On the origin of subgrain boundaries during conventional solidification of austenitic stainless steels

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Abstract. The origin of subgrain formation during conventional casting and solidification of stainless steels was studied using two austenitic stainless steels with 0 and 4 mass-% Al. Whereas the Al-free alloy showed no subgrain formation, the Al-added alloy developed a high density of subgrains separated by low-angle grain boundaries. The occurrence of subgrains in the Al-added alloy was justified by its ferritic mode of solidification as predicted by thermodynamic calculations and confirmed by dynamic scanning calorimetry measurements. The subgrains might be a consequence of the plastic deformation of soft primary ferrite dendrites by the fluid flow and their subsequent inheritance by the austenite. Alternatively, they might have been induced during the austenite formation from delta ferrite, most likely via a peritectic reaction. The absence of subgrains in the Al-free alloy was justified by its austenitic mode of solidification.

1. Introduction

Bending and fragmentation of dendrite arms are well demonstrated to happen during solidification processes like stir casting [1] and spray forming [2] which are inherently associated with external forces. These can give rise to the formation of low-angle grain boundaries (LAGBs) inside the grains. In the absence of external forces during conventional casting, LAGBs are apparently not expected. However, internal forces caused by fluid-dendrite interactions, specifically in the mushy zone, may bring about mechanisms by which such a deformation could arise [3]. Two possible mechanisms are the rotation of the principal growth direction by thermo-solutal advection and the direct mechanical damage to the growing dendrite by the fluid flow [4]. In the thermo-solutal advection mechanism, a deviation in isotherms caused by the fluid flow results in the bending of dendrites. Direct mechanical deformation in the latter mechanism arises when the liquid flows next to the dendrite and causes friction-induced stresses.

Deformation of dendrite during solidification is theoretically and experimentally investigated is some studies [5,6]. For instance, Dragnevski et al. [5] modeled the dendrite-fluid flow interactions during solidification of Cu-O and Cu-3wt.%Sn melts in a variety of supercoolings in the approximate range of 47-160 K. After a series of calculations, they concluded that the thermo-solutal advection cannot account for the deformation of dendrites in the studied supercooling range. Within a certain range of supercoolings (50 K in Cu–O and 75–85 K in Cu–3wt%Sn), however, the required stress for
the bending of dendrite arms was supplied by the fluid flow. At these supercoolings, the fine size of dendrites and the high melt velocities supply the required stress for the mechanical damage of dendrites. Due to the small supercoolings associated with conventional solidification, the mechanical deformation of dendrites is unlikely during conventional solidification processes. This belief, however, was challenged by Doherty later [7]. In his critical article, he listed a couple of studies in which the formation of in-grain misorientations is reported for conventional casting processes. For example, in a statistical work, a higher than usual frequency of LAGBs is seen during direct chill (DC) casting of commercial pure Al [8]. It should be noted that high cooling rates as well as relative movement of mold wall with respect to the casting are the factors which may influence the solidification process. When the casting is still solidifying, these external forces can extend into the semi-solid mushy zone and slightly bend the dendrite arms [6]. In at least one of the references cited by Doherty, namely [9], it seems that misorientation substructures have truly formed during directional solidification of 99.9% pure Al. The development of grain boundaries with misorientations less than 15° is clearly shown in that work using electron backscattered diffraction (EBSD) method. Additionally, it is certainly possible that large solidification contractions can lead to significant internal stresses, particularly when dendrites impingement occurs. The extreme case of internal stress development is the occurrence of hot tearing where the lack of mushy zone feeding can lead to the cracking of the sample [10].

In the present study, differences in the tendency of austenitic stainless steels to form in-grain misorientations are discussed in view of the differences in their solidification modes.

2. Experimental methods

Two austenitic stainless steels with the chemical compositions shown in Table 1 were cast in a vacuum induction melting (VIM) furnace. Electron backscattered diffraction (EBSD) and electron channeling contrast imaging (ECCI) investigations were conducted on as-cast samples using a Zeiss LEO-1530 GEMINI field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) observations were carried out in a JEOL field emission TEM (FETEM) at an operating voltage of 200 kV. TEM foils were prepared using mechanical grinding to a thickness of below 100 μm followed by twin-jet electrolytic polishing using a solution of 5% perchloric acid in 95% acetic acid at room temperature. The equilibrium phase diagram of the alloy system was calculated using the Thermo-Calc software. Differential scanning calorimetry (DSC) experiments were done in a 404 C Pegasus calorimeter with heating and cooling rates of 50 K/min and 10 K/min, respectively.

Table 1. Chemical composition of the cast alloys in mass- %.

| Alloy | C  | Al | Mn  | Cr  | Ni  | Si  |
|------|----|----|-----|-----|-----|-----|
| 0Al  | 0.43 | 0.02 | 6.63 | 17.76 | 9.27 | 0.40 |
| 4Al  | 0.42 | 3.95 | 6.24 | 16.91 | 8.69 | 0.39 |

3. Results and discussion

3.1. Subgrains characterization

Figures 1(a,d) show ECC images of the alloys in the as-cast condition. The corresponding inverse pole figure (IPF) maps and grain boundary misorientation maps obtained by EBSD are shown in Figures 1(b-c,e,f). The results indicate significant differences in the microstructures of the alloys. Based on the ECC images alone, the 4Al alloy appears to have a significantly finer grain size than the 0Al alloy. Based on the EBSD maps, however, the grain size of both alloys is relatively comparable if the small island grains in the 4Al alloy and the in-grain small misorientations are neglected. According to the boundary map in Figure 1(f), the island grains in the 4Al alloy are twin-related to the surrounding matrix. The most obvious difference between the microstructures is the massive development of subgrains in the 4Al alloy and their absence in the Al-free variant. The subgrains observed in the 4Al alloy arises from the presence of a high density of LAGBs (Figure 1(f)). LAGBs are normally observed after annealing of cold-worked metals at temperatures below the recrystallization temperature, where
recovery is the dominant restoration mechanism [11]. By contrast, the subgrains in the 4Al alloy have already formed in the as-cast condition prior to any deformation and annealing.

The LAGBs, which are otherwise difficult to observe by optical microscopy, become visible after soaking at temperatures where precipitates form [12]. This is due to the formation of precipitates at LAGBs. To enable the precipitation of Cr-rich carbides in both alloys, they were aged at 650 °C for 8 hours. The optical micrographs of the aged specimens (Figure 2) indicate the existence of subgrains only in the 4Al alloy. Optical micrographs also indicate that the substructures are not uniformly distributed throughout the γ grains and that there also exist regions free of subgrains. Some regions without subgrains are indicated by arrows in Figure 2(b).

**Figure 1.** Microstructure of as-cast alloys; (a,d) ECC images; (b,e) corresponding EBSD IPF maps; (c,f) corresponding grain boundary distribution maps. Colors in IPF maps denote the crystallographic directions parallel to the plane of view. High-angle grain boundaries (HAGBs), LAGBs, and Σ3 twin boundaries are represented by black, gray, and red lines, respectively.

**Figure 2.** Optical micrograph of (a) 0Al and (b) 4Al alloys after annealing at 1250 °C for 5 minutes and heat treating at 650 °C for 6 hours. Samples were etched with V2A agent. Before annealing, samples were homogenized at 1200 °C for 1 h.

The TEM micrograph in Figure 3 shows a subgrain boundary in the Al-added steel. Depending on the nature of dislocations, the boundary can be regarded as a tilt or twist boundary for edge and screw
dislocations, respectively [13]. The similarity of the selected area electron diffraction (SAED) patterns taken from the regions marked A and B in Figure 3(b) and the similarity of dislocation arrangements on both sides of the boundary indicates that this boundary is a LAGB. Accordingly, the pattern of LAGBs in the 4Al alloy does not act as effective obstacles to dislocation motion as both alloys exhibit comparable flow stresses [14,15]. Similarly, the presence of solidification-induced LAGBs with misorientations below 6° has been reported to have a negligible influence on the tensile properties of Ni-based single crystal superalloys [16].

Figure 3. TEM bright field micrograph of 4Al (a) subgrain boundary (b) interaction of a boundary and moving dislocations. SAD patterns are taken from spots A and B in two adjacent austenite grains.

The most common justification for the occurrence of in-grain features is the bending of dendrite arms by the fluid flow in the mushy zone. Nevertheless, since both alloys were cast and fabricated using the same processing conditions (i.e. the same casting and heat treatment conditions), the occurrence of the subgrains only in 4Al alloy is rather an inherent characteristic of the 4Al alloy. In the following, we discuss two possibilities for the origin of in-grain boundaries in the 4Al alloy.

3.2. Dendrite arm bending during solidification
As discussed before, subgrain formation in as-cast alloys has often been linked to the dendrite arm bending during solidification. The required force for this deformation could be provided by external or internal forces, depending on casting and solidification conditions. Although there is no consensus on whether the internal forces in conventional solidification suffice to deform dendrites, it appears that no better alternative is available. According to Doherty [7], “It would seem very difficult to account for these small in-grain misorientations in conventionally solidified dendrites, if they did not arise by dendrite arm bending”. In this regard, the misorientation substructures observed in the 4Al alloy may be attributed to the slight bending of dendrite arms. The absence of in-grain misorientations in the 0Al alloy might then be justified by differences in the solidification mode of the steels. The pseudo-binary
equilibrium phase diagram in Figure 4 predicts that the solidification of 0Al and 4Al alloys begins with the formation of austenite and ferrite dendrites, respectively. To confirm the validity of Thermo-Calc predictions, specimens of both alloys were continuously heated in DSC to study their transformation/melting behavior. Both steels exhibit small endothermic peaks at slightly below 1300 °C, which mark the dissolution of Cr-rich carbides. At temperatures above approximately 1339 °C, the 0Al alloy exhibit a large endothermic peak which marks the onset of melting (solidus temperature). Melting of austenite is complete at approximately 1480 °C. Due to the absence of any phase transformation between the melting start and finish points, the austenite in the 0Al alloy is stable up to the liquidus temperature, namely it melts without preceding or simultaneous formation of ferrite. In the case of the 4Al alloy (Figure 5(b)), in contrast, a slope change and an extra endothermic peak occurred between the solidus and liquidus temperatures. The slope change at ~1367 °C and the peak at ~1397 °C can be attributed to the transformation of austenite into ferrite during melting of the 4Al alloy, namely the higher thermodynamic stability of ferrite compared to austenite just below the liquidus temperature. Based on the DSC results, the first phase to form during solidification of the 4Al alloy is ferrite, although it transforms to austenite before the solidus temperature is reached. In contrast, the solidification of the 0Al alloy starts with the formation of austenite which remains stable down to RT. Due to the high C concentration of the alloys and the likelihood of cooling curves being influenced by severe decarburization in the liquid state, interpretations regarding the sequence of transformations during solidification were made based on the sequence of transformations during the reverse process, rather than that during cooling from the liquid range.

![Figure 4. Pseudo-binary phase diagram of Fe–16.9Cr–8.7Ni–6.2Mn–0.42C alloy system as a function of Al concentration. The actual position of alloys are indicated by dashed lines in diagram.](image-url)

For austenitic and ferritic stainless steels with a roughly similar chemical composition, the yield strength of austenite has been reported to exceed that of the ferrite at temperatures above nearly 600 °C [17]. Although the mechanical properties available in Ref. [17] are limited to 900 °C, it is likely that the strength of austenite remains higher than that of ferrite at still higher temperatures, including the solidification temperature range. Therefore, it can be implied that the stresses induced by fluid flow have not been high enough to yield the austenite dendrites in the 0Al alloy but high enough to cause the plastic deformation of the softer ferritic dendrites in the 4Al alloy. The subgrains induced by the plastic deformation of primary dendrites of ferrite in the 4Al alloy are subsequently inherited by austenite and persist down to RT.
3.3. Phase transformation during cooling

The effect of solidification and transformation sequence on the final microstructure of welded steels has been extensively studied [18–24]. These investigations have mainly focused on the morphology and volume fraction of ferrite, due to their relevance to the crack susceptibility and in-service properties of welds with duplex microstructure [25]. Although most of the previous studies have focused on welded metals, the principles of solidification are equally applicable to cast metals. Based on the succession of the formation of phases, the solidification mode of steels can be divided into three categories, namely austenitic (A), ferritic (F), and ferritic-austenitic (F-A) modes. In steels with the A-mode of solidification, austenite is the primary phase nucleating from the melt and remains stable during further cooling. The delta ferrite, if any, may only form from the remaining liquid as a secondary phase or as one of the constituents of a eutectic phase transformation. In such cases, the delta ferrite will assume a roundish or vermicular morphology and appears between the cellular dendrites of austenite [26]. The microstructure of F-mode steels, on the other hand, is composed of large grains with a lath-like morphology. In some cases, Widmanstätten γ-austenite also forms from the ferrite in the solid state [27]. In steels with the F-A solidification mode, ferrite is formed as the primary phase and austenite nucleates afterwards either in the melt or in the solid state. The morphology of ferrite in the latter case might be circular and/or lath-like [28]. The Cr$_{eq}$/Ni$_{eq}$ ratio is believed to govern the solidification mode and final microstructure of steels, where Cr$_{eq}$ and Ni$_{eq}$ are chromium and nickel equivalents as originally proposed by Schaeffler [29]. For Cr$_{eq}$/Ni$_{eq}$ values below 1.48 and above 1.95, the solidification modes are expected to be A and F, respectively. For steels with Cr$_{eq}$/Ni$_{eq}$ values between 1.48 and 1.95, the F-A mode of solidification is expected [26–28].

The alloying elements in the present steels can be classified into γ-stabilizers and α-stabilizers, whose balance controls the final microstructure. The γ-stabilizers are C, Mn, and Ni and the α-stabilizers are Al, Cr, and Si. Since the chemical composition of both steels is almost identical except for the Al content, it is plausible to assume that the 4Al alloy has a higher value of Cr$_{eq}$/Ni$_{eq}$ and is consequently more susceptible to the F-mode of solidification. The expectations based on the ferrite potential and the predictions based on the thermodynamic equilibrium calculations (Figure 4) were indeed confirmed by the DSC results in Figure 5.

As mentioned before, the subgrain pattern was found to be a distinctive characteristic of the Al-added steel. This dissimilarity may originate from the difference in their mode of solidification. Based on the presented results, the sequence of phase transformations during cooling of the 0Al alloy from the liquid state can be summarized as L → L + γ → γ. For the 4Al alloy, the transformation sequence changes to L → L + δ → L + δ + γ$_{l}$ → L + γ$_{l}$ → γ$_{l}$ + γ$_{H}$, where γ$_{l}$ denotes the austenite formed in the presence of δ-ferrite and γ$_{H}$ denotes the austenite deposited directly from the melt after the transformation of δ-ferrite into γ$_{l}$.

![DSC curves for (a) 0Al and (b) 4Al steels in the heating section. The heating rate was 50 K/min.](image-url)
As schematically represented in Figure 6, the subgrains within the coarse austenitic grains of the 4Al alloy can be attributed to the replacement of $\delta$-ferrite by $\gamma_I$. Although the formation of $\gamma_I$ can be via a solid state transformation ($\delta \rightarrow \gamma_I$), it is more likely via a peritectic reaction initiating at interfaces of $\delta$-ferrite and liquid ($L + \delta \rightarrow \gamma_I$). Small misorientations between the independently nucleated regions of austenite will then lead to the formation of LAGBs at the points of impingement. The subgrain-free regions in the 4Al alloy (Figure 2(b)), on the other hand, can be the $\gamma_I$ regions in the schematic of Figure 6, namely the austenite formed directly from the melt after the full exhaustion of $\delta$-ferrite.

![Figure 6](image)

**Figure 6.** Schematic showing the microstructural evolution of the 4Al alloy during solidification: (a) formation of $\delta$-ferrite primary dendrites at the beginning of solidification; (b) nucleation of austenite ($\gamma_I$) with the involvement of $\delta$-ferrite leading to the creation of LAGBs represented by thin lines; (c) transformation of the remaining liquid into austenite ($\gamma_{II}$) free of subgrains. Thick lines in (b) and (c) denote the HAGBs.

4. Conclusions
Microstructures of two austenitic stainless steels with Al (4Al) and without Al (0Al) were examined using various characterization methods and the differences were discussed in view of the dissimilar solidification modes. Whereas the 0Al alloy had a uniform distribution of coarse $\gamma$ grains free of subgrains, the austenite grains in the 4Al alloy contained subgrains separated by low-angle grain boundaries. The occurrence of subgrains in the 4Al alloy was justified by its ferritic mode of solidification as predicted by thermodynamic calculations and confirmed experimentally by dynamic scanning calorimetry measurements. The subgrains can be a consequence of the plastic deformation of soft primary ferrite dendrites by the fluid flow and their subsequent inheritance by the austenite. Alternatively, they can be induced during the austenite formation from $\delta$-ferrite, most likely via a peritectic reaction, in which case the impingement of austenite grains at small misorientation angles would lead to the formation of subgrains. The subgrains were absent in the 0Al alloy with an austenitic mode of solidification.
5. References

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