Solidification Behaviour and Microstructural Development of Iron-based Alloys under Conditions Pertinent to Strip Casting – 200 Series Stainless Steels

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The castability and microstructures produced from strip casting simulations of three compositions in the 200 series stainless steels have been examined. The nucleation density was similar for all three compositions. The as-cast microstructure showed very fine austenite grains of 10–20 μm in width. Retained delta ferrite was observed in the inter-dendritic regions, and was likely to be stabilised by the segregation of Cr into these regions. An analysis of the crystallography expected of different solidification sequences is presented, but a strict adherence to the Kurdjumov-Sachs orientation relationship was not found in these samples.

KEY WORDS: strip casting; stainless steel; 200 series; rapid solidification; nucleation; heat flux.

1. Introduction

We present here the second paper of a three part series that investigates the direct strip casting behaviour of a range of specialty steels. A brief introduction to the strip casting of steels was provided in our previous paper, and for further information the reader is referred to that publication.1) To avoid repetition, we will only remind the reader here of the most important features of strip casting: this technology significantly reduces the energy required to convert liquid metal to sheet products,2) it has the advantage of reduced capital costs, and imparts uniquely high cooling rates on the alloy which can significantly reduce elemental segregation, oxidation, and cracking. It is largely for environmental reasons that this technology is becoming of increased interest, and in this series of three papers we examine its applicability to a wide variety of specialty steels. In this paper, we examine the 200 series stainless steels.

The 200 series stainless steels are an austenitic group with compositions in the range: 5–15 wt% Mn, 15–20 wt% Cr, and 3–6 wt% Ni.3) Compared to 304 stainless, the 200 series has a considerably reduced Ni content, and this is offset by the addition of Mn, and often N and Cu, all these elements being austenite stabilizers.4) As well as being significantly cheaper than its austenitic counterparts, the 200 series alloys (201-, 202- and 205-grades) can offer about 30–40% higher yield strength than the commonly used 304 stainless steel grade, and could also offer acceptable ductility and formability. However, it is generally recognised that 200 series stainless steels may not have the same level of corrosion resistance, deep-drawability, weldability and lustre as 304.3,5) Consequently, the most successful applications for the 200 stainless are likely to be in relatively mild corrosive environments where the degree of forming is moderate to low. Possible applications include cutlery, cookware, water tanks, indoor architectural, automotive trim, rebar, bus bodies and frameworks, and fuel tanks.3,4) Chemical compositions of the standard 200 grades and the commonly used 304 stainless are presented for comparison in Table 1.

While the suitability of direct strip casting to produce 304 stainless steel products has been investigated in great length,5–8) other stainless grades have received little attention. Also, the literature suggests that there has not yet been a study that investigates strip casting behaviour of 200 grades. For these reasons we have chosen to investigate the cheaper 200 series stainless steel family. Although the 200

Table 1. Chemical compositions of the standard 200 series stainless steel grades, compared with 304 stainless steel.3)

<table>
<thead>
<tr>
<th>Grades</th>
<th>Chemical Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>AISI 201/UNS S20100</td>
<td>0.15 max</td>
</tr>
<tr>
<td>AISI 202/UNS S20200</td>
<td>0.15 max</td>
</tr>
<tr>
<td>AISI 204 Cu/UNS S20430</td>
<td>0.15 max</td>
</tr>
<tr>
<td>AISI 205/UNS S20500</td>
<td>0.12–0.25</td>
</tr>
<tr>
<td>AISI 304/UNS S30400</td>
<td>0.08 max</td>
</tr>
</tbody>
</table>
series are considered to be an austenitic grade, it will be demonstrated here that under strip casting conditions, the alloys produced have retained delta ferrite and are, strictly speaking, a duplex stainless steel in the as-cast condition.

2. Experimental Methodology

Three variations of 200 series stainless steel were tested, and these are detailed in Table 2. Alloys 17Cr–5Ni–6Mn and 17Cr–5Ni–9Mn are within the composition ranges specified for AISI 201 and AISI 202 respectively. Alloy 17Cr–5Ni–9Mn–3Cu has slightly higher Ni content (4.5 wt%) when compared to the specifications for AISI 204Cu (1.5–3.5 wt%).

For each alloy grade a series of melt immersion experiments was carried out, comprising a total of 30 tests. In between immersions, the melt was kept under an argon atmosphere to minimise oxidation and slag formation. During the immersion the atmosphere above the melt was changed to nitrogen. Experiments were carried out at a melt temperature of 1510°C (±5°C) corresponding to a superheat of approximately 80°C. The solidification substrate was copper, and the roughness of the substrate corresponded to ~0.4 Ra. For each chemical composition the first immersion was carried out with a chemically cleaned substrate, for chemical cleaning a solution of oxalic acid was used. All subsequent tests were carried out with the substrate mechanically cleaned with a wire brush. This is with the exception of a series of 3 immersions that were carried out without prior cleaning of the substrate to evaluate the effect of oxide build-up on the substrate for the 200 series steels. All tests were carried out at a casting speed of 1 m/s. For further information on the experimental methodology, heat flux calculation, surface roughness, and furnace particulars, the reader is referred to the first publication in this three paper series.1)

After casting, the samples were evaluated for the nucleation density by optical microscopy of the contact surface between the molten steel and the substrate. To examine the microstructure of the samples through the thickness of the casting, selected specimens were sectioned and mounted in the transverse direction. These samples were then metallographically prepared using standard polishing techniques. Polished sections were electrolytically etched to reveal the as-cast microstructures using a mixture of 50% nitric acid in water and a voltage of 2V at room temperature.

Selected as-cast specimens were also examined using scanning electron microscopy (SEM). This technique was used to examine the inter-dendritic segregation using energy dispersive spectroscopy (EDS) and also to examine the development of intermetallic species. This analysis was carried out on an FEI Quanta FEG SEM.

3. Results

3.1. Castability and Surface Distortion

The cast samples were typically 0.8 to 1 mm thick with a total residence time below the melt surface of 159 ms at the sample centre. This corresponds to a solidification rate (K-factor) of 15 to 20 mm/min0.5. The average K-factors for the three alloys are shown in Fig. 1(a). Also shown are the K-factors for the 3 immersions carried out with substrates that were ‘not-cleaned’ (NC) between immersions. It can be seen that increasing the alloy content decreases the K-factor,

![Fig. 1. Average solidification rate and heat flux data for the four testing conditions.](image)

| Table 2. Chemical compositions of the 200 series stainless steel alloys tested (wt%). |
|----------------------------------|---|---|---|---|---|---|---|---|---|---|
| Alloy Type                        | Cr | Ni | Mn | Cu | Si | Al | N  | C  | S  | P  |
| 17Cr–5Ni–6Mn (AISI 201)          | 17.7 | 4.8 | 6.0 | 0.014 | 0.770 | 0.152 | 0.195 | 0.105 | 0.017 | 0.007 |
| 17Cr–5Ni–9Mn (AISI 202)          | 17.3 | 4.6 | 8.6 | 0.014 | 0.757 | 0.123 | 0.197 | 0.105 | 0.024 | 0.007 |
| 17Cr–5Ni–9Mn–3Cu (AISI 204Cu)    | 16.6 | 4.5 | 8.4 | 2.85  | 0.745 | 0.100 | 0.208 | 0.103 | 0.020 | 0.002 |
and that the samples produced from ‘not-cleaned’ substrates did not show a significantly different solidification rate to those that were cast on cleaned substrates.

The surface of the samples is shown in Fig. 2. These photographs indicate that for some samples a smooth cast surface was not obtained. These deviations from a smooth surface are considered to be casting defects. The tendency for the formation of relatively large 10–20 mm size distortions as well as the more significant 2–5 mm size surface defects generally increased with increasing alloy content.

When solidification was carried out with ‘not-cleaned’ substrates, a well-defined 2–3 mm size surface defect formed on these samples. The fine-scale, 2–5 mm size surface defects are thought to be due to stresses associated with high temperature solid-state phase transformations and/or high heat fluxes resulting from the melting of oxides accumulated on the substrate surfaces (these two aspects are presented later in this paper). A summary of the surface defects observed on the as-cast samples is detailed in Table 3.

### Table 3. Summary of casting defects observed in the as-cast samples.

<table>
<thead>
<tr>
<th>Casting condition</th>
<th>Large &gt;10 mm sized warping/distortion</th>
<th>2–5 mm surface defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>17Cr–5Ni–6Mn</td>
<td>4 from 10 (40%)</td>
<td>0 from 10 (0%)</td>
</tr>
<tr>
<td>17Cr–5Ni–9Mn</td>
<td>9 from 10 (90%)</td>
<td>0 from 10 (0%)</td>
</tr>
<tr>
<td>17Cr–5Ni–9Mn–3Cu</td>
<td>3 from 7 (43%)</td>
<td>4 from 7 (57%)</td>
</tr>
<tr>
<td>17Cr–5Ni–9Mn–3Cu (NC)</td>
<td>0 from 3 (0%)</td>
<td>3 from 3 (100%)</td>
</tr>
</tbody>
</table>

3.2. Heat Flux during Solidification

Typical examples of the heat flux curves obtained during the casting simulations are shown in Fig. 3(a). The heat fluxes increased rapidly to a peak value within the first 10 to 15 ms, which corresponds to the point of establishing good contact between the substrate and the liquid metal. The peak heat flux reflects the nature of the contact and wetting of the melt on the substrate. For the next 30 to 40 ms heat transfer rates decreased rapidly, and continued to decrease thereafter but at a slower rate. Peak and average heat fluxes
measured for all tests conducted during the experimental series varied between 15–30 and 8–10 MW/m² respectively, and the data are summarised in Fig. 1(b). There was a noticeable variability in peak heat flux between subsequent dips for the 17Cr–5Ni–9Mn alloy, and this is reflected in a slightly larger error shown in Fig. 1(b).

The effect of not cleaning the substrate between dips was significant, and increased the peak heat flux markedly. However, the average heat flux was not significantly affected. The average heat flux over the entire solidification period reflects the total heat removed during solidification, and this corresponds well with the average solidification rate or K-factor, Fig. 3(b).

3.3. Nucleation of Solidification

Figure 4 shows examples of surface nucleation structures obtained for the three 200 series alloys cast with wire-brush cleaned substrates, and for the higher alloyed steel cast with ‘not-cleaned’ substrates. The point of nucleation of solidified grains on the contact surface of the sample is evident under an optical microscope as a central dark spot. These spots are surrounded by dendrites which grow outwards until they impinge upon neighbouring grains. Nucleation densities and average nucleation spacing estimated from several images across the samples surface, and peak heat fluxes are also presented. All three alloys cast with wire-brush cleaned substrates exhibited a random nucleation pattern and dendritic solidification structures. The key parameters estimated from the surface microstructures (225–325 per mm² nucleation density and 55–67 μm average nucleation spacing) and the peak heat fluxes of 18–28 MW/m² are reasonably similar for all three alloys (Figs. 4(a)–4(c)). The sample produced with the ‘not-cleaned’ substrate (Fig. 4(d)) exhibited large areas of intimate contact along the direction of the immersion as opposed to the discrete contact points observed on the samples produced with cleaned substrates.

3.4. As-cast Microstructure

Polished transverse sections of selected 200 stainless samples, taken perpendicular to the immersion direction,

![Figure 5](image)

**Fig. 5.** Optical micrographs of as-cast microstructures obtained for the alloys and conditions indicated. All microstructures shown at the same magnification, scale bar = 200 μm. Substrate side shown at top of the image.
were examined microstructurally in three different ways. Firstly, they were examined optically after electrolytic etching, a process that revealed the dendritic structure that develops during solidification. Next, the samples were polished back to a flat surface and examined in the SEM to examine the microstructure at higher magnifications using orientation contrast. These two techniques revealed significantly different microstructures. Finally, the samples were examined using electron backscattered diffraction (EBSD).

The optical microstructures are presented in Figs. 5 and 6. These specimens were obtained from the same samples that were used to examine the surface nucleation structures shown in Fig. 4. These four microstructures were obtained from the three different alloys cast with wire-brush cleaned substrates, and for the higher alloyed steel (17Cr–5Ni–9Mn–3Cu) cast with ‘not-cleaned’ substrates. Two of these microstructures obtained at a higher magnification are presented in Fig. 6. The width (perpendicular to the casting direction) of the columnar dendrite colonies originating from the substrate side appear to be in the range of 50–100 μm which is consistent with the nucleation spacing discussed in section 3.3.

A very fine dendritic structure is developed on the substrate side of the sample, and this progressively coarsens towards the melt side as the local solidification cooling rate decreases. The secondary dendrite arm spacing (SDAS) at approximately half sample thickness is in the range of 6.6 to 8.3 μm for all four microstructures, and this is consistent with the SDAS previously reported for twin-roll cast AISI 304 austenitic stainless steel.7)

Under optical microscopy the microstructure was noticeably coarser on the melt side of the sample, and in the case of the Cu-containing alloy there appeared to be a columnar to equiaxed transition, Fig. 5(c). Also visible is an undefined zone near the substrate side of the sample (see Figs. 5(d) and 6(b)) cast with ‘not-cleaned’ substrate where the dendritic structure is not resolved and this is possibly due to very high solidification rates resulting from oxide melting around contact areas.

The microstructures examined using SEM, with conditions optimised to reveal orientation contrast are shown in Fig. 7. These differ significantly from the dendritic struc-
tures that were revealed from electrolytic etching. Although the original dendritic structure can still be resolved, it is apparent that the microstructure is much finer than was obvious from the optical microscopy. Higher magnification imaging revealed that the grains were very fine, grain width often in the range of 10–20 μm (which is comparable to that of the primary dendrite arm spacing) and elongated in the direction of the dendrite growth, Fig. 8. This was confirmed using EBSD, Fig. 9. Such fine grain structures are not normally encountered on strip cast products, and this will have significant positive impact on microstructure and mechanical property development during further processing of cast products (these aspects in detail will be presented in future publications).

Higher magnification imaging revealed that in between the dendrites there was often a layer of a different phase present, and this was confirmed by EBSD to be ferrite, Fig. 10. The volume fraction of ferrite was in the order of 5%, and typically had a width of less than a micron.

The inter-dendritic regions were examined further with energy dispersive spectroscopy (Fig. 11), and this showed them to be enriched in Cr and depleted in Ni. This is consistent with the phase identification of these regions being ferrite. There was no measurable segregation of Mn, Cu or Si to the inter-dendritic regions. The electron microscopy also revealed that there were small 1–2 μm particles dispersed throughout the microstructure, and these were identified to be manganese sulphides, Fig. 11.

4. Discussion

The first two sections of this discussion describe the microstructural development of these complicated alloy compositions. There are two aspects to this discussion that could become easily confused. The first is the “phase stability” which describes, at equilibrium, what crystal structure we expect the alloy to have. The second discussion point is the “solidification sequence” which attempts to determine the sequence of solid state phase transformations that may (or may not) occur during cooling from the solidification temperature to room temperature. We note here that both “phase stability” and “solidification sequence” use the Ni and Cr equivalency technique to make their respective predictions. We therefore remind the reader that there are two sets of Ni and Cr equivalencies listed here, one for each prediction.

After the “solidification sequence” has been predicted using the Ni and Cr equivalencies, we make an additional assessment of the microstructure based on crystallography. Essentially, EBSD is used to assess if the predicted sequence of solid state phase transformations is consistent with the observed crystallography.

4.1. Phase Stability

The Schaeffler Diagram, modified by De Long,

![Fig. 8. High magnification SEM micrograph of alloy 17Cr–5Ni–6Mn. Images were obtained using the backscattered detector, with conditions optimised for orientation contrast.](image)

![Fig. 9. EBSD orientation map of 17Cr–5Ni–6Mn in the mid-thickness of the specimen. The substrate side of the sample is towards the top, and the solidification direction is downwards.](image)

![Fig. 10. EBSD orientation map of 17Cr–5Ni–6Mn in the mid-thickness of the specimen. The measured angle of misorientation between phases from the map shown in (a) is detailed in (b). The measured axis of misorientation between the phases from the map shown in (a) is given in (c). The theoretical axis and angle of misorientation predicted by the Kurdjumov-Sachs (KS) orientation relationship is given in (d).](image)
martensite for a wide range of stainless steel alloy compositions. The Cr and Ni equivalents defined in Eqs. (1) and (2) have been determined for the three alloys studied in the present work, and these are listed in Table 4. These values in conjunction with the Scheffler diagram indicate that all three compositions examined are predicted to be fully austenitic. This is consistent with the dominant phase observed being face centred cubic. The small fraction of delta ferrite that was observed using electron microscopy is likely to form as a result of solute segregation in the inter-dendritic regions during solidification locally stabilising the BCC phase.

\[
\begin{align*}
C_{\text{eq}} &= \text{Cr} + 1.37\text{Mo} + 1.5\text{Si} + 2\text{Nb} + 3\text{Ti} \quad \text{(Solidification sequence)} \quad \cdots (3) \\
N_{i_{\text{eq}}} &= \text{Ni} + 22\text{C} + 14.2\text{N} + 0.31\text{Mn} + \text{Cu} \quad \text{(Solidification sequence)} \quad \cdots (4)
\end{align*}
\]

It has been found that determination of which sequence of transformation takes place can be readily predicted by using the Cr and Ni equivalent methodology. Note here that the weightings applied to determine the Cr and Ni equivalents are different for phase stability and the solidification sequence. The weightings used to calculate the Cr and Ni equivalent values for solidification sequence are given in Eqs. (3) and (4), and the resulting values for the three alloys studied here are listed in Table 4.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr_{eq}</th>
<th>Ni_{eq}</th>
<th>C_{req}/Ni_{eq}</th>
<th>C_{req}</th>
<th>Ni_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>17Cr–5Ni–6Mn</td>
<td>18.86</td>
<td>11.75</td>
<td>1.61</td>
<td>18.86</td>
<td>16.81</td>
</tr>
<tr>
<td>17Cr–5Ni–9Mn</td>
<td>18.44</td>
<td>12.39</td>
<td>1.49</td>
<td>18.44</td>
<td>17.97</td>
</tr>
<tr>
<td>17Cr–5Ni–9Mn–3Cu</td>
<td>17.72</td>
<td>15.17</td>
<td>1.17</td>
<td>17.72</td>
<td>19.46</td>
</tr>
</tbody>
</table>

4.2. Solidification Sequence

The solidification sequence and phase stability of stainless steel alloys have been well studied, with the use of Cr and Ni equivalents being commonly used parameters to predict these behaviours over a wide composition range. The solidification sequence of stainless steels can occur in a number of ways, depending on the composition and cooling rate. Di Schino et al.\textsuperscript{11)} have listed the possible solidification sequences:

Mode A: L → L + δ → δ + γ \quad C_{req}/Ni_{eq} > 2.01
Mode B: L → L + δ → L + δ + γ → δ + γ → γ \quad C_{req}/Ni_{eq} between 1.71 and 2.00
Mode C: L → L + γ → L + γ + δ → γ + δ → γ \quad C_{req}/Ni_{eq} between 1.38 and 1.70
Mode D: L → L + γ → γ \quad C_{req}/Ni_{eq} < 1.37
entation of ~43° about <115>, see Fig. 10(d). For the EBSD measurements shown in Fig. 10, the KS relationship was not observed. The misorientation across phase boundaries in this region had three distinct groupings, and none corresponded to the KS relationship. It is unclear from these observations if the alloy went through one or two solid state phase transformations during cooling, and the solidification sequence of complex alloy systems will be the focus of forthcoming publications.

4.3. Substrate Condition

The effect of substrate cleanliness was examined in this series of experiments, and the build-up of oxide on the substrate after repeated casting resulted in an increase in the measured peak heat flux, Fig. 1(b). However, this did not correspond to an increase in the average solidification rate; in fact, the average solidification rate slightly decreased, Fig. 1(a). This phenomenon has previously been examined during the casting of a 304 stainless alloy. In that case it was shown that although a molten oxide layer can enhance the initial wetting of the steel on the substrate, the rapid cooling of the substrate and solidified shell very quickly causes the solidification of the oxide layer, and this results in a significant decrease in the heat flux. This is supported by the heat flux curves that show for the ‘not-cleaned’ substrates the heat flux after about 30 ms is lower than for the cleaned substrates, despite the opposite being true at a time scale of 10–15 ms (see Fig. 3(a)). Further, the cast samples produced with ‘not-cleaned’ substrates invariably had 2–3 mm size surface defects (see Table 3). It therefore can be concluded that the presence of such oxides on the roll surface of a twin-roll caster is detrimental to the castability of the alloy system, and should be avoided during casting.

5. Conclusions

A series of three stainless steel alloys, corresponding to compositions within AISI 201, AISI 202 and AISI 204Cu, have been rapidly solidified under conditions that are pertinent to strip casting. It has been concluded that:

- The three alloys tested were castable under strip casting conditions. The alloys however had propensity to form surface defects. Increasing the alloy content decreased the solidification rate, but increased the incidence of casting defects.

- When the substrates are cleaned before casting, the heat flux and nucleation density are almost the same for the three alloy compositions tested. However when the substrate is ‘not-cleaned’ in between immersions, there is a significant rise in the peak heat flux, and this is correlated with a rise in the incidence of casting defects.

- The dendrite colonies formed during solidification were relatively large, being 50 to 200 μm in width and 200 to 800 μm long. However, crystallographic orientations measurements revealed as-cast grain structure to be uncharacteristically fine with grain width in the range of 10–20 μm.

- Electron backscattered diffraction revealed that the microstructure consisted of a complicated set of crystallographic relationships between the austenite and ferrite grains.

- Although the composition of the alloys were all predicted to be austenitic, inter-dendritic regions of delta ferrite were observed in all specimens. This is proposed to be the result of solute segregation to the inter-dendritic regions during solidification locally stabilising the ferrite phase.

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