Microstructural Development and Solidification Cracking Susceptibility of a Stabilized Stainless Steel

Solidification modeling results are utilized to relate fusion zone composition to mushy zone characteristics and resultant solidification cracking susceptibility in Alloy 20Cb-3

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ABSTRACT. The solidification behavior and fusion zone solidification cracking response of Alloy 20Cb-3 was investigated by Varestraint testing, differential thermal analysis (DTA) and microstructural characterization techniques including light optical microscopy (LOM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Autogenous 20Cb-3 welds were evaluated, along with composite fusion zones prepared with 20Cb-3 base metal and INCO 112 filler metal. The 20Cb-3 alloy initiate solidification by a primary L→γ reaction and completed solidification at ~1300°C (2372°F) by a eutectic-type L→(γ+NbC) transformation. The composite 20Cb-3/INCO 112 fusion zone also exhibited the primary L→γ and eutectic-type L→(γ+NbC) reactions, but solidification did not terminate until 1223°C (2233.4°F), with a second eutectic-type reaction consisting of L→(γ+Laves). The solidification paths of each fusion zone composition were calculated and plotted on a γ-Nb-C pseudoternary liquidus projection as an aid to understanding the influence of alloy composition on the progression of solidification transformations, and the predicted results were in good agreement with the experimentally determined solidification reaction sequences. Both the autogenous 20Cb-3 and composite 20Cb-3/INCO 112 fusion zones exhibited a higher degree of solidification cracking susceptibility than 304 stainless steel. The 20Cb-3/INCO 112 composite fusion zone displayed the highest cracking propensity. A recently developed model was utilized to calculate the variation in fraction liquid with distance within the crack-susceptible solid + liquid (mushy) zone for each fusion zone composition. The modeling results directly showed that the presence of the low temperature L→(γ+Laves) reaction in the 20Cb-3/INCO 112 fusion zone extended the mushy zone out to large distances, thus accounting for the higher crack lengths observed in this composite fusion zone sample during Varestraint testing. These results were used to understand the relation between fusion zone composition, solidification behavior and the resultant solidification cracking response.

Introduction

Alloy 20Cb-3 is a high-Ni austenitic stainless steel stabilized with Nb additions and is utilized for aggressive corrosion environments in the chemical and process industries. Because of the high Ni content, the weld metal solidifies in the fully austenitic mode and is, therefore, prone to solidification cracking (Ref. 1). In applications where filler metal is utilized, the alloy was originally welded with the 302 class filler metals, in which no special effort was placed on control of minor elements. Subsequent work by Brown, et al. (Ref. 1), showed that the cracking resistance of welds in 20Cb-3 increased when 320 electrodes were used with reductions in Nb, Si and P, along with increases in Mn. This work led to the development of a 320LR electrode, in which these elemental concentrations were controlled for improved weldability.

The solidification cracking susceptibility of fully austenitic weld metal depends on the solidification temperature range and terminal solidification events that occur at the grain boundaries and interdendritic regions (Refs. 2, 3). This is particularly true for austenitic alloys containing Nb, which are known to form Nb-rich phases such as NbC and Laves at the terminal stages of solidification (Refs. 4–6). These secondary solidification phases typically form in a eutectic-type morphology with the austenite matrix. Of the two possible phases that can form, the Laves phase is known to be more detrimental because it forms at a lower temperature and, thus, widens the solidification temperature range (Refs. 4, 7). The propensity for forming each type of constituent (i.e., NbC and/or Laves) and the resultant solidification cracking susceptibility is highly dependent on the nominal alloy composition (Refs. 4, 8).

However, no published data are available that link the solidification behavior of Alloy 20Cb-3 to solidification cracking susceptibility. Thus, in this work, Varestraint weldability evaluations are combined with microstructural characterization and differential thermal analysis results to establish an understanding of solidification behavior/hot cracking relations of Alloy 20Cb-3.

Experimental Procedure

Materials

Table 1 lists the chemical compositions of the base metals and shielded metal arc welding (SMAW) electrodes utilized in this work. All of the measured compositions are within the values specified for these alloys. The base metals

KEY WORDS

Alloy 20 Cb-3
E320LR
INCO 112
Laves Phase
Maximum Crack Length
Stainless Steel
Solidification Cracking
Varestraint Testing
were received in the mill-annealed condition. The 3.2-mm-thick base metal samples were used for autogenous Varestraint tests, while the 7.9-mm-thick base metals were utilized for preparation of composite Varestraint samples, as explained below. Two electrodes were evaluated: E320LR and INCO 112 (AWS ENiCrMo-3). The E320LR is typically used in SMAW applications for Alloy 20Cb-3, while the INCO 112 was evaluated as part of a program to investigate the use of high-Mo electrodes for improved corrosion resistance. The electrode compositions listed represent the core wire (i.e., flux was removed for the analysis). It should be noted that the final weld metal composition depends on the core wire composition, the flux composition, the base metal composition and the extent of dilution between the base metal and filler metal. Thus, as described below, the actual weld metal composition was determined directly through electron probe microanalysis to account for these factors. Each electrode type had a 3.2-mm diameter.

Varestraint specimens of 165 mm length x 25 mm width were prepared from the 3.2-mm-thick sheet for autogenous weldability evaluations. As shown schematically in Fig. 1, composite specimens were prepared with the 7.9-mm-thick plate and two electrode types by first depositing single-pass welds along the center of 25-mm-wide samples under the following SMAW parameters: 120 A, 25 V, 3 mm/s travel speed and 10-deg electrode angle. The SMAW process was conducted semiautomatically. Travel speed and electrode angle were controlled by an automated travel carriage, and electrode feed rate was controlled by a manual screw feeder. This procedure produced welds of uniform and repeatable width. After welding, the plates were cold-straightened and the weld crown machined just flush with the plate surface. The reverse side of the plate was then machined to achieve a 3.2-mm-thick specimen for Varestraint tests.

Weldability Evaluations

Varestraint tests (Refs. 9, 10) were conducted for each sample type (20Cb-3 autogenous, 20Cb-3/E320LR, 20Cb-3/INCO 112) over an applied strain range of 0.74% to 2.5%. The maximum strain of 2.5% was selected on the basis of a large number of tests at varying strain levels (conducted using essentially identical testing equipment, welding conditions and weld sizes) on a range of alloys with similar solidification characteristics and solidification microstructures (Refs. 6, 11, 12). These results have shown that in these test conditions, for alloys that solidify over similar temperature ranges and exhibit maximum crack length (MCL) values spanning the range observed in this study, the MCL is generally saturated at the 2.5% strain level. At these strain levels, it is normally expected that cracking will span a major fraction of the mushy zone. The gas tungsten arc welding (GTAW) process was used with the following parameters: 100 A, 8.5 V, 3 mm/s travel speed, 3.2-mm-diameter 2% thoriated tungsten with a 60-deg tip angle and argon shielding gas. The 20Cb-3/E320LR and 20Cb-3/INCO 112 composite samples were lightly etched and cleaned in acetone prior to the tests, to accurately center the tungsten electrode on the composite fusion zone. With this procedure, the GTA weld utilized for the Varestraint tests was contained completely within the previous weld deposited by the SMAW process. MCL was used as the indicator of cracking susceptibility and was measured at 100X, using
a light optical microscope (LOM) interfaced with a quantitative image analysis (QIA) system.

**Differential Thermal Analysis (DTA)**

A small sample of all-weld-metal was removed from the 20Cb-3/INCO 112 SMAW fusion zone for differential thermal analysis, by electro-discharge machining. The cross-sectional dimensions required to obtain an all-weld-metal deposit were determined metallographically. The 3.2-mm-thick 20Cb-3 base metal was also evaluated by DTA. The DTA was conducted on a Netzsch STA 409 thermal analyzer, using argon cover gas and an alumina crucible. The sample size was $\approx 0.65$ gram and pure Ni was used as the reference material. The samples were heated to 1440°C (2624°F) at a rate of 5°C (9°F)/min, at which point they were completely molten. The samples were then cooled at 20°C (36°F)/min through the solidification temperature range. The weight of the sample was simultaneously monitored by a thermogravimetric balance to ensure that no weight change occurred during the test.

The DTA system was calibrated by determining the melting temperature of pure Ni and was found to be within 2°C (3.6°F) of the literature value. Consistent with previous work on similar alloy systems, reaction temperatures were taken as deviations from the local baseline (Refs. 4–7).

**Microstructural Characterization**

Specimens were removed from the Varestraint samples for microstructural characterization by light optical microscopy (LOM) and scanning electron microscopy (SEM). The samples were mounted in planar view to examine the solidification cracks, which intersected the sample surface. All samples were polished to a 0.04-µm finish using colloidal silica and electrolytically etched at $\approx 3$ V in a 10% chromic acid/90% water solution. SEM was conducted at 30 kV in the secondary electron mode on carbon-coated samples with a JEOL 6300 field emission gun high-resolution microscope. The area fraction of minor constituent in the welds was determined on a LECO 2001 QIA system. Area fraction was assumed to be equal to volume fraction.

A 20Cb-3 autogenous Varestraint sample and a 20Cb-3/INCO 112 composite sample were examined in more detail by electron probe microanalysis (EPMA). The 20Cb-3/INCO 112 composite specimen was examined in the as-deposited condition (i.e., before machining flush with the base metal surface) to obtain an EPMA trace across the entire fusion zone. The objective of this broad trace was to determine the extent (if any) of macrosegregation within the fusion zone of the dissimilar metal weld. For this EPMA trace, the electron beam was scanned over an area of 415 µm$^2$ to smooth out effects from dendritic microsegregation and provide an average composition for the relatively large scan area. This scan was conducted from the fusion line to the surface of the weld. Localized composition gradients due to dendritic microsegregation were also investigated (i.e., with no beam raster). This was accomplished by marking small areas of parallel dendrites on polished and etched samples with a precision microscope scribe. The EPMA samples were then re-polished to a 0.04-µm finish and carbon coated. EPMA was conducted on a JEOL 733 microprobe equipped with four wavelength-dispersive spectrometers.
The microscope was operated at an accelerating voltage of 15 kV and beam current of 20 nA. Under these conditions, the interaction volume of the EPMA technique is approximately 1 µm³. Composition traces were performed perpendicular to several cellular dendrites. The Kα lines were used for all elements analyzed, except Mo and Nb, where Lα lines were used. Raw data were reduced to weight percentages (wt-%) using a ZAF algorithm. EPMA was conducted on second-phase particles in the DTA specimens by the same procedure.

Results

Weldability

Figure 2 shows the Varestraint results. As a basis for comparison, data are also shown for 304 stainless steel evaluated under identical conditions. As shown in Table 1, the 304 stainless steel used here for comparison contained 0.04 C, 9.3 Ni and 18.5 Cr (in wt-%). At this composition, the WRC diagram predicts a primary ferrite solidification mode, which leads to the excellent solidification cracking resistance displayed in Fig. 2. The 20Cb-3 type samples show similar levels of weldability, while the 20Cb-3/INCO 112 composite fusion zone shows the highest cracking susceptibility. The similarity in weldability for the 20Cb-3 and 20Cb-3/320LR is not surprising, considering the similarity in the 320LR and 20Cb-3 compositions; therefore, the 20Cb-3/320LR results will not be discussed further.

Differential Thermal Analysis

Figures 3A and 3B show DTA cooling curves acquired on the 20Cb-3 and 20Cb-3/INCO 112 composite samples, respectively. The DTA curve for the 20Cb-3 alloy exhibits a large exothermic peak at 1408°C (2566.4°F), which is associated with formation of the primary austenite dendrites. No secondary solidification reaction was identified on the DTA trace. The DTA curve for the 20Cb-3/INCO 112 composite fusion zone sample exhibits a large exothermic peak at 1376°C (2508.8°F) from solidification of the primary austenite dendrites, and solidification is completed at 1223°C by a terminal solidification reaction.

Microstructural Characterization

Figure 4 presents LOM photomicrographs of typical solidification cracks induced by the Varestraint tests. Higher magnification SEM photographs of these crack tips are shown in Fig. 5. The cracks always coincided with second phases located at the grain boundary and interdendritic regions. The 20Cb-3/INCO 112 composite fusion zone also exhibited small amounts of this globular phase in addition to a secondary phase that existed in a eutectic-type morphology with the austenitic matrix. The following values of vol-% second phase were measured on 20 random fields of each weld metal: 20Cb-3 autogenous – 0.9% ± 0.2%; 20Cb-3/INCO 112 – 3.3% ± 0.3%. In the 20Cb-3 autogenous fusion zone, this measurement represents only the amount of the isolated second-phase particles. In the 20Cb-3/INCO 112 sample, this value represents the amount of the isolated second-phase particles plus the eutectic constituent.

The EPMA trace conducted from the 20Cb-3/INCO 112 weld interface area to weld surface (with the electron beam scanned over an area of 415 µm²) is presented in Fig. 6. A relatively narrow transition zone (TZ in Fig. 6A) of ~400 µm exists where the composition varies from the 20Cb-3 base metal to that of the 20Cb-3/INCO 112 fusion zone. After this region, the fusion zone composition is fairly constant with distance. This indicates that good mixing occurs in the liquid state between the 20Cb-3 base metal...
and INCO 112 electrode, so that macroscopic concentration gradients in the weld are not significant. This result has also been reported in previous work on welds deposited by consumable electrode processes (Refs. 5, 13). Thus, the EPMA data can be used to determine a bulk fusion zone composition. This is presented in Table 2, where the average of EPMA values collected after the 1000 µm position in Fig. 6 are listed. From the values listed in Table 2, an average dilution value of 0.55 ± 0.05 was determined. The dilution was calculated by

\[
D = \frac{E_{fz} - E_{bm}}{E_{fm} - E_{bm}}
\]

where \(E\) represents the concentration of each element in the fusion zone (fz), filler metal (fm) and base metal (bm). The dilution value determines the relationship of EPMA data in good agreement with the measured cross-sectional areas of the melted metal (fm) and base metal (bm). The dilution was calculated above from EPMA data where \(E\) represents the concentration of each element in the fusion zone (fz), filler metal (fm) and base metal (bm). The dilution value was determined from Equation 1, in turn, can be used to estimate the carbon content in the fusion zone from knowledge of the base metal and filler metal composition and is also listed in Table 2. As explained in the next section, the carbon content in the fusion zone plays a key role in the fusion zone microstructural development and solidification cracking response of these alloys, but when present in such low concentrations, its concentration cannot be accurately determined experimentally by EPMA techniques. Thus, the dilution value is useful for estimating the fusion zone carbon content. Estimated values of the phosphorus and sulfur concentration in the fusion zone are also provided in Table 2, since these elements can be important from a solidification cracking perspective.

Figures 7 and 8 are EPMA traces conducted across several dendrites in the 20Cb-3 autogenous and 20Cb-3/INCO 112 weld metals, respectively. As an example, Fig. 9 shows a region of parallel dendrites that were analyzed by EPMA. Typical examples of dendrite core and interdendritic areas are noted in the EPMA composition traces. For each weld metal type, the dendrite cores are significantly depleted in Mo and Nb. The elements Ni and Cr show very little tendency for microsegregation, while the Fe segregates moderately in the opposite directions of Nb and Mo (i.e., to the dendrite core regions). The behavior of Cu varies. In the Fe-rich 20Cb-3 weld metal, Cu segregates to interdendritic areas rather strongly. In the Ni-rich 20Cb-3/INCO 112 weld, Cu segregates only slightly.

The DTA samples exhibited characteristics similar to the welds where second phases formed in the interdendritic areas. However, as shown in Fig. 10, the second-phase particles were larger due to the slower cooling rates. The 20Cb-3 DTA sample exhibited an isolated second-phase field — Fig. 10A. The 20Cb-3/INCO 112 sample also exhibited this isolated second phase, in addition to a large blocky phase that existed in a eutectic-type arrangement with the austenite matrix. The eutectic morphology was not as well developed in the DTA sample shown in Fig. 10B as the weld metal sample shown in Fig. 5B, because of the slower cooling rate of the DTA sample. The size of the secondary phases in the DTA specimens were large enough (≈5–15 µm) to permit chemical analysis by EPMA (resolution ≈1–2 µm), and typical results for each of the phases observed are summarized in Table 3. The Nb content of the isolated second phase in each fusion zone (87 wt-% Nb) is consistent with the NbC phase, which is well known to form during solidification of austenitic alloys containing Nb and C (Refs. 4, 6, 7, 14, 18). The second phase observed in a eutectic morphology with the austenite matrix, which was found only in the 20Cb-3/INCO 112 fusion zone, had a Nb content of 23.5 wt-%, consistent with the Laves (A2B) phase. As with the NbC phase, it is well established that Laves forms as a secondary solidification constituent in Nb-bearing austenitic alloys (Refs. 4, 6, 7, 14, 18).

**Discussion**

**Solidification**

The two fusion zone compositions evaluated in this work (20Cb-3 and 20Cb-3/INCO 112) exhibit two types of solidification sequences that are similar to those expected in the simple ternary Ni-Nb-C system (Ref. 15) and recent work conducted on a wide range of experimental multicomponent N-bearing superalloys (Ref. 8). The liquidus projection for the Ni-Nb-C system is shown in Fig. 11. The projection exhibits three primary-phase fields that are of interest here: γ, NbC and Ni3Nb. A primary C (graphite) phase field exists at high C contents, which is not of importance. Additions of Fe, Cr and Si to the Ni-Nb-C system are well known to promote Laves at the expense of Ni3Nb in commercial superalloys, as well as the experimental alloys utilized in this work (Refs. 16, 17). Thus, by replacing Ni3Nb with Laves, the Ni-Nb-C liquidus projection can be utilized as a guide in developing a description of the solidification reactions in these alloys.

The 20Cb-3 alloy initiates solidification by formation of primary austenite dendrites (large exothermic peak in the DTA cooling curves). As explained in detail below and documented for other austenitic alloys containing Nb and C (Refs. 6–8, 18), the distribution coefficients (k) for Nb and C are less than unity, indicating that these elements preferentially segregate to the liquid during solidification.
secondary solidification phases observed in the DTA sample. There is only a small amount of NbC (0.9 vol-%) that forms in this alloy. At this low quantity, there is insufficient heat released during the reaction to permit identification of the L → γ + NbC transformation in the DTA cooling curve.

The start of solidification is similar for the 20Cb-3/INCO 112 composite fusion zone, where the primary L → γ stage of solidification induces progressive enrichment of Nb and C in the interdendritic liquid, until the L → (γ + NbC) eutectic-type reaction occurs. However, for this fusion zone composition, solidification does not terminate with this reaction. Instead, the interdendritic liquid continues to be enriched in Nb (and depleted in C) until the L → (γ + Laves) reaction occurs, at which point solidification is complete. As with the 20Cb-3 sample, the NbC forms in very small amounts and, therefore, cannot be detected by the DTA. The solidification behavior of these alloys can be understood in more detail with the aid of a recently developed pseudoternary γ-Nb-C solidification model (Ref. 8). The model requires several key input parameters — equilibrium distribution coefficients, k, for the solutes Nb and C, a liquidus surface to identify the lines of twofold saturation separating primary phase fields and appropriate solute redistribution relations — that describe solute transport in the liquid and solid during solidification.

Cieslak, et al. (Ref. 18), have previously determined the distribution coefficient for C, kC, by DTA techniques in alloy IN625 and found that kC = 0.21. Considering the similarity in composition between IN625 and the pertinent alloys in this study, and that each alloy solidifies as primary austenite, this value should serve as a good estimate for the segregation potential of C in the alloys of interest to this work. The EPMA data can be used with simple solidification concepts to determine values for kNb. It has been noted (Ref. 6) that the diffusion of Nb and other solid-solution alloys in austenite is negligible; therefore, solute redistribution can be described with the Scheil equation as

\[ C_s = kC_0(1-f_s)^{k-1} \]  

where \( C_s \) is the solid composition at the solid/liquid interface, \( C_0 \) is the nominal composition, k is the equilibrium distribution coefficient and \( f_s \) is the fraction solid. Equation 2 assumes that solid-state diffusion and dendrite tip undercooling are insignificant, equilibrium is maintained at the solid/liquid interface and there is complete mixing in the liquid. At the start of solidification, \( f_s = 0 \) and \( k = C_{core}/C_0 \), where \( C_{core} \) is the composition at the dendrite core, at which the first solid forms from liquid at the nominal concentration. The dendrite core compositions, nominal compositions and k values for the major alloying elements are summarized in Table 4.

As previously noted, the major alloying elements (Fe,Ni,Cr) show little tendency for segregation and their k values are, therefore, close to unity. The value of \( k_{Nb} \) is of particular interest to the present work, since each of the secondary phases that form at the terminal stages of solidification (NbC and Laves) is Nb-rich. The value of \( k_{Nb} \) is 0.55 in the Ni-rich 20Cb-3/INCO 112 fusion zone, but only 0.33 in the Fe-based 20Cb-3 alloy. This indicates that Nb segregates more aggressively to the liquid in the 20Cb-3 alloy than in the 20Cb-3/INCO 112 composite fusion zone. Considering the differences in solubility of Nb in the Fe-Nb and Ni-Nb systems, this behavior is not surprising. For example, the maximum solid solubility of Nb in γ-Ni is 18.2 wt-% Nb, at 1286°C (2364.8°F) (Ref. 19). In contrast, γ-Fe can only dissolve a maximum of 1.5 wt-% Nb at a comparable temperature of 1210°C (2210°F) (Ref. 19). Thus, based on these significant differences, it is expected that Fe-rich alloys would exhibit a lower solubility of Nb than Ni-rich alloys. As the Fe-rich γ dendrites begin to form, less Nb is taken into the liquid and, as a result, more is rejected to the liquid (in comparison to the Ni base alloys), thus, leading to a decrease in the value of \( k_{Nb} \).

Quantitative treatment of solute redistribution during solidification of these alloys requires two sets of expressions: one to describe the solidification path (i.e., variation in liquid composition) during primary L → γ solidification and one to describe the variation in fraction liquid, \( f_s \), with liquid composition, \( C_s \), during the L → (γ + NbC) eutectic-type reaction. The model utilized here is based on a previous treatment proposed by Mehrabian, et al. (Ref. 20), with modifications being made to account for the high diffusion rate of carbon in the solid. The approach
is briefly outlined below, with further details of the model provided elsewhere (Ref. 8).

The solidification path during primary L → γ solidification is obtained by first writing the expressions describing the relation between fraction liquid, \( f_l \), and liquid composition, \( C_l \), for each solute (Nb and C). As previously discussed, diffusion of Nb in the solid is negligible and the relation between \( f_l \) and \( C_l,Nb \) is given by the counterpart of Equation 2:

\[
f_l = \left( \frac{C_l,Nb}{C_{o,Nb}} \right)^{\frac{1}{k_{Nb}}} \quad \text{(3)}
\]

where \( C_{o,Nb} \) is the nominal Nb concentration. This relation also assumes that dendrite tip undercooling is negligible, thermodynamic equilibrium is maintained at the solid/liquid interface and diffusion is infinitely fast in the liquid. For transport of C, diffusion in the solid is typically fast enough to maintain equilibrium (Ref. 21), and the equilibrium lever law provides the relation between \( f_l \) and \( C_{l,C} \):

\[
f_l = \frac{C_{o,C} - k_{C}C_{l,C}}{(1-k_{C})C_{l,C}} \quad \text{(4)}
\]

At any particular temperature during solidification, the fraction liquid, \( f_l \), can have only one value. Thus, following the same approach developed by Mehrabian, et al. (Ref. 20), Equations 3 and 4 are equated and solved for \( C_{l,Nb} \) to obtain the solidification path relation for the primary L → γ stage of solidification:

\[
C_{l,Nb} = C_{o,Nb} \left[ \frac{C_{o,C} - k_{C}C_{l,C}}{(1-k_{C})C_{l,C}} \right]^{k_{Nb}^{-1}} \quad \text{(5)}
\]

Thus, when the distribution coefficients \( k_{C} \) and \( k_{Nb} \) are known along with the nominal alloy content (\( C_{o,Nb} \) and \( C_{o,C} \)), Equation 5 can be used to calculate the Nb content in the liquid for any given value of carbon content in the liquid (i.e., the solidification path). Once the primary solidification path intersects the line of twofold saturation between γ and NbC, additional terms are needed in the mass balance equations to account for formation of two solid phases (\( \gamma + NbC \)) from the liquid and a finite difference technique is utilized to solve the differential mass balance equations. This has been described in detail elsewhere (Ref. 8).

Table 4 — Summary of Dendrite Core Compositions, Nominal Compositions and k Values (Composition values in wt-%)

<table>
<thead>
<tr>
<th>Element</th>
<th>( C_{o} )</th>
<th>( C_{o,C} )</th>
<th>( k )</th>
<th>( C_{o} )</th>
<th>( C_{o,C} )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>40.2</td>
<td>43.3</td>
<td>1.08</td>
<td>24.0</td>
<td>25.8</td>
<td>1.08</td>
</tr>
<tr>
<td>Ni</td>
<td>33.2</td>
<td>32.3</td>
<td>0.97</td>
<td>46.3</td>
<td>44.8</td>
<td>0.98</td>
</tr>
<tr>
<td>Cr</td>
<td>19.9</td>
<td>19.1</td>
<td>0.96</td>
<td>20.2</td>
<td>20.8</td>
<td>1.03</td>
</tr>
<tr>
<td>Mo</td>
<td>2.08</td>
<td>1.79</td>
<td>0.86</td>
<td>5.20</td>
<td>4.50</td>
<td>0.87</td>
</tr>
<tr>
<td>Cu</td>
<td>3.26</td>
<td>2.71</td>
<td>0.83</td>
<td>1.70</td>
<td>2.00</td>
<td>1.18</td>
</tr>
<tr>
<td>Nb</td>
<td>0.49</td>
<td>0.16</td>
<td>0.33</td>
<td>2.20</td>
<td>1.21</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The solidification path of each alloy initiates at the nominal alloy composition, where \( f_l = 1 \) and progresses toward the line of twofold saturation separating the γ and NbC primary phase fields, as the interdendritic liquid becomes enriched in Nb and C. For the 20Cb-3/INCO 112 composite fusion zone, the nominal C content is relatively low and the Nb content is relatively high. Thus, the liquid does not become significantly enriched in C and the solidification path of this alloy remains close to the γ-NbC “binary” side of the liquidus surface. The primary solidification path barely intersects the γ-NbC twofold saturation line at a relatively high temperature. As a result, the temperature interval for the primary L → γ stage of solidification is small for alloys with a high C/Nb ratio. Based on previous DTA data where the variation in L → (\( \gamma + NbC \)) temperature along the twofold saturation line was established (Ref. 8), the L → (\( \gamma + NbC \)) transformation...
**Weldability**

In terms of alloy parameters, fusion zone solidification cracking susceptibility depends primarily on the solidification temperature range and amount/distribution of liquid in the solid + liquid mushy zone where cracking occurs (Refs. 2, 3). Under a fixed temperature gradient (i.e., processing parameters), the solidification temperature range controls the size of the mushy zone. The mushy zone is bounded by the liquidus temperature and the terminal solidus temperature. However, not all of the mushy zone is susceptible to cracking. As noted by Borland (Ref. 2), cracking occurs within regions that are between the coherent temperature and the terminal solidus temperature. The coherent temperature is the temperature at which the primary dendrites initially make contact and interlock to provide a coherent network. Since the coherent temperature is below the liquidus temperature, cracking will occur through some fraction of the solid + liquid mushy zone. In view of this description, the terminal solidus temperature is an important quantity in terms of solidification cracking susceptibility. Alloys that exhibit a terminal eutectic reaction at a low temperature widen the region over which cracking can occur and which, in turn, increases cracking susceptibility.

The amount and distribution of terminal liquid — typically at or near a eutectic composition — will govern the ease with which a crack can propagate through the region bounded by the coherent temperature and terminal solidus temperature. When the solid/liquid surface tension is low and/or the amount of terminal liquid high, the liquid tends to form a continuous film that covers a relatively large portion of the grain boundary and interdendritic regions. This type of morphology interferes with the formation of solid/solid boundaries, thus reducing the ability of the boundaries to support solidification stresses and increasing cracking susceptibility. However, an upper limit on the amount of terminal eutectic liquid often exists, above which cracking tendency can be reduced by the process of back-filling (Ref. 22). A model has recently been developed (Ref. 23) that can be used to estimate this size of the mushy zone and variation in fraction liquid with distance within the mushy zone as an aid to understanding the relation between alloy composition and cracking susceptibility. The model is briefly outlined below and then applied to understand the relation between alloy composition and solidification cracking susceptibility for the two fusion compositions of interest in this work.

Ignoring possible interactive effects among the solutes and assuming that the liquidus slopes are constant, the liquidus equation for any multicomponent system is given by

\[ T_l = T_o + \sum m_{ij} C_{ij} \]

where \( T_l \) is the liquidus temperature, \( m_{ij} \) is the liquidus slope for the \( i \)th solute in the system, \( C_{ij} \) is the concentration of the \( i \)th solute in the liquid, and \( T_o \) is the melting temperature of the pure solvent. As described above, the amount of liquidus temperature of the alloy (i.e., its liquidus slope is negative) (Refs. 7, 18, 23). Thus, Nb, Si and C are treated as the solutes in these alloys, and the remaining elements in the solid solution with \( \gamma \) are treated as the \( \gamma \)-solvent.

The diffusion of Nb and Si in the solid during solidification is insignificant and the solute redistribution of these elements can, therefore, be described with the Scheil equation. The relation between \( C_{ij} \) and fraction liquid, \( f_l \), for these two elements during primary \( L \rightarrow \gamma \) solidification is given by

\[ C_{i,j} = C_{o,i}f_l^{(k_{i,j} - 1)} \]

where \( k_{i,j} \) is the liquidus slope at the temperature. When the solidus temperature is given by

\[ f_l = \frac{C_{o,i}}{f_k + \frac{C_{o,C}}{f_l k_C (1 - f_l)}} \]

Inserting Equations 7a–c into 6 yields a relation between temperature and fraction liquid:

\[ T_l = T_o + m_{Nb}C_{o,Nb}f_l^{(k_{Nb} - 1)} + m_{Si}C_{o,si}f_l^{(k_{Si} - 1)} + m_{C}C_{o,c}f_l^{(k_{C} - 1)} \]

Equation 8 relates the fraction liquid to temperature during primary solidification as a function of nominal alloy composition, liquidus slopes and equilibrium distribution coefficients. The values for the equilibrium distribution coefficients, liquidus slopes and \( T_o \) values determined in previous work (Refs. 8, 18, 23) are summarized in Table 5.

The variation in fraction liquid with
distance in the mushy zone during the primary L → γ stage of solidification can be determined by combining Equation 8 with the temperature gradient. The temperature gradient is given by the ratio of cooling rate, \( \varepsilon \), to growth rate, R, where the growth rate at the weld centerline (where the maximum crack length typically develops) is generally equivalent to or approximated by the travel speed. The travel speed utilized here is 3 mm/s. The cooling rate in the welds can be determined experimentally through measurements of the dendrite arm spacing, \( \lambda \), using the following semi-empirical relation developed for Type 310 stainless steel (Ref. 24), an alloy that also solidifies as primary austenite:

\[
\lambda = \frac{80e^{-0.33}}{C/s}
\]

where \( \lambda \) is in µm and \( \varepsilon \) is the cooling rate in °C/s. Type 310 stainless steel has a nominal composition of Fe-21Ni-25Cr, which is similar to the 20Cb-3 alloy composition. Values of \( \lambda \) were determined by making measurements at the weld centerline in the 20Cb-3 autogenous fusion zone. The average \( \lambda \) was 13 µm, indicating that under these processing conditions, the welds cool at a rate of ~250°C (450°F)/s. Thus, the temperature gradient, \( G = (\varepsilon/R) \), is ~80°C/mm. At the trailing edge of the weld pool, the liquid is at the liquidus temperature, \( T_L \). Assuming \( G \) is constant and taking \( x = 0 \) at \( T = T_L \), the relation between temperature and distance, \( x \), in the mushy zone is given by

\[
x = \frac{T_L - T}{G}
\]

Thus, Equations 8 and 10 can be combined to determine the variation in \( f_L \) with distance in the mushy zone during the primary solidification stage. When the L → γ + NbC reaction begins, the relation between \( f_L \) and \( T \) is given as previously modeled (Refs. 8, 23). The L → γ + Laves reaction occurs over a relatively narrow temperature range and is, therefore, estimated to occur isothermally. Thus, the point at which the liquid composition satisfies conditions for the L → γ + NbC reaction is taken as the end of the mushy zone and the value of \( f_L \) at that point corresponds to the amount of the γ + Laves constituent that forms “isothermally” at that location. Lastly, the \( f_L \)-x relation developed for the eutectic-type transformation is joined to the \( f_L \)-x relation for primary solidification to construct the entire \( f_L \)-x curve in the mushy zone.

Figure 13 schematically illustrates the variation in fraction liquid with distance that is calculated with the procedure explained above. (For simplicity, the condition is illustrated for a system in which the eutectic solidifies isothermally.) At the liquidus temperature (i.e., the boundary between the liquid weld pool and solid + liquid mushy zone), the fraction liquid is equal to one and \( x = 0 \). As distance increases beyond this boundary, there is a mixture of solid and liquid, which is uniquely defined by temperature. At the position where the actual temperature coincides with the eutectic temperature, solidification is complete and the fraction liquid is equal to zero. For the multicomponent systems considered here, the eutectic solidifies over a range of temperatures and thus over a range of positions (not shown for simplicity). As previously discussed (Ref. 7), it should be emphasized that the schematic illustration in Fig. 13 is not intended to suggest that single primary cells or dendrites will traverse the entire mushy region, but the diagram is intended to reveal the features calculated with the approach described above. Due to the simplifying assumptions (i.e., constant liquidus slopes and distribution coefficients), the method utilized here is only semi-quantitative. However, as shown below, the results provide realistic estimations of the mushy zone sizes and are very useful for making comparisons among alloys with composition variations.

Figure 14 compares the variation in fraction liquid in the mushy zone for the 20Cb-3 and 20Cb-3/INCO 112 fusion zones. As previously noted, cracking does not necessarily occur through the entire mushy zone, but is generally expected to occur through some fraction of the mushy zone that is bounded by the terminal solidus temperature and the terminal solidus temperature. In this regard, the terminal solidus temperature is important since it controls the location of the extremity of the mushy zone and, thus, will affect the distance over which cracking can occur. As explained below, these plots reflect how this factor is influenced by alloy composition. In addition, the calculations also reveal important information concerning the variation in fraction liquid with distance within this region, and this characteristic controls the ease with which a crack can propagate through the crack-susceptible region.

Figure 14A shows the variation in fraction liquid with distance over the entire range of solidification (0 < \( f_L < 1 \)), while Fig. 14B shows an expanded view near the terminal stages of solidification (0 < \( f_L < 0.1 \)). The distance over which the primary L → γ stage of solidification occurs is noted in Fig. 14B for each alloy. As described previously, the 20Cb-3 alloy terminates solidification near the edge of the mushy zone with the L → γ + NbC reaction, while the last remaining liquid in the 20Cb-3/INCO 112 composite fusion zone is enriched in Nb to the point where solidification ends with the L → γ + Laves transformation. The influence of alloy composition on the distribution of liquid and size of the mushy zone is readily evident — particularly in Fig. 14B for the terminal stages of solidification (i.e., near the edge of the mushy zone where cracking occurs). Note that the 20Cb-3 alloy always has a lower level of liquid present, particularly at the edge of the mushy zone. As demonstrated in Fig. 12, the 20Cb-3 alloy — with a relatively high C/Nb ratio — exhibits a solidification path that extends far into the C-rich side of the pseudo-ternary liquidus projection where the primary L → γ solidification path intersects the line of twofold saturation between γ and NbC at high temperatures. As a result, the L → γ + NbC reaction occurs at a relatively high temperature (~1300°C) and the reaction is, therefore, initiated at a short distance behind the liquid weld pool. Once the reaction starts, the very small amount of remaining liquid is consumed over a short distance (small temperature range). Thus, the solid + liquid mushy zone in the 20Cb-3 alloy is relatively small. As a result, the region over which cracking can occur is also small and the resistance to cracking is, therefore, relatively good. The calculated size of the mushy zone, ~2 mm, is similar to the measured maximum crack length of 1.8

<table>
<thead>
<tr>
<th>Quantity</th>
<th>20Cb-3</th>
<th>20Cb-3/INCO 112</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_{\text{Ni}} ) (wt%)</td>
<td>-5.0</td>
<td>-8.3</td>
</tr>
<tr>
<td>( m_{\text{Si}} ) (wt%)</td>
<td>-14.1</td>
<td>-23.4</td>
</tr>
<tr>
<td>( m_{\text{C}} ) (wt%)</td>
<td>-20.5</td>
<td>-34.1</td>
</tr>
<tr>
<td>( k_{\text{Ni}} )</td>
<td>0.33</td>
<td>0.55</td>
</tr>
<tr>
<td>( k_{\text{Si}} )</td>
<td>0.58</td>
<td>0.71</td>
</tr>
<tr>
<td>( k_{\text{C}} )</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>( T_c ) °C</td>
<td>1447.5</td>
<td>1437.7</td>
</tr>
</tbody>
</table>
mm. While the calculations are not expected to provide exact values of the mushy zone, the similarity in these two values suggests that the calculated values are reasonable. In addition, reference to Fig. 2 indicates that the 20Cb-3 alloy may not have been tested to the full-saturation strain level and, therefore, its MCL may be slightly larger than that shown by the current Varestraint results. However, previous work on similar alloys [Refs. 6, 11, 12] has shown that a 2.5% applied strain level is at saturation strain. By comparison, the C/Nb ratio of the 20Cb-3/INCO 112 composite fusion zone is much lower. As a result, the primary solidification path travels closer to the γ-Nb “binary” edge of the pseudo-ternary projection, where the eutectic transformations occur at lower temperatures [1223°C for the terminal L → (γ + Laves) reaction]. Thus, the edge of the mushy zone is extended out to larger distances.

This is readily evident for the 20Cb-3/INCO 112 curve shown in Fig. 14B. Since the crack-susceptible zone is contained within the low-temperature region of the mushy zone, extension of this low-temperature region out to larger distances translates into higher solidification cracking susceptibility and a larger MCL. The calculated mushy zone size of ~3.5 mm is reasonably close to the maximum crack length of ~3 mm. Again, the calculated size of the mushy zone is not expected to be exact and cracking will not occur through the entire mushy zone, but the similarity in these two values indicates the calculations are realistic.

The approach developed here permits prediction of mushy zone characteristics and resultant weldability as a function of alloy composition. In particular, alloys with a high C/Nb ratio exhibit better weldability than alloys with low C/Nb ratios. The influence of Fe concentration can also be considered through the distribution coefficient for Nb, kN, since kN is known to decrease as the Fe concentration increases (Ref. 8). This can provide a useful method for optimizing alloy or filler metal composition for minimizing fusion zone solidification cracking susceptibility. Note that the influence of welding parameters can also be considered through their influence on the temperature gradient. For example, the temperature gradient decreases with increasing heat input. This, in turn, will cause the crack-susceptible region to enlarge and increase the maximum crack length. However, these processing parameter effects are fairly straightforward and well understood, and the model is expected to be more useful for providing insight into composition-weldability relations that are more complicated and difficult to predict.

**Summary**

The solidification behavior and solidification cracking response of autogenous 20Cb-3 and composite 20Cb-3/INCO 112 fusion zones were investigated by Varestraint testing, differential thermal analysis and microstructural characterization techniques. The 20Cb-3 alloy initiated solidification by a primary L → γ reaction. Due to its relatively high C/Nb ratio, the interdendritic liquid became highly enriched in C, until solidification terminated at ~1300°C by a eutectic-type L → (γ + NbC) transformation and none of the γ/Laves constituent formed. In contrast, the lower C/Nb ratio of the composite 20Cb-3/INCO 112 fusion zone caused the interdendritic liquid to become more highly enriched in Nb, so that solidification terminated at a lower temperature (1223°C) by the eutectic-type L → (γ + Laves) reaction. The higher resistance to solidification cracking displayed by the autogenous 20Cb-3 fusion zone is attributed to its rel-
atively high C/Nb ratio and concomitant ability to avoid formation of the low temperature L → (γ + Laves) reaction, thus decreasing the size of the crack susceptible solid + liquid mushy zone.

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References


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