Effect of Phase Solidification Sequence in Stainless Steel on Grain Refining Efficiency

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ABSTRACT

Grain refinement of the as-cast structure of Cr-Ni stainless steel alloys solidified with primary FCC, BCC and mixed FCC/BCC phases was experimentally studied using a melt treatment that promotes the formation of heterogeneous nuclei. This melt treatment was designed using solidification simulations with FACTSAGE 7.1 thermodynamic software. Refinement of the primary solid phases was achieved in both cast ferritic and austenitic grades. However, imposing a mixed solidification sequence of FCC and BCC phases resulted in a macrostructure without a recognizable Columnar-to-Equiaxed Transition zone (CET). Non-metallic inclusions in the casting were analyzed using automated SEM/EDS method, and compared with the thermodynamic simulations. A computational fluid dynamics (CFD) analysis was employed using ANSYS 18.1 Fluent software to simulate the thermal gradient (G) and isotherm velocity (V) in the casting, and their values were plotted on a Hunt’s criteria map and compared qualitatively to experimental CET position for the different steels.

INTRODUCTION

The macrostructure of a stainless steel casting is typically characterized by three distinct regions of grain structure. The first is the chill zone, which occurs at the mold interface where solidification begins. These grains tend to be small in size because of high solidification rates and high undercooling of the melt near the mold wall. Some of these grains manage to continue growing into the melt as dendrites. These dendrites form the second zone, which contains a columnar grain structure. If favored, these grains will grow until all the liquid metal is fully consumed. However, this columnar growth can be impeded by the formation of equiaxed grains in the third zone in the melt ahead of the growing columnar dendrites. Equiaxed grains can form when thermal conditions are favorable and/or effective heterogeneous nuclei are present to encourage the nucleation of solid within the melt. Grain refinement promotes a large equiaxed zone which, in some cases, can completely suppress growth of the columnar zone. This manipulation of grain size and shape affects both the castability and mechanical properties of the final steel casting, and is therefore a crucial aspect of the casting process.

Numerous studies have been conducted to better understand how to control the Columnar-to-Equiaxed Transition zone (CET) in a variety of metals. One grain refining technique commonly used in industry to control CET in aluminum alloys is the use of a TiB2 inoculant to introduce solid heterogeneous nuclei in the liquid metal or by forming heterogeneous nuclei in-situ in the liquid. This solidification based grain refining technique is a flexible and low-cost method for steel mills and steel foundries to improve the properties of their final product compared to heat treatment, which is high cost. However, for heterogeneous nucleation to be effective, several factors must be taken into consideration. (1) The nuclei must survive long enough for nucleation of the desired phase to occur. Preferably, the nuclei should be stable at the temperature when inoculation occurs thus limiting the potential for dissolution of the solid particle back into the melt. (2) The nuclei must have a low lattice disregistry or similar crystal structure with the nucleating phase. (3) A low interfacial energy that promotes nucleation of the desired phase on to the surface of the nuclei must exist. In comparison to nonferrous metals, steels have a significantly higher melting temperature. Therefore, the types of inclusions that satisfy the previously listed factors while also surviving at steelmaking temperatures are limited. In addition, alloying elements in steel can affect both solidification behavior and solid-state reactions. This makes selecting an effective heterogeneous nuclei even more difficult because of the potential for multiple phases changing, forming, competing, and/or interacting in the melt upon solidification.
In this study, a grain refining process was applied to three Cr-Ni stainless steel alloys that each target a different solidification sequence: primary ferrite, primary austenite, and mixed ferrite→austenite (F→A) solidification mode. The purpose of these experiments was to determine the effect of solidification sequence on grain refining capability for a specifically designed grain refining melt practice. The tools used for this investigation include thermodynamic software, SEM/EDS inclusion classification, EBSD grain orientation, and Differential Scanning Calorimetry (DSC). A computational fluid dynamics (CFD) analysis was performed using ANSYS 18.1 Fluent software to estimate the thermal gradient (G) and isotherm velocity (V) vs. position in the mold during solidification. These values of G and V were then plotted using Hunt’s Criterion to estimate the grain refining capability for stainless steel alloys with ferritic, austenitic, and mixed F→A solidification modes.

**METHODOLOGY**

**Grain Refining Process**

Grain refinement of cast ferritic stainless steel by titanium nitride has proven to be highly effective in recent studies.\(^9,10\) Research conducted by the authors has shown that titanium nitride nuclei can grain refine as-cast austenitic stainless steels\(^1\) as well as ferritic stainless steels. The authors also performed thermodynamic simulations to predict the precipitation sequence of heterogeneous nuclei during solidification of the melt. In this study, a grain refining method based on \textit{in-situ} formation of titanium nitrides (TiN) on preexisting (MgO·Al\(_2\)O\(_3\)) spinel inclusions using a controlled sequence of melt additions prior to casting.\(^1\) This co-precipitation is favorable because the lattice disregistry between spinel and TiN is low (5.1%).\(^1\) TiN co-precipitated on spinel inclusions then act as suitable heterogeneous nucleation sites for both solid ferrite and solid austenite phases based on a low lattice disregistry between TiN and the solid ferrite (3.9%) or solid austenite (7.7%) phases.\(^1\) TiN is also stable in liquid steel at relatively low concentrations of dissolved titanium and nitrogen when compared to other potential heterogeneous nuclei.\(^9\)

Schematic plot of the designed melting procedure is shown in Figure 1 and has been adopted for the use in this experiment. Figure 2 shows the precipitation sequence of inclusions simulated using FACTSAGE 7.1 during ladle treatment of a stainless steel melt for three dissolved nitrogen contents. This includes the initial formation of spinel inclusions in the melt, followed by TiN co-precipitation on spinel in the melt before solidification begins.

![Figure 1. Designed solidification-based, grain refining melt practice targeting co-precipitated TiN nuclei](image)

![Figure 2. FACTSAGE 7.1 simulated inclusion formation during ladle treatment of the melt prior to solidification](image)
Experimental Set-up and Procedure

The charge for each experimental heat consisted of specific quantities of induction iron, low carbon ferrochrome, electrolytic nickel, ferromolybdenum, electrolytic manganese, and ferrosilicon. These materials were melted in a 45 kg (100 lb) capacity induction furnace. The top of the induction furnace was covered and shrouded in argon gas to reduce oxygen pickup from the atmosphere. The charge material was melted, de-oxidized with aluminum, calcium treated, and argon stirred to produce a melt with low dissolved oxygen, sulfur, and inclusion contents. Argon stirring was employed to remove de-oxidation products and pre-existing inclusions from the melt. Nitrogen was then dissolved into the melt using a nitrided ferrochrome alloy in the furnace. The melt was de-slagged, and the furnace was then tapped into a ladle. The dissolved oxygen picked up by the melt during the furnace to ladle transfer was consumed by the oxidation of aluminum and magnesium during stage one ladle treatment to form spinel. The second ladle addition of ferrotitanium to introduce titanium to the melt was therefore protected from reoxidation improving Ti recovery. The titanium reacted with the dissolved nitrogen in the melt to form TiN, which then co-precipitated on the surfaces of the existing spinel inclusions. The melt was then poured into a no-bake sand mold at an aim temperature that was approximately 100 °C above the liquidus of the alloy. A consistent superheat was used to control the amount and size of inclusions prior to solidification in the mold, and to help prevent flotation or clustering of inclusions to keep the inclusions well-dispersed throughout the casting.

A CAD model of the no-bake sand mold is shown in Figure 3. This mold produces a heavy section, cylindrical casting with dimensions of 100 mm (4 in.) diameter and a 200 mm (8 in.) height. An insulated riser dome is used to manage thermal conditions within the mold to ensure that final solidification of the liquid metal occurs in the riser thus minimizing porosity in the casting. The riser dome has approximate dimensions of 150 mm (6 in.) diameter and 100 mm (4 in.) height. The combined height of the pouring cup and sprue is greater than 300 mm (12 in.) to ensure complete filling of the mold cavity. It is a bottom-filled gating system with the runner positioned tangent to the cylindrical mold cavity to promote mixing inside the mold which helps keep inclusions well-dispersed throughout the solidified casting.

Targeted Chemistry

Three experimental heats were performed using the same melt practice and amounts of additions made for cleaning and refining steps. Selected spinel and TiN content at liquidus were defined in previous research conducted for grain refining trials of CF3M (316L) grade stainless steel using similar mold design and grain refining practice. The only difference between the three heats described in this article is the initial metallic charge used to establish the base chemistry of the melt. The targeted base chemistries of these heats are listed in Table I.

<table>
<thead>
<tr>
<th>Heat #</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>MgO·Al₂O₃</th>
<th>TiN</th>
<th>Primary Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>1.18</td>
<td>0.53</td>
<td>17.7</td>
<td>2.0</td>
<td>16.3</td>
<td>≈ 0.006</td>
<td>≈ 0.09</td>
<td>FCC</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>1.35</td>
<td>0.60</td>
<td>19.3</td>
<td>2.3</td>
<td>9.5</td>
<td></td>
<td></td>
<td>BCC+FCC</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>1.40</td>
<td>0.60</td>
<td>25.9</td>
<td>2.3</td>
<td>0.0</td>
<td></td>
<td></td>
<td>BCC</td>
</tr>
</tbody>
</table>

These chemistry values were selected based on equilibrium cooling calculations using Thermo-Calc 2016a software. TCFE8: Steels/Fe-Alloys database was chosen for calculation of liquid and solid solutions in the melt. The results of phase content versus temperature calculated from the simulations can be seen in the plots of Figure 4.
Figure 4. Phase formation upon equilibrium solidification and cooling of the melt at 1773 K (1500 °C) to 1473 K (1200 °C) for (a) Heat #1, (b) Heat #2, and (c) Heat #3.

From the plots, each heat exhibits a different solidification mode and cooling behavior. Austenitic heat #1 and ferritic heat #3 demonstrates a single-phase solidification mode from liquidus to solidus \((\Delta \rightarrow \gamma)\) temperatures. Heat #2 illustrates a more complex solidification and cooling path. The melt begins to solidify primary \(\delta\)-ferrite phase at liquidus temperature till it reaches an intermediate temperature \((\Delta \rightarrow \gamma)\). At the intermediate temperature, secondary \(\gamma\)-austenite phase begins to solidify from the liquid. A series of phase transformations are possible from the intermediate to solidus \((\Delta \rightarrow \gamma)\) temperatures. Primary \(\delta\)-ferrite phase begins to disappear in tandem with the liquid phase as secondary \(\gamma\)-austenite phase continues to form. This is a classical scenario of a peritectic reaction that has been observed to occur in certain grades of steel.\textsuperscript{[14]} The peritectic phase transition has been interpreted to occur in the following series of events.\textsuperscript{[14,15]} A thin film of \(\gamma\)-austenite begins to form at the interface between the liquid and \(\delta\)-ferrite dendrite due to the peritectic reaction as a result of liquid super-saturation. Peritectic transformation starts once the \(\delta\)-ferrite dendrite surface is completely covered with a thin \(\gamma\)-austenite film. These transformations occur by solid-solid reaction of the \(\delta\)-ferrite dendrite to \(\gamma\)-austenite by diffusion through the peritectic phase and/or by continued solidification of \(\gamma\)-austenite into the liquid. However, regardless of the overall decline in the \(\delta\)-ferrite phase, the formation of \(\delta\)-ferrite phase from the liquid and/or by a eutectic reaction is also possible. Once the liquid disappears at solidus temperature, solid-solid transformation of \(\delta\)-ferrite to \(\gamma\)-austenite continues till equilibrium is achieved or the temperature decreases to the point where diffusion can no longer drive the transformation.

Potential reactions and transformations from the plots in Figure 4 are outlined in Table II.

<table>
<thead>
<tr>
<th>Heat #</th>
<th>1600°C → ①</th>
<th>① → ②</th>
<th>① → ①</th>
<th>① → ②\textsuperscript{[14,15]}</th>
<th>② → 1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L</td>
<td>L → (\gamma)</td>
<td>-</td>
<td>-</td>
<td>(\gamma)</td>
</tr>
<tr>
<td>2</td>
<td>L</td>
<td>-</td>
<td>L → (\delta)</td>
<td>L → (\delta + \gamma)</td>
<td>(\delta \rightarrow \gamma)</td>
</tr>
<tr>
<td>3</td>
<td>L</td>
<td>L → (\delta)</td>
<td>-</td>
<td>-</td>
<td>(\delta)</td>
</tr>
</tbody>
</table>
RESULTS

Casting Chemistry and Inclusion Analysis
Chemistry values were obtained using a Spectrometer, LECO C-S combustion analyzer, and LECO N-O combustion analyzer. Samples were taken at heights of 1 inch, 3 inch, and 5 inch with relation to the bottom of the casting. The chemistry at each height was sampled three to five times, and then averaged into a single chemistry value. The chemistry value from each height was then averaged together to estimate the chemistry of the overall casting. These values are summarized in Table III. Actual casting chemistries nearly match the targeted base chemistry for each experimental heat.

Table III. Casting chemistry from each experimental heat, wt.%

<table>
<thead>
<tr>
<th>Heat #</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.038 ± 0.005</td>
<td>1.33 ± 0.04</td>
<td>0.43 ± 0.01</td>
<td>17.8 ± 0.1</td>
<td>2.1 ± 0.05</td>
<td>15.7 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.034 ± 0.008</td>
<td>1.42 ± 0.03</td>
<td>0.51 ± 0.01</td>
<td>19.0 ± 0.2</td>
<td>2.3 ± 0.05</td>
<td>8.7 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.036 ± 0.006</td>
<td>1.72 ± 0.04</td>
<td>0.57 ± 0.01</td>
<td>25.4 ± 0.1</td>
<td>2.5 ± 0.04</td>
<td>0.2 ± 0.0</td>
</tr>
</tbody>
</table>

Keeping all conditions the same for each heat is of crucial importance in examining the effect that changing charge chemistry, and therefore solidification sequence, has on the grain refining efficiency of the current developed grain refining process. This process targets the formation of TiN inclusions as heterogeneous nuclei. An analysis of samples taken at the center of each casting was performed to verify that similar nuclei conditions were achieved in each heat design. Counting and classifying inclusions was performed using an ASPEX SEM/EDX automated inclusion analyzer. A rule file was established with a carbon content limit to prevent recording porosity on the sample. A total of 2,000 inclusions were counted on a scan area between 5 to 8 mm² for each sample. Inclusions statistics for each sample are shown in Table IV.

Table IV. ASPEX inclusion analysis statistics taken from the center of the casting for each experimental heat

<table>
<thead>
<tr>
<th>Heat #</th>
<th>Scan Area, mm²</th>
<th>Inclusion Total Area, μm²</th>
<th>Inclusion Content, %</th>
<th>Inclusion Average Diameter, μm</th>
<th>NND of Inclusions, μm</th>
<th>Inclusion Density, #/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.903</td>
<td>8,568</td>
<td>0.108</td>
<td>2.01 ± 1.15</td>
<td>23.2 ± 21.6</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>5.232</td>
<td>5,443</td>
<td>0.104</td>
<td>1.63 ± 0.90</td>
<td>22.6 ± 16.3</td>
<td>374</td>
</tr>
<tr>
<td>3</td>
<td>6.454</td>
<td>6,889</td>
<td>0.107</td>
<td>1.77 ± 1.09</td>
<td>22.7 ± 18.2</td>
<td>307</td>
</tr>
</tbody>
</table>

The total area of inclusions recorded was divided by the scan area to estimate inclusion content. These values were consistent for each heat at approximately 0.1%. This means that each sample has a similar area fraction of inclusions. The average diameter and nearest neighboring distance (NND) of the recorded inclusions is also similar between samples. Small average diameter (< 3μm) and large NND (> 20μm) suggests that the inclusions are well-dispersed throughout the casting. However, the differences in inclusion density for each sample indicates that the inclusions in heat #1 were better distributed throughout the casting than in heat #2. Classification of the types of inclusions recorded for each sample are summarized by the bar chart in Figure 5. This chart shows the cumulative element content for the total number of inclusions recorded.

Figure 5. Cumulative element content found within all the inclusions recorded during ASPEX inclusion analysis
The main elements found within the recorded inclusions are Ti-N-Mg-Al-O. Since the grain refining process made additions in steps, the elements Mg-Al-O are from spinel inclusions and the elements Ti-N are from TiN inclusions. This has also been verified by plotting the composition of each inclusion on to the ternary plots shown in Figure 6. These plots show that the two main types of inclusions are grouped around the Ti-N binary (TiN) and within the Ti-Al-Mg ternary (spinel). Formation of manganese sulfides contributed to trace amounts of Mn-S elements. It is possible that a small amount of metastable titanium oxide formed in the melt with dissolved oxygen that was not consumed during the formation of spinel. However, most of the titanium reacted with the dissolved nitrogen to form TiN as is shown in the ternary plots of Figure 6. An energy-dispersive X-ray spectroscopy (EDS) line scan of a typical inclusion with TiN co-precipitated on a spinel inclusion is shown in Figure 7. This type of inclusion was observed in all three experimental castings.

![Figure 6](image1.png)

Figure 6. Ternary plots of inclusion composition recorded from a sample taken at the center of the casting during ASPEX inclusion analysis for (a) Heat #1, (b) Heat #2, and (c) Heat #3

![Figure 7](image2.png)

Figure 7. EDS line scan of TiN co-precipitated onto spinel inclusions formed in each casting of the experimental heats

**Comparison of the Grain Structure**

Each casting was sectioned and macro-etched to reveal the extent of grain refinement. The sample is a vertical cross-section of the casting from the bottom to a height of 125 mm (5 in). Each sample was etched at room temperature in a solution of 5 parts hydrochloric acid, 2 parts hydrogen peroxide, and 3 parts distilled water. Macrostructure photos were taken optically using red and green light filters to expose grain orientations. Resulting photos of the samples are shown in Figure 8.
A grain refined macrostructure was achieved in the castings where a single-phase solidification mode was promoted in the melt (i.e. one solid phase solidifies from the liquid). A superimposed structure of columnar and equiaxed crystals persisted when dual-phase solidification mode was favored in the melt (i.e. two solid phases present with liquid). Additional optical images shown in Figure 9 were taken at the center of each casting at 15x magnification with a Dino-Lite Digital Microscope using red, green, and blue light filters. The effect of lattice disregistry of TiN with austenite compared to ferrite can be observed by the difference of heat #1 with coarser grains and heat #3 with finer grains. It is well known that TiN has a lower disregistry with ferrite phase than austenite phase making it a more effective heterogeneous nuclei during the solidification of ferritic stainless steel.\(^{[16]}\) However, heat #2 exhibited a combination of fine, round grains surrounded by directional, columnar crystals. EBSD mapping shown in Figure 10 verified the structure in heat #2 had 0.5 to 2 mm diameter grains dispersed among larger, elongated crystals.
Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) (TA Instruments SDT-Q600) was performed on each heat to verify the results from the solidification simulations illustrated in Figure 4. This was done to verify that heat #2 undergoes a mixed ferrite-austenite (FA) solidification mode. Small (0.1 – 0.15 g) samples were taken from each casting. DSC tests were performed in an argon atmosphere during the heating cycle from room temperature to 1500 °C and then cooled back to room temperature at a rate of 10 °C/min during the cooling cycle. The raw results obtained from the DSC test during the cooling cycle are shown in Figure 11.

This data was used for determination of transformation temperatures and latent heat. The peaks in Figure 11 represents the temperatures where a phase change is occurring and latent heat of the transformation overcomes the sensible heat. The point at which the slope of the line drastically changes upon solidification and the peak begins is the liquidus temperature. Solidus temperature is located at the tail end of the peak when the slope of the line goes from negative to approximately zero. These curves indicate that the steels from each experimental heat exhibits different solidification behaviors. Most notably, the liquidus and solidus temperatures of the dual-phase solidification mode heat #2 occurs in between the liquidus and solidus temperatures of the single-phase solidification mode heat #1 and heat #3. This is the same trend that was observed in the previous Thermo-Calc simulations. Shown in Table V, the liquidus and solidus temperatures from the DSC analysis of each material are compared against the simulated values. In addition, latent heat values calculated from the DSC data were compared for each steel. Thermodynamic simulation predicted the difference in latent heat during solidification for heat #1 (L→FCC) and heat #3 (L→BCC) is approximately 30 J/g. The difference in latent heat values between heat #1 and heat #3

**Figure 10. Localized EBSD map showing grain size in sample taken from Heat #2**

**Figure 11. DSC analysis performed for experimental steels showing heat flow upon solidification**
calculated from DSC data is 31 J/g. However, the difference in latent heat values between heat #1 and heat #2 calculated from the DSC data is 16 J/g which resulted from the mixed F → A solidification mode.

Table V. Comparison of the liquidus and solidus temperatures determined from simulations and experimental data

<table>
<thead>
<tr>
<th>Heat #</th>
<th>Thermo-Calc</th>
<th>DSC Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature, °C</td>
<td>Temperature, °C</td>
</tr>
<tr>
<td>1</td>
<td>1420</td>
<td>1412</td>
</tr>
<tr>
<td>2</td>
<td>1450</td>
<td>1440</td>
</tr>
<tr>
<td>3</td>
<td>1500</td>
<td>1470</td>
</tr>
</tbody>
</table>

Both the simulated results and the DSC data suggests that heat #2 solidifies with two phases in the liquid: ferrite and austenite. It is unclear from the DSC data which is the primary phase. However, based on quenching experiments performed by Fu et al. to classify solidification mode of stainless steel by chromium and nickel equivalences, heat #2 will solidify by a mixed F → A solidification mode.\[17\]

DISCUSSION

The structure of heat #2 in Figure 9(b) is peculiar in that it appears to contain both columnar and equiaxed grains without a visible, classic CET. This type of behavior has been observed before in several weld experiments dealing with austenitic stainless steels that favor a dual-phase solidification mode of primary ferrite and secondary austenite.\[18\-20\] In some of these steels, ferrite transformed to austenite by solid-solid reactions upon cooling. Welding experiments using austenitic stainless steel with a primary ferrite solidification mode were conducted by Villafuerte et al. to investigate similar etched grain structures.\[21\] In type 321 steel welds, it was found that the etched structure consisted of equiaxed primary ferrite grains dispersed randomly in a matrix of columnar austenite grains. It was concluded that titanium-rich inclusions, believed to be TiN, found at the center of ferrite dendrites acted as heterogeneous nuclei in the formation of equiaxed ferrite grains. The cause of the columnar austenite grains was attributed to solidification conditions (G and V) of the secondary austenite phase that may not intersect with the CET curve, thus producing only a columnar structure.\[21\] Another factor considered is that the low fraction of liquid remaining when the secondary austenite phase forms cannot nucleate and grow enough equiaxed austenite grains to stop the heat flow driven growth of columnar austenite grains.\[21\]

Another experiment by Inoue et al. investigated solidification morphologies of stainless steel welds by examining the relationship of growth direction between ferrite and austenite.\[22\] In the liquid pool, primary ferrite dendrites reject nickel into the liquid thus favoring austenite formation in the interdendritic regions. This austenite nucleated epitaxially from existing austenite grains outside of the melt zone and formed new austenite dendrites which grew in the interdendritic region between ferrite dendrite boundaries. This model predicts that the austenite growing in the interdendritic region is not crystallographically restricted by the growing primary ferrite phase. This implies that the austenite phase will continue to follow a preferential growth direction determined by the direction of heat flow even when the growth direction of the primary ferrite phase changes.\[22\] Inoue et al. referred to this growth mechanism as “Independent Two-phase Growth”. This concept was verified by casting two ingots of austenitic stainless steel containing 19wt% Cr and 11wt% Ni. The first ingot was base material while the second ingot targeted the formation of TiN inclusions to refine the primary ferrite phase. Unrefined, lacy or vermicular ferrite was observed in the first casting while fine, equiaxed ferrite containing TiN at the center formed in the second casting. However, columnar grains of secondary austenite phase were observed in both castings making up an overall unrefined macrostructure.\[22\] Therefore, because of this growth independence, solidification of equiaxed ferrite grains and columnar austenite grains can occur simultaneously. Furthermore, according to the explanation given by Villafuerte et al., the solidification conditions of the secondary austenite phase will favor the growth of columnar grains as opposed to the nucleation and growth of austenite from the surfaces of TiN inclusions. This solidification mechanism is significantly different from the classical descriptions of peritectic and eutectic growth in two-phase alloys where prime phase crystallography is dominating. Yet, independent two-phase growth fits to the experimentally observed macrostructure in heat #2. To verify this hypothesis, the thermal conditions of phase solidification in the experimental casting were simulated.

The earliest work to thermally and chemically model the CET under realistic casting conditions was performed by J.D. Hunt.\[23\] In his work, the interaction of the columnar front with equiaxed grains formed by heterogeneous nuclei was examined. Using an analytical approach to study single-phase dendritic and eutectic columnar growth in an Al-Cu alloy, J.D. Hunt was able to describe a variety of variables that effect the position of the CET in the solidified alloy. These variables include growth velocity, temperature gradient, alloy composition, number of nuclei, and type of nuclei. Hunt suggested that
growing columnar grains can only be stopped if a critical volume fraction of equiaxed grains exist in the melt ahead of the growing columnar front. This volume fraction was theoretically estimated to be 0.49 which corresponds to the value of the thermal gradient $G$ in Eq. (1) required to stop columnar growth:

$$G < 0.617 N_o^{1/3} \left\{1 - \frac{(\Delta T_n)^3}{(\Delta T_C)^3}\right\} \Delta T_C$$

(1)

where: $N_o$ is the heterogeneous nuclei density per unit volume, $\Delta T_n$ is the undercooling required for heterogeneous nucleation, and $\Delta T_C$ is the constitutional undercooling at the dendrite tips.

Considering the thermal conditions and redistribution of alloying elements in multi-component alloys, Eq. (1) was rewritten to a form in Eq. (2), which is known as the Hunt’s Criterion for CET:

$$G/V^{0.5} < 0.617 N_o^{1/3} C_o \left\{\frac{8m(k - 1)\Gamma}{D}\right\}$$

(2)

where: $V$ is the dendrite tip velocity, $C_o$ the alloy composition, $m$ the liquidus slope, $k$ the distribution coefficient, $D$ the liquid diffusion coefficient, and $\Gamma$ the Gibbs-Thomson parameter.

The authors estimated the values for $G$ and $V$ for stainless steel solidification within a mold by using computational fluid dynamics (CFD) through ANSYS 18.1 Fluent software to simulate the temperature field of the liquid metal during the solidification of the casting. This same approach was used in this study. However, instead of tracking the solidification of a single solid phase, simulations were performed for the sequential solidification of two solid phases in the liquid (primary and secondary). It was assumed that solidification of the primary phase would occur up until approximately 0.5 volume fraction where the secondary phase would then appear. The results shown in Figure 12 for primary phase (red squares) and secondary phase (black triangles) at different locations from the wall towards the center of the cylindrical casting. Because latent heat upon solidification releases energy and the mold has a low thermal conductivity, heat will accumulate in the liquid metal thus causing solidification velocity of the secondary phase to be significantly lower which favors columnar growth. This graph also has two qualitative CET lines for FCC and BCC solidifying steels. These two lines have different positions because of the difference in nucleation activity of TiN nuclei for FCC and BCC crystals. At the same thermal conditions, heterogeneously nucleated BCC will favor the formation of an equiaxed structure. Assuming independent two-phase growth model, this Hunt’s map explains the structure observed in heat #2. For heat #2, the primary BCC phase would be near the necessary amount of equiaxed grains required to stop columnar growth of the primary BCC phase for all points (red squares) above the intersection of the CET (BCC) curve. Assuming independent columnar growth of the secondary FCC phase, the thermal and growth conditions of the remaining liquid will not be sufficient to favor an equiaxed FCC structure.

Figure 12. CFD simulated thermal and growth conditions for primary and secondary phases occurring within the mold vs. qualitative CET lines plotted based on observed CET position for FCC and BCC phases.
It can be seen from the Hunt map that both phases experience different thermal gradient and growth velocity conditions. Since the growth of the ferrite phase does not affect the growth of the austenite phase, it is reasonable that complete grain refinement in dual-phase steels can only be achieved by stopping columnar growth of both phases. The observed superimposed or “mottled” structure in heat #2 suggests that grain refining conditions were achieved only for the primary ferrite phase. However, the secondary austenite phase path in Figure 12 suggests that a large columnar zone will be established before the conditions for equiaxed austenite growth are established. Therefore, the absence of a well-defined CET occurs and the existence of a superimposed structure of both equiaxed ferrite and columnar austenite grains prevails. This structure was observed in the macrograph for ferrite-austenite solidification mode heat #2 while a traditional CET was established in the single-phase solidification mode austenitic heat #1 and ferritic heat #3. More effective grain refinement techniques are needed to move the CET curve into an area that will favor the formation of a refined structure in steels with a mixed ferrite-austenite solidification mode.

CONCLUSION

The effect on grain refining capability of heterogeneous nuclei in stainless steel was investigated for three experimental heats each targeting a different solidification sequence. Preliminary analysis of solidification sequence using thermodynamic software indicates that austenitic heat #1 and ferritic heat #3 will solidify by single-phase solidification mode while heat #2 exhibits a dual-phase ferrite-austenite solidification mode. This analysis was validated by DSC analysis and observations reported in literature. The presence of similar nuclei in each heat was verified by ASPEX inclusion analysis. Images taken of the etched macrostructure for each casting shows that heat #1 and heat #3 achieved grain refinement while heat #2 did not. This was explained by the independence of growth between the primary ferrite and secondary austenite phases which results in more difficult thermal and growth conditions for equiaxed growth of the secondary phase. The absence of a CET and a mix of equiaxed ferrite grains and columnar austenite grains in the final structure can therefore be explained. This was validated by observing intersections on a G-V Hunt map using CFD simulated thermal gradients, $G$, and growth velocities, $V$, for each solidifying phase in the mold vs. Hunt’s Criterion of a qualitative CET line plotted for both solid phases.

REFERENCES


