Formation of two-phase coupled microstructure in AISI 304 stainless steel during directional solidification

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Formation and evolution details of a two-phase coupled microstructure in AISI 304 stainless steel are studied by quenching method during directional solidification. Results show that the coupled growth microstructure, which is composed of thin lath-like ferrite (δ) and austenite (γ), crystallizes first in the form of colony from the melt. As solidification develops, the retained liquid transforms into austenite gradually. On cooling, solid-state transformation from ferrite to austenite results in the disappearance of part thinner ferrites and the final two-phase coupled microstructure is formed after the solid-state transformation. The formation mechanism of the two-phase coupled microstructure is analyzed based on the nucleation and constitutional undercooling criterion (NCU) before steady-state growth of each phase is reached.

I. INTRODUCTION

Microstructures of austenitic stainless steels have been the object of considerable renewed interest within the last few years because the mechanical properties and corrosion resistance of this alloy are basically determined by the complicated as-cast microstructures.1–6 However, the solidification behavior of austenitic stainless steels is complicated because of the occurrence of a variety of ferrite morphologies during the solidification and subsequent solid-state transformation. Interpretation of the formation mechanism of the different ferrite morphologies is difficult due to the nonequilibrium solidification conditions and the subsequent solid-state transformation on cooling.6–10 Many efforts have been devoted to reveal the formation mechanism of various ferrite morphologies.

Frederiksson11 studied the development of the skeletal ferrite morphology and concluded that the skeletal ferrite was resulted from a diffusion-controlled reaction with partitioning of Ni to the austenite and Cr to the ferrite, leaving only a Cr-rich, Ni-lean ferrite core along the dendrite center. Ma et al.12 studied the microstructure evolution in AISI 304 stainless steel during directional solidification by a quenching method. They concluded that the phase transformation sequence in this system is the precipitation of primary ferrite dendrites, ferrite-austenite eutectic reaction, and the direct formation of austenite occur in sequence during directional solidification of the austenitic stainless steel. As solidification develops, the eutectic ferrites disappear and the final morphology of the ferrite is skeletal, resulting from the primary dendritic ferrite after the incomplete solid-state transformation from ferrite to austenite. However, Ma et al.12 have not analyzed what microstructures will form with a further increase of the cooling rate. Using STEM analysis, Brooks et al.6,10 investigated the alloy element partitioning within the skeletal ferrite structure and lathy structure, where ferrite is arranged in an entangled pattern in austenite matrix. They concluded that the skeletal ferrite and lathy ferrite structures are the results of primary ferrite solidification and a subsequent solid-state transformation during cooling. More recently, Baldissin et al.13 also observed the lathy microstructures in rapidly solidified AISI 304 stainless steel by casting the melt into a copper conic mould. They suggested that this morphology was a result of the solid-state transformation...
from ferrite to austenite. However, the reports on the formation details of the two-phase microstructure where ferrite is arranged in a parallel pattern have not been found so far. Additional studies of the transformation behavior in ferrite morphology would be of interest.

In the present article, quenching and directional solidification experiments in AISI 304 austenitic stainless steel were carried out to investigate the solidification details of the two-phase coupled microstructure. Then, the formation mechanism was theoretically analyzed based on the nucleation and constitutional undercooling criterion.

II. EXPERIMENTAL

In the experiment, a commercial AISI 304 stainless steel, with the compositions (wt%) of Cr 17.93, Ni 8.76, Mn 0.77, Si 0.56, C 0.048, P 0.031, S 0.013, and Fe balance, was used. The rod machined to 7.0-mm diameter and 140-mm long was contained in an alumina tube for directional solidification. Directional solidification experiments were performed under the controlled argon atmosphere. The temperature gradient of liquid was 20 K/mm, and the withdraw velocity was 200 μm/s. After initial heating and temperature stabilization at 1923 K, the sample was pulled down at the constant velocity for steady growth. To observe the evolution details of the two-phase coupled growth microstructure during solidification and subsequent solid-state transformation, the alumina tube was dropped into a brine-quenching bath when the desired volume fraction was solidified.

The directionally solidified samples sectioned longitudinally were electrolytically etched with 10% oxalic acid reagent after being mechanically ground and polished. The solidified microstructures were analyzed with optical microscopy and scanning electron microscopy (SEM).

III. RESULTS

Quenched solidification microstructures of the directionally solidified specimen at different stages with the temperature gradient of 20 K/mm and withdraw velocity of 200 μm/s are shown in Fig. 1. As shown in Fig. 1(a), it is clear that the two-phase coupled growth microstructure forms from the melt first and is surrounded by the quenched liquid that is caused by the high cooling rate. As the solidification proceeds, the retained liquid transforms to austenite gradually, as shown in Fig. 1(b). When the retained liquid disappears completely after solidification, the subsequent solid-state transformation from ferrite to austenite will be expected on cooling. Figure 2 represents the magnified image of the coupled growth microstructure to show the phases clearly. The solid-state transformation details are displayed in Fig. 3. Figure 3(a) is the initial stage of the solid-state transformation. Plenty of lath-like ferrites are distributed on the austenite matrix in the form of colony, as shown in Fig. 3(a). With the development of the solid-state transformation, some thinner ferrites transform into austenite, as shown in Figs. 3(b) and 3(c). The final microstructure that is composed of the thin lath-like ferrite and austenite is shown in Fig. 3(d), which is the result of both the solidification behavior and sequent solid-state transformation on cooling.

IV. DISCUSSION

A. Solidification mode

To simplify a multicomponent austenitic stainless steel system into the Fe-Cr-Ni ternary system, the solidification mode usually can be classified into the following four types using Ni equivalent (Ni\text{eq}) and Cr equivalent (Cr\text{eq}) \textsuperscript{14,15}:

![Fig. 1. Quenched microstructures of the directionally solidified AISI 304 stainless steel at different stages: (a) precipitation of the two-phase coupled microstructure from the melt; and (b) transformation of part retained liquid to austenite.](image-url)
A mode: \( L \rightarrow L + \gamma \rightarrow \gamma \ \text{Cr}_{eq}/\text{Ni}_{eq} < 1.25 \)

AF mode: \( L \rightarrow L + \gamma \rightarrow L + \delta + \gamma \rightarrow \gamma + \delta \)
\( \rightarrow \gamma \ \text{Cr}_{eq}/\text{Ni}_{eq} < 1.48 \)

FA mode: \( L \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \delta + \gamma \)
\( \rightarrow \gamma \ \text{Cr}_{eq}/\text{Ni}_{eq} < 1.95 \)

F mode: \( L \rightarrow L + \delta \rightarrow \delta + \gamma \rightarrow \gamma \ \text{Cr}_{eq}/\text{Ni}_{eq} > 1.95 \)

For the AISI 304 stainless steel used in the experiments, \( \text{Cr}_{eq} \) is calculated as 18.77 wt%, \( \text{Ni}_{eq} \) as 10.59 wt%, and \( \text{Cr}_{eq}/\text{Ni}_{eq} \) as 1.77. Therefore, under equilibrium solidification conditions, the AISI 304 stainless steel falls into FA mode according to the above solidification types. Thus, the precipitation of primary dendritic ferrite should occur first. After the formation of primary dendritic ferrite, three-phase reaction was expected with the further decrease of the melt temperature. In contrast to the equilibrium solidification conditions, phase formation under rapid solidification conditions depends not only on alloy composition but also on the solidification conditions such as cooling rate and melt undercooling before solidification. When the cooling rate is sufficiently high, the solidification behavior will deviate from the equilibrium solidification, and, as a result, nonequilibrium solidification will become dominant with the occurrence of possible new solidification microstructures.

**B. Formation mechanism of the two-phase coupled microstructure**

It is well known that cooling rate or melt undercooling before solidification has an important effect on the solidification microstructures in alloys. The formation of the two-phase coupled microstructure in AISI 304 stainless steel is related to the larger undercooling in the melt before solidification compared with the skeletal ferrite. Formation of the two-phase coupled microstructure and the skeletal ferrite can be analyzed based on the nucleation and constitutional undercooling criterion (NCU) in the constant Fe vertical section, as shown in Fig. 4. If the...
melt undercooling before solidification has not reached the difference between the liquidus temperature of ferrite and the eutectic trough temperature indicated by point a in Fig. 4, primary dendritic ferrite will occur first. With further decrease of the melt temperature, the coupled growth microstructure between ferrite and austenite will take place subsequently. This solidification process has been revealed by Ma et al. using a quenching method in AISI 304 stainless steel during directional solidification. However, when the melt undercooling before solidification is higher than the difference between the liquidus temperature of ferrite and the eutectic trough temperature, two-phase microstructure can be directly formed without the occurrence of the primary dendritic ferrite according to the solidification path in vertical section of Fe-Cr-Ni phase diagram at 70 wt%Fe. During the initial stage of the formation of the two-phase coupled microstructure, ferrite first nucleates from the melt and grows gradually into the melt, as shown schematically in Fig. 5(a), so that Cr is absorbed and Ni is rejected to the liquid, resulting in Cr depletion and Ni enrichment at the interface of ferrite, which is favored for the formation of austenite. With the development of solidification, melt temperature will change down the ferrite liquidus line. When the melt undercooling is higher than the undercooling required for the nucleation of austenite, $\Delta T_{\text{neu}}$, before ferrite reaches a steady state, as shown by the point b in Fig. 4, austenite will nucleate and grow at the interface of ferrite, which is shown schematically in Fig. 5(b). Then, melt temperature changes following austenite liquidus line after the nucleation of austenite. Cr becomes enriched and Ni becomes depleted at the interface of austenite, which is favored for the formation of ferrite. From the solidification path shown in Ref. 16, it is known that the melt temperature is undercooled for ferrite phase when the austenite phase forms. Therefore, simultaneous growth of ferrite and austenite phases in the liquid will occur at this temperature. The primary dendritic ferrite precipitation in two-phase region, which is found under equilibrium conditions, is suppressed due to large undercooling and the coupled growth of lath-like ferrite and austenite consequently takes place. Note that this effect does not necessarily mean that coupled growth microstructure will take place as long as melt undercooling exceeds the critical value mentioned above. A solidification sequence will change as primary austenite from primary ferrite if the melt undercooling is higher than the difference between the liquidus temperature of the equilibrium ferrite phase and the $T_0$ temperature of metastable austenite phase $\Delta T > \Delta T_{0,\gamma} = T_{1,\delta} - T_{0,\gamma}$. This solidification
sequence transition from primary ferrite to primary austenite has been confirmed under a sufficiently cooling rate.\textsuperscript{17} When austenite becomes primary phase, the coupled growth microstructure will not occur and the dendritic or cellular austenite forms.

To examine the element distribution in the two-phase coupled microstructure, composition measurement was performed using EDS on an S-3400N SEM (Hitachi, Tokyo, Japan) at an accelerating voltage of 20 kv. All of the measurements were carried out on the spots of interest including ferrite and austenite between the two ferrites. The distribution of Cr and Ni crossing ferrite and austenite, as shown in Fig. 6(b), demonstrates that Cr is enriched and Ni is depleted within ferrite and Cr is depleted and Ni is enriched within austenite. This result is in agreement with the formation process of the coupled growth microstructure consisting of lath-like ferrite and austenite analyzed above. It should be noted that the width of lath-like ferrite is approximately 0.5 $\mu$m, which is less than the x-ray resolution of approximately 1 $\mu$m in the EDS analyzer. Therefore, the measured concentration in the narrow ferrite phase is a mixture of ferrite and austenite concentration. Although there are errors in composition measurement, resulting from volume averaging between ferrite and austenite phases, the results can show quantitatively the partitioning tendency for Cr and Ni during the formation of the two-phase coupled microstructure. In addition, Fig. 6(b) shows that big scatter of the concentrations of Cr and Ni in ferrite occurs. The scatter of the Cr concentration data in ferrite is not caused by solute partitioning during solidification because the partition coefficient of Cr in ferrite ($k_{Cr}$) is close to 1,\textsuperscript{19} but it is a result of the volume averaging between ferrite and austenite phases during composition measurement\textsuperscript{18} because the width of lath-like ferrite is less than the x-ray resolution. The scatter of the Ni concentration in ferrite is caused by both solute partitioning during solidification and the volume averaging between ferrite and austenite phases because the partition coefficient of Ni in ferrite ($k_{Ni}$) is less than 1\textsuperscript{19} and the width of lath-like ferrite is less than the x-ray resolution.

C. The effect of solid-state transformation

It is well known that solid-state transformation from ferrite to austenite markedly affects the microstructure evolution and ferrite morphology in austenitic stainless steels. During the solid-state transformation, the austenite grows into both the liquid and the thinner lath-like ferrite, which is accompanied by the rejection of Cr and the acceptance of Ni. This growth behavior results in the disappearance of the thinner lath-like ferrites in the final microstructure.\textsuperscript{1} The solid-state transformation process is controlled by element diffusion in alloys. Therefore, the diffusion process is limited by the cooling conditions in the melt. Under nonequilibrium solidification conditions, the diffuse-controlled transformation from ferrite to austenite is incomplete because the element diffusion is suppressed by the high cooling rate. Only the thinner lath-like ferrite transforms into austenite during the solid-state transformation. The thicker ferrite cannot be dissolved completely and is retained to room temperature, forming the final two-phase microstructure.

V. CONCLUSIONS

In this article, we have revealed the detailed formation and evolution process of the two-phase coupled microstructure between lath-like ferrite and austenite in AISI 304 stainless steel by a quenching technique under directional solidification. Primary dendritic ferrite is suppressed due to the large cooling rate, and the coupled growth microstructure between thin lath-like ferrite and austenite is formed directly from the melt. As solidification proceeds, the retained liquid gradually transforms into austenite. Solid-state transformation from ferrite to austenite is not complete because of the suppression of diffusion-controlled solid-state transformation by the
high cooling rate. This incomplete solid-state transformation causes the disappearance of the thinner lath-like ferrite. A coupled growth mechanism for the two-phase coupled microstructure is proposed that ferrite and austenite form from the melt simultaneously when the melt undercooling exceeds the critical value.

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