DTA-HTCM Experiments

In the present work, a HTCM was been used for in-situ observation and in real-time the planar to cellular to dendritic transition of the progressing solid/liquid interface in SASS. By comparing thermodynamic calculation with experimental results, we can analyse the phase transformation and secondary phase formation of SASS during solidification process.

![Images of solidification process](a) (b)

**Fig 5.3.2** Increased undercooling (a) and shallow undercooling (b) of S31254

![DTA output graph](Fig 5.3.3 DTA output for S31254)
Figure 5.3.2 and Figure 5.3.3 are DTA-HTCM outputs for S31254. As shown in Figure 5.3.2, the nucleation patterns of δ- ferrite varies with different undercooling. Large undercooling leads to refined microstructure and decreased undercooling for γ nucleation. In Figure 5.3.3, the red line represents sample temperature (Ts) and the black line represents temperature difference (dT). The sample temperature and the temperature difference were plotted as a function of time. During the heating stage, one part of input heat was absorbed by the sample to melt itself and another part was used to increase the sample’s temperature. Hence, the sample temperature is smaller than reference temperature and the value of dT is negative and an endothermic peak shows up. As temperature decreases, the solidification proceeds accompanied by heat release. Hence, the temperature of tested sample is higher than the reference, the value of dT is positive and an exothermic peak shows up. Fast cooling leads to increased undercooling and slow cooling leads to shallow undercooling.

![Graph showing DTA output of S31254 with different cooling rates](image)

Fig 5.3.4 DTA output of S31254 with the cooling rates of 20°C/min, 100°C/min, 200°C/min and 300°C/min

As shown in Figure 5.3.4, four different cooling rates, 20°C/min, 100°C/min, 200°C/min and 300°C/min respectively, were applied for the solidification process of S31254 SASS. The heating rate is fixed. Each experiment was divided into 3 stages, heating stage, holding stage and cooling stage. To melt the sample, the holding temperature was set as 1430°C. In this curve, the black line represents reference temperature, the red line represents sample temperature and the blue line represents temperature difference (dT = Sample Temperature – Reference Temperature). As shown in this curve, since the heating rate is identical, the patterns of endothermic peak are roughly the same and the value of endothermic peak point dT are also the same, -39°C. During the cooling
stage, right after the temperature drops down, an exothermic peak shows up, and this peak represents the nucleation of \( \gamma \). As cooling rate increases, the temperature difference of \( \gamma \) nucleation increasing and the interval of nucleation decreasing and releasing more heat. The major exothermic peak is following the nucleation peak. By comparing these 4 experiments, we can see that larger cooling rate leads to sharper exothermic peak, smaller solidification interval and more energy was released.

Solidification is a heat releasing process, as the increasing of cooling rate, the nucleation proceeds more rapidly and releases more heat, as shown in the peaks of solidification process of Figure 5.3.4. The faster the cooling rate, more heat released during solidification.

(a)

(b)

(c)
CHAPTER 5 RESEARCH OF S31254 SUPER-AUSTENITIC STAINLESS STEEL

Fig 5.3.5 HTCM revealing the solidification process of S31254 SASS under the cooling rate of (a) 20°C/min (b) 100°C/min (c) 200°C/min (d) 300°C/min

For S31254 SASS, as shown in Figure 5.3.5, the melting point is around 1400°C. Along with the increasing of cooling rate, the nucleation temperature decreased, and the microstructure became finer. In Figure 5.3.5(a), large dendritic arms were observed under the cooling rate of 20°C/min. As the cooling rate increased to 100°C/min (Figure 5.3.5(b)), the dendritic arms became much smaller. In Figure 5.3.5(c) and (d), under the cooling rates of 200°C/min and 300°C/min, the nucleation happens all over the liquid pool and leaves no time for dendrites to grow. The HTCM experimental results and the DTA outputs of SASS suggest that increased undercooling could lead to a refined microstructure and decreased undercooling for γ (austenite) nucleation. The results revealed the variability in undercooling for γ nucleation.

5.3.3 Concentric HTCM

Concentric HTCM is new technique which was used to study the peritectic reactions. For S31254 SASS, the steel contains 100% γ. When it was heated, the γ transformed into δ-ferrite and started melting partially (Figure 5.3.6(a)). As shown in Figure 5.3.6(b), the solidification mode of SASS is totally different comparing with DSS. During the solidification process, the δ-ferrite phase forms firstly, as solidification proceeds, γ grows at the interface of δ-ferrite and liquid phase. Austenite grows into δ-ferrite via peritectic and grows towards liquid phase. The solid-state growth of γ proceeds at a much higher rate than liquid-state growth. Through changing the cooling rates, different solidification structures were observed.
Fig 5.3.6 HTCM images revealing melting (a) and solidification (b) behaviour of S31254

Fig 5.3.7 HTCM revealing the solidification process of S31254 under 5°C/min cooling rate

When the cooling rate is 5°C/min, it will give the dendrites enough time to grow. Typical peritectic solidification pattern was observed under this low cooling rate (Figure 5.3.7).
As shown in Figure 5.3.8, under a cooling rate of 20°C/min, the liquid/solid interface is irregular, and solidification starts with the growth of solid in the liquid pool’s edge. Nucleation happens in the centre of liquid pool and followed by the edge shortly. After the nucleation, the liquid between nuclei solidifies later. The inter-dendritic liquid more likely to form intermetallic or precipitates which have lower melting point.
Fig 5.3.9 Concentric HTCM revealing the solidification process of S31254 under the cooling rate of (a) 50°C/min (b) 100°C/min (c) 200°C/min (d) 500°C/min

Comparing to DTA-HTCM, the technique of Concentric HTCM can generate better quality video (Figure 5.3.9). For enhanced cooling rates which are greater than 50°C/min, the microstructure growth mode is same. The liquid/solid interface is irregular, and solidification starts with the growth of solids and nucleation will happen in the centre of liquid pool and followed by the edge shortly.

5.3.4 Thermodynamic calculation

The output of Table 5.1 was calculated by Thermo-Calc which can be used to estimate the mole, mass and the volume fraction of all phases and even can calculate the mole and mass fraction of every component for each specific phase. For example, at the temperature of 800°C, there are four stable phases of S31254 SASS, austenite (FCC_A1#1), nitride (HCP_A3#2), Laves phase (LAVES_PHASE_C14#1) and sigma phase (SIGMA#1). The version of Thermo-Calc software employed in this research is 2018a and database is TCFE9: Steels/Fe-Alloys V9.0.
Take this system as 1 mole, the mass is 56.6g and the volume is 7.32E-6 m3. The total Gibbs energy of this system at the temperature of 800℃ is -55640.42J. The Enthalpy is 28785.35J. At the temperature of 800℃, the system has 0.80241 moles austenite, 0.02392 moles nitrides, 0.0004 moles Laves phase and 0.17327 moles sigma phase.

For austenite phase, the composition includes the elements of Fe, Ni, Cr, Mo, Mn, Cu and N. It has two constitutions, one sublattice is \((Cr,Cu,Fe,Mn,Mo,Ni)_1\) and another one is \((N,VA)_1\).

For nitrides (HCP_A3#2), the composition contains the elements of Cr, N, Mo, Fe, Mn, Ni and Cu. This Cr and N-domain phase has two sublattice, \((Cr,Cu,Fe,Mn,Mo,Ni)_1\) and \((N,VA)_{0.5}\).

For Laves phase, Mo, Fe, Cr, Ni, Cu and Mn elements forms two sublattice, \((Cr,Cu,Fe,Mn,Mo,Ni)_2\) and \((Cr,Cu,Fe,Mn,Mo,Ni)_1\).

For sigma phase, high amount of Mo element along with Fe, Cr, Ni and Mn element forms 3 sublattice, \((Cr,Fe,Mn,Ni)_{10}\), \((Cr,Mo)_4\) and \((Cr,Fe,Mn,Mo,Ni)_{16}\).

Table 5.1 Composition of stable phases of S31254 SASS at 800℃ calculated by Thermo-Calc

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<tr>
<th>Stable Phases</th>
<th>Moles</th>
<th>Mass</th>
<th>Volume Fraction</th>
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Composition

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<th>Mass Fraction</th>
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<td>0.2111</td>
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<td>Cr</td>
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</tr>
<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Mn</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.0077</td>
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</tr>
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<td>N</td>
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### Constitution

<table>
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### Composition

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### Constitution

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<tr>
<td>LAVES_PHASE_C14#1 0.00040</td>
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### Composition

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### Constitution

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### Composition

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<th>Mass</th>
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</table>
Table 5.2 shows the amount of all phases as a function of temperature start from 660°C to 1100°C. Comparing with S32101 DSS, the solidification process of S31254 SASS is much more complicated. As temperature rises, Cr$_2$N, Laves phase and sigma phase dissolve and transform to austenite. Laves phase completely dissolves at the temperature of 800°C and Cr$_2$N totally dissolves at the temperature of 1027°C. The sigma phase forms at elevated temperature and still exists at 1100°C with tiny amount of 0.00318 mol.

Table 5.2 The amount of all phases of S31254 SASS in the temperature range of 660°C -1100°C, calculated by Thermo-Calc software
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<th>F</th>
<th>E</th>
<th>F</th>
</tr>
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</table>
5.4 Discussion

5.4.1 Secondary phases induced cracking

Super Austenitic Stainless Steels such as S31254 are extensively applied to some nuclear industries which required excellent resistance to aqueous corrosion. These types of relatively high-nickel steels contain 6~7%wt Mo to improve corrosion resistance. However, during the solidification process of continuous casting, Mo segregates preferentially to the liquid due to the low solubility of Mo in austenite phase. In addition, the diffusion rate of Mo in austenite is very low and won’t allow it to diffuse back toward the dendrite cores to eliminate the concentration gradient. Finally, some Mo-enrich and Mo-deplete secondary phases form[88-90]. Some of the secondary phases and intermetallics are quite brittle and could lead to cracking (as shown in Figure 5.4.1). To tackle this cracking problem, the composition of the defects was studied firstly.
In Figure 5.4.2, 4 points around the defect were chosen to do the spectrum analysis. In Point 1, the amount of Cr is 21.38wt%, Ni is 16.85wt% and Mo is 7.02wt%. Comparing to the composition of S31254 SASS, the content of Cr and Mo are a little bit higher and the amount of Ni is smaller. In spectrum 2, the content of Cr is 3.28wt%, Ni is 3.54wt% and Mo is 2.12%. Point 2 is extremely
deplete of Cr, N and Mo. Same as spectrum 2, spectrum 3 also has a few amounts of Cr and Ni and even didn’t detect Mo element. The content of Cr, Ni and Mo in spectrum 4 are less than S31254. Among all 4 points, only point 1 has lager amount of alloying elements Cr and Mo. All other points have less alloying element.

Fig 5.4.3 SEM revealing the element dispersion around the defect for elements (a) Iron, (b) Nickel, (c) Molybdenum and (d) Chromium
CHAPTER 5 RESEARCH OF S31254 SUPER-AUSTENITIC STAINLESS STEEL

To understand the distribution of Cr, Mo and Ni elements distribution around the cracking. SEM linear scanning function was used to analyse the content. As shown in Figure 5.4.3, the green map represents iron content, the celeste map represents nickel content, the purple map represents molybdenum content and the red map represents chromium content. The cracking interface is located at the distance of 18μm. The element distribution changes suddenly at the interface. The region around the defect contains large amount of Fe and Ni element and small amount of Mo element. The content of Mo element is about 7wt% on average which is the exact composition of S31254 SASS. At the interface, the Fe and Ni content drop to a very low level. And Mo content increases to a very high level. The Ni content increases a little comparing to the outside of the defect. The cracking region has more Mo and Cr elements and less Ni element.

5.4.2 Solidification mode of S31254 SASS

By using “Scheil Solidification” function in Thermo-Calc, the solidification process of S31254 SASS can be calculated. As shown in Figure 5.4.4, around 1390°C, the two lines diverge which is due to microsegregation. In Thermo-Calc software, FCC_A1 represents austenite, BCC_A2 represents delta-ferrite and HCP_A3 represents Cr2N. During the solidification process, delta-ferrite...
will form around 1360°C and at the temperature of 1320°C, sigma phase forms. As temperature decreasing to 1280°C, the delta-ferrite will fully transform into austenite.

5.4.3 Intermetallics and precipitation

In stainless steels, both χ phase and σ phase are the intermetallics which form the most frequently upon thermal ageing. EBSD is a convenient way to distinguish them[2]. Recent studies showed that even the χ phase forms earlier than the σ phase, it also can transform to σ phase due to prolonged ageing [91-93]. The χ phase contains more Mo element than σ phase [81].

The σ phase has been studied by lots of researchers for a long time due to its significant influence. Sims [94] pointed out that when the electron hole number (Nv), which is an indicator for the formation of σ phase, exceeds 2.5, no σ phase will form. His point of opinion was verified by T. Yamane et al [95] in a 25Cr-20Ni austenite stainless steel. Because of the enrichment of Cr, the diffusion of Cr is taken as a factor of its formation. Sasikala et al [96] reported that the diffusion of other substitutional elements like Mo can also affect the formation of σ phase. On the same time, Vitek [97] and David and David et al [98] pointed out that the ferrite-to-sigma phase transformation is limited by the step of the σ phase nucleation which means the enrichment of Cr in ferrite is not a sufficient condition for σ phase formation. The formation of σ phase in austenite related to the grain size and shape in austenitic stainless steels [99]. Small grain size can provide more grain boundaries for σ phase to form.

Since the application of high-nitrogen stainless steels has been extended, lots of types and grades of stainless steel has been invented. Thus, more and more researchers are focused on the precipitation of nitrides. The precipitation of cellar Cr2N is, in most case, detrimental.

For the S31254 SASS, to obtain a clear surface morphology, the sample was etched in a solution of 15mL HCl + 10mL acetic acid + 5mL HNO₃ + 2 drops of glycerol. The solution was prepared by mixing HCl and glycerol thoroughly before adding HNO₃. The sample was either immersed in the etchant or swabbed for few seconds. As shown in Figure 5.4.5, after 2 (a) and 6 (b) seconds etching, a large number of vermicular lines emerge. These lines more likely to be due to the segregation of some alloying elements, Mo for example.
The EDS mapping in the SEM was used to analyse the chemical composition of the austenite matrix and vermicular lines. Figure 5.4.6 shows five spectrums for 5 different points, from spectrum 5 to spectrum 8, respectively. Spectrum 4, 5 and 7 detect the composition of different locations on vermicular line. Spectrum 6 and spectrum 8 locate on austenite matrix. The Cr contents of spectrum 6 and 8 are 15 and 14wt%, respectively. The Mo contents are both 6wt%. For spectrum 4, 5 and 7, the Cr contents are 20, 20 and 19wt%, respectively. Mo contents are 7.5, 10 and 8wt%. The vermicular particle is rich in Cr and Mo, indicating that the Cr and Mo in the surrounding austenite matrix segregated to the vermicular shape particle. In addition, the depletion of Cr and Mo in austenite matrix could cause the decrease of pitting corrosion resistance. It has been reported [100] that at least four different types of precipitates were observed and they are sigma phase, Laves phase, chi phase and Cr₂N nitride. The volume fraction of sigma and Laves phases are greater than
the other two. Since the composition of vermicular particle is vary with location, it could have more than just one phase.
Fig 5.4.6 Average composition of austenite matrix and vermicular line as determined by energy dispersive spectroscopy (EDS)

In S31254 SASS, a secondary phase has been observed. Metallographic preparation for SEM-EDS analysis of the samples was performed with standard metallographic mounting and polishing techniques. EDS can be used to analyse the composition of various secondary phases. The samples were etched with 10% oxalic acid in deionized water at 5V for 0.5 to 20 seconds. As shown in Figure 5.4.7, by using SEM-EDS mapping, it is obvious that the vermicular line is a different phase from the austenite matrix which has a wide distribution of size and morphology. In these two regions, both have high amount of Cr and Mo and accompany with depletion of Ni. Previous studies[38] have indicated that the enrichment of Cr and Mo can increase the tendency of the precipitation of σ phase. Enrichment of Cr and Mo, depletion of Ni and Body centred tetragonal microstructure are three features of σ phase and it normally formed with eutectoid transformation by decomposition of δ to γ and σ at interfaces, or within transformed γ. The decomposition of γ is the main cause of σ phase formation. When large amount of Cr, sometimes Mo, diffuse within the γ matrix, the Cr-rich compounds will form. As indicated by SEM-EDS mapping, the secondary phase formed on the austenite matrix of S31254 SASS is σ phase. The enrichment of Cr and Mo in σ phase leads to depletion of Cr and Mo in the austenite matrix and this can increase the susceptibility to corrosion. The intermetallic σ phase is brittle. It can affect the fatigue, strength and corrosion behaviour of S31254 SASS[101]. So, the formation of σ phase is one of the factors that leads to the cracking.
Except \(\sigma\) phase, the intermetallic Laves phase also has a large volume fraction and forms earlier than the precipitates of \(\sigma\) phase. In previous report\cite{100}, among \(\sigma\) phase, \(\chi\) phase, Laves phase and Cr\(_2\)N nitride, the Laves phase is the first formed secondary phase and followed by the formation of \(\sigma\) phase. The Mo content in Laves phase could reach as high as 21.5-27.4wt\%, it was partitioned into Laves phase particles and leads to the enrichment of Mo.

The Cr\(_2\)N nitride precipitated close to Laves phase particles, in other words, the Laves phase formed earlier than Cr\(_2\)N nitride and the formation of Cr\(_2\)N nitride seems to be favoured by the presence of Laves phase. The diffusion of Mo element form \(\gamma\) matrix into Laves phase leads to the depletion of
Mo in $\gamma$ matrix and could promotes the formation of $\sigma$ phase and Cr$_2$N nitride which are enrich of Cr. Finally cause the enrichment of Ni in $\gamma$ matrix. Another proof of $\sigma$ phase is the phenomenon of localized melting of S32154 SASS. The secondary phase can be observed very clearly by concentric HTCM only if the tested sample was well-polished. In Figure 5.4.8, when the samples were heated, the precipitates will melt in different stages. Not all the ‘marks’ will melt at the same temperature, in another word, the different melting points of the ‘marks’ means there are more than one secondary phase in these ‘marks’. When the temperature hits 1240°C, all the marks will melt as clusters. Among all secondary phases, only $\sigma$ phase’s melting point can reach this high. For the distribution of $\sigma$ phase, it is not even.

![Fig 5.4.8 Concentric HTCM revealing localize melting of sigma phase](image)

In S32154 SASS, Laves phase and nitrides also can affect the property of the product. By using the “property diagram” function in Thermo-Calc, we can predict the secondary phases’ formation. As shown in Figure 5.4.9, the $\sigma$ phase forms in 1105.93°C, the amount of $\sigma$ phase is larger than the other two phases and can reach 0.18 mol. The Laves phase forms in 799.6°C and the amount of it is 0.1mol. HCP_A3#2 represents Cr$_2$N nitrides in Thermo-Calc and it forms in 1025.50°C. The amount of Cr$_2$N nitrides is smaller than $\sigma$ and Laves phases, around 0.025mol.
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Fig 5.4.9 Secondary phase formation of S31254 SASS calculated by Thermo-Calc

5.4.4 Influence of alloying elements on secondary phase formation

Fig 5.4.10 Phase diagram of S31254 SASS as the function of (a) Mo mass percentage and (b) N mass percentage calculated by Thermo-Calc
Thermo-Calc can calculate different phase diagrams for different alloying elements. In Figure 5.4.10, the blue line represents Laves phase and the brown line represents SIGMA phase and through changing the mass percent of alloying elements, each phase will form at different temperatures. In frame (a), during the process of solidification, as mass percentage of Mo increasing, both Laves phase and sigma phase will form earlier, in another word, at higher temperature. Lower content of Mo (less than 3.7wt%) has greater effect on Laver phase formation and Higher amount of Mo (more than 3.7wt%) has greater effect on sigma phase. When the content of Mo is 6wt%, the Laves phase formation temperature is 810°C and the sigma phase will form at the temperature of 1050°C. In frame (b), as mass percentage of N increasing, the Laves phase formation temperature increases slightly and the sigma phase formation temperature decreases.
5.5 Conclusions

For S31254 SASS, the solidification mode is liquid + δ-ferrite → γ. It solidifies via peritectic and the cooling rate affects the nucleation and microstructure of δ-ferrite. Higher cooling rate represents larger undercooling and increased undercooling leads to finer microstructure. As cooling rate increased, the nucleation temperature decreased, and the microstructure became finer.

Through the calculation of Thermo-Calc, the precipitation temperatures of σ phase, Cr2N nitrides and Laves phase are 1105.93°C, 1025.50°C and 799.60°C, respectively. The amount of σ phase is largest, then is Laves phase, followed by Cr2N nitrides. During the solidification process of S32154 SASS, Laves phase and nitrides can affect the property of the product. We can predict the secondary phases’ formation through thermodynamic calculation. The σ phase forms in 1105.93°C, the amount of σ phase is larger than the other two phases and can reach 0.18 mol. The Laves phase forms in 799.6°C and the amount of it is 0.1 mol. Cr2N forms in 1025.50°C. The amount of Cr2N nitrides is smaller than σ and Laves phases, around 0.025 mol.

During the process of solidification, as mass percentage of Mo increasing, both Laves phase and sigma phase will form earlier, in another word, at higher temperature. Lower content of Mo (less than 3.7wt%) has greater effect on Laver phase formation and Higher amount of Mo (more than 3.7wt%) has greater effect on sigma phase. When the content of Mo is 6wt%, the Laves phase formation temperature is 810°C and the sigma phase forms at the temperature of 1050°C. As mass percentage of N increasing, the Laves phase formation temperature increases slightly and the sigma phase formation temperature decreases.

According to DTA outputs, larger cooling rate leads to sharper exothermic peak, smaller solidification interval and more energy was released. As cooling rate increases, the temperature difference of δ-ferrite nucleation increases, the interval of nucleation decreases, and more heat released. Below the temperature of 1110°C, SIGMA phase separates out and the amount changes with temperature. Then comes with another secondary phase, Cr2N, around 1020°C, Laves phase will precipitate at 800°C. All these phases have a detrimental effect on the material properties. This is consistent of thermodynamic calculation.

SEM-EDS mapping shows that the cracking region has more Mo and Cr elements and less Ni element.
The formation of $\sigma$ phase in austenite related to the grain size of austenitic stainless steel. Small grain size provides more grain boundaries for $\sigma$ phase to form.
References

REFERENCES


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