Formation of a blocky ferrite in Fe–Cr–Ni alloy during directional solidification

J.W. Fu a, b, Y.S. Yang a,*, J.J. Guo b

a Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Abstract

Formation and evolution details of a blocky microstructure in AISI 304 stainless steel are studied by quenching method during directional solidification. Results show that a coupled growth microstructure, consisting of lathy ferrite and austenite, forms first from the melt. At solid-state transformation stage, most lathy ferrite disappears due to the phase transformation from ferrite to austenite. With further decreasing of the temperature, plenty of fine ferrite colonies occur in the original austenite region. The formation of the blocky ferrite indicates that reverse solid-state transformation from austenite to ferrite takes place. This transformation is due to the segregation and the instability of austenite during the growth of austenite under low cooling rate. The fine ferrite colonies transform into blocky ferrite at room temperature. TEM and EDS analyses were carried out to identify the phases and determine the phase composition, respectively.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Austenitic stainless steels form an important class of engineering materials in several energy systems and considerable attention has been given to the microstructural formation and development to obtain sound products with required performances in the last few years. The solidification microstructure of austenitic stainless steels varies greatly and typically consists of ferrite phase and austenite phase. The complex microstructure of as-cast austenitic stainless steels is caused by both the solidification behavior and subsequent solid-state transformation which are controlled by composition and cooling rate [1–8]. The complicated phase transformation behavior of austenitic stainless steels results in a variety of ferrite morphologies such as blocky ferrite, skeletal ferrite, and lathy ferrite. Through extensive studies, it is now recognized that the ferrite morphology has a great effect on the hot cracking susceptibility, corrosion resistance, and low temperature fracture toughness of the class of steel [9]. Therefore, a series of investigations on the formation mechanism of ferrite morphology has been conducted.

The development of the skeletal ferrite morphology has been studied using directional solidification technique and welding technique [6,10]. It was suggested that the skeletal ferrite 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. This core becomes the stable skeletal ferrite at room temperature. Lippold and Savage [11,12] studied the solidification behavior of austenitic stainless steel weldments and related the formation of the skeletal ferrite morphology to massive transformation from ferrite to austenite. They suggested that the skeletal ferrite is a result of Cr-enriched, Ni-depleted dendrite core formed in the initial transient stage of solidification. Based on the solute partitioning which occurs upon cooling, it was concluded that the skeletal ferrite and lathy ferrite are caused by primary ferrite solidification and a subsequent diffusion-controlled solid-state transformation during cooling [6,13]. The formation and evolution details of lathy ferrite in AISI 304 stainless steel during directional solidification have been revealed using quenching technique and the formation mechanism of the two-phase coupled growth microstructure has been theoretically analyzed based on the nucleation and constitutional undercooling criterion [14]. Recently, Baldissin et al. [15] have observed a blocky ferrite through casting the AISI 304 stainless steel melt into a conical-shaped copper mold. They suggested that formation of this ferrite morphology was a result of the
suppression of the solid-state transformation from ferrite to austenite due to higher cooling rate.

The formation processes of skeletal ferrite, lathy ferrite, and blocky ferrite are all related to solid-state transformation between ferrite and austenite. This solid-state transformation is a result of the nature of the $\delta$ and $\gamma$ solvus, as can be seen from the constant Fe vertical section of Fe–Cr–Ni phase diagram, as shown in Fig. 1 [16]. From the path on the vertical section of Fe–Cr–Ni phase diagram at 70 wt% Fe, it is known that solid-state transformation from ferrite to austenite will occur first on cooling after solidification in 18-8 austenitic stainless steel. With further cooling, transformation from austenite to ferrite should reach subsequently based on the path on the vertical section of Fe–Cr–Ni phase diagram at 70 wt% Fe. However, reports on the evolution details of phase transformation from austenite to ferrite have not been investigated to date, and further studies of the transformation behavior in blocky ferrite are of interest. In this work, quenching and directional solidification techniques were carried out to investigate the formation and evolution details of the blocky ferrite formed in AISI 304 stainless steel.

2. Experimental procedure

In this work, a commercial AISI 304 stainless steel was used. The alloy was first remelted in a vacuum induction furnace under a pure argon atmosphere to cast rods of 8.0 mm in diameter and 160 mm in height. The measured chemical composition (wt%) of the as-cast rods was 17.93 Cr, 8.76 Ni, 0.77 Mn, 0.56 Si, 0.048 C, 0.031 P, and 0.013 S. The as-machined rods of 6.0 mm diameter and 140 mm in length were contained in an alumina tube for directional solidification. Directional solidification experiments were carried out under the controlled argon atmosphere. The temperature gradient of the liquid was 20 K/mm, and the withdrawal velocity was 20 $\mu$m/s. After heating and stabilization at 1923 K, the sample was pulled down at a constant velocity for steady growth. In order to observe the solidification details of the two-phase coupled growth microstructure and solid-state transformation process between ferrite and austenite, the alumina tube was dropped into a brine quenching bath at the end of the experiment.

The directionally solidified samples were sectioned longitudinally and electrolytically etched with 10% oxalic acid reagent after being mechanically ground and polished. The solidification microstructures were analyzed by optical microscopy (OM). The phases were identified using a TECNAI $G^2$ 20 transmission electron microscope (TEM). EDS analysis was performed to determine the final composition of each phase.

3. Results

As-quenched solidification microstructures of the directionally solidified specimen at different stages are shown in Fig. 2. A two-phase microstructure, consisting of the coupled growth between thin lathy ferrite and austenite, forms first from the melt and is surrounded by the liquid, as shown in Fig. 2(a). In order to identify the phases in the coupled growth microstructure in Fig. 2, TEM analysis was carried out, as shown in Fig. 3. Selected area diffraction patterns on the marked areas in Fig. 3(a) indicate that they are identified as ferrite and austenite phases. Ferrite and austenite correspond to B and A in Fig. 2. Label C is reserved from the liquid phase due to the high cooling rate caused by quenching during solidification. In order to analyze the solute distribution during the formation of the coupled growth microstructure,
The composition analysis was performed on the marked ferrite, austenite, and the quenched liquid in Fig. 4 using EDS. The results of composition analysis are listed in Table 1. It can be found that both Cr and Ni are enriched in the retained liquid. This means that during the formation of the coupled growth microstructure Cr and Ni are rejected to the liquid region, which finally solidifies into austenite. This result is in agreement with the liquid composition during the formation of the two-phase coupled microstructure in AISI 304 stainless steel during directional solidification [14].

The structure of the coupled growth microstructure can be shown by TEM micrograph in Fig. 3(a). It is shown that ferrite is arranged in the form of lath in the coupled growth microstructure. As solidification develops, the rest of the liquid transforms into austenite gradually, as shown in Fig. 2(b). When the rest of the liquid phase transforms to austenite completely the solidification process is completed and the solid-state transformation will take place subsequently.

The as-quenched solid-state transformation process is shown in Fig. 5. Fig. 5(a)–(f) corresponds to 100, 200, 300, 400, 500, and 600 K below the temperature at which solidification is completed, respectively. At the initial stage of solid-state transformation, ferrite is arranged in the form of lath in the austenite matrix, as shown in Fig. 5(a). With the development of solid-state transformation on cooling, lathy ferrite transforms to austenite gradually, as shown in Fig. 5(b). Meanwhile, some fine ferrite colonies precipitate from the original austenitic region between lathy ferrites, as shown in Fig. 5(b). With the decrease of the temperature, ferrite colonies increase gradually, as shown in Fig. 5(c) and (d). As the temperature decreases further, ferrite inside the lathy structure region dissolves, only the Cr-rich blocky regions are retained, which will transform into blocky ferrite with further cooling, as shown in Fig. 5(e). Fig. 5(f) shows the final microstructure after solid-state transformation. The dark ferrite phase is arranged in blocky pattern in the austenite matrix.

### 4. Discussion

#### 4.1. Solidification mode

For austenitic stainless steels, the solidification mode using Ni equivalent (Ni_{eq}) and Cr equivalent (Cr_{eq}) to simplify a
multi-component system into the Fe–Cr–Ni ternary system [17,18] can be divided into the following four types [4]:

A mode:

\[
L \rightarrow L + \gamma \rightarrow \gamma
\]

\[\text{Cr}_{eq}/\text{Ni}_{eq} < 1.25\]

AF mode:

\[
L \rightarrow L + \gamma \rightarrow L + \delta + \gamma \rightarrow \gamma + \delta \rightarrow \gamma
\]

\[1.25 < \text{Cr}_{eq}/\text{Ni}_{eq} < 1.48\]

FA mode:

\[
L \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \delta + \gamma \rightarrow \gamma
\]

\[1.48 < \text{Cr}_{eq}/\text{Ni}_{eq} < 1.95\]

F mode:

\[
L \rightarrow L + \delta \rightarrow \delta \rightarrow \delta + \gamma \rightarrow \gamma
\]

\[\text{Cr}_{eq}/\text{Ni}_{eq} < 1.95\]

The relative position of the four solidification modes is illustrated on the pseudo-binary phase diagram, as shown in Fig. 6. \(\text{Ni}_{eq}\) and \(\text{Cr}_{eq}\) can be estimated using the following equations [19]:

\[
\text{Ni}_{eq} = \%\text{Ni} + 35 \times \%\text{C} + 20 \times \%\text{N} + 0.25 \times \%\text{Cu}
\]  

(1)

\[
\text{Cr}_{eq} = \%\text{Cr} + \%\text{Mo} + 0.7 \times \%\text{Nb}
\]  

(2)

For the present AISI 304 stainless steel, \(\text{Cr}_{eq}=17.93\) wt% and \(\text{Ni}_{eq}=10.44\) wt%, giving \(\text{Cr}_{eq}/\text{Ni}_{eq}=1.72\). Under equilibrium solidification conditions, the AISI 304 stainless steel falls into FA mode according to the above solidification modes. Therefore, the formation of primary ferrite, plus three-phase (ferrite, austenite, and liquid) reaction at the terminal solidification stage will occur. Following this three-phase reaction, subsequent solid-state transformation is reached when the temperature is decreased further. However, the solidification velocity or melt undercooling has an important effect on the solidification behavior of austenitic stainless steels [8,10,14,20–23]. When the solidification velocity is sufficiently high, the solidification behavior will deviate markedly from equilibrium solidification, and non-equilibrium solidification
will dominate the solidification process and new microstructures may be generated. It can be found from Fig. 2 that a two-phase coupled growth microstructure forms from the melt first without the occurrence of primary dendritic ferrite. The formation of this two-phase coupled growth microstructure indicates that the primary dendritic ferrite that forms in the two-phase region existing under equilibrium solidification conditions is suppressed by the high cooling rate. The formation mechanism of the two-phase coupled growth microstructure has been theoretically analyzed based on the nucleation and constitutional undercooling criterion in our previous work [14]. It can be found that the solidification stage during the formation of the blocky ferrite is similar to the formation of the lathy ferrite by comparing the formation process of the two ferrite morphologies. Therefore, whether lathy ferrite or blocky ferrite will occur is determined by the solid-state transformation stage.

4.2. Solid-state transformation stage

For austenitic stainless steels, solid-state transformation results in various microstructures and ferrite morphologies. For the present alloy, a diffusion-controlled transformation from ferrite to austenite should come forth with further cooling after solidification based on the phase transformation path on the constant Fe vertical section of Fe–Cr–Ni phase diagram [16]. At the initial stage of solid-state transformation, the growth of austenite into ferrite, including primary ferrite and the ferrite in the two-phase coupled growth microstructure, is accompanied by means of the motion of planar or near planar interface between ferrite and austenite [1,24]. With the decreasing temperature, more ferrite transforms to austenite by solute diffusion, and the lathy ferrite zone becomes narrower. This diffusion-controlled interface motion results in the disappearance of a majority of lathy ferrite formed in the solidification stage. The morphological stability of austenite depends on local composition, since higher Cr and lower Ni in ferrite locally can increase the stability of planar interface motion [24]. With the development of solid-state transformation, the fine ferrite colonies precipitate in the austenite region. The formation of the fine ferrite colonies from austenite clearly indicates that a reverse transformation from austenite to ferrite takes place. Fredriksson [10] pointed out that there are two transitions during phase transformation of 300 series stainless steels. The first one is from ferrite to austenite and the other one is from austenite to ferrite. The first transition is mainly due to the increased stability of austenite relative to ferrite as the temperature decreases and the second reverse transformation is related to the segregation during the growth of austenite and the stability of austenite phase with the decrease of the temperature. The local segregation increases and the stability of austenite phase decreases with the decrease of the temperature [10]. Solid-state transformation from austenite to ferrite should occur with further cooling in AISI 304 stainless steel based on the vertical section of Fe–Cr–Ni phase diagram at 70 wt% Fe, as shown in Fig. 1 [16]. However, there are few reports revealing the reverse transformation from austenite to ferrite in AISI 300 series stainless steels up to now because this transformation is controlled by cooling rate and the required low cooling rate is hard to achieve under normal solidification conditions.

It is shown that two-phase coupled growth microstructure occurs at the initial solidification stage during the formation of both the lathy ferrite and the blocky ferrite microstructures. The solid-state stage will determine whether blocky ferrite or lathy will form. The difference of the cooling conditions between the two different ferrite morphologies lies in the withdraw velocity during directional solidification. The phase transformation is controlled by solute diffusion in the alloys and the diffusion process is limited by the cooling conditions. When the cooling rate is sufficiently high, phase transformation from ferrite to austenite is incomplete and only part lathy ferrite formed in the solidification stage transforms to austenite. Meanwhile, phase transformation from austenite to ferrite will be suppressed and austenite will be retained to room temperature. This phase transformation can account for the formation mechanism of lathy ferrite morphology in AISI 304 stainless steel [14]. However, when the cooling rate is sufficiently low, phase transformation from ferrite to austenite is approximately complete and almost all lathy ferrite formed in the solidification stage transforms to austenite completely. With further cooling, the stability of austenite decreases and austenite transforms to ferrite at low cooling rate. As the ferrite inside the lathy structure region dissolves gradually, only the Cr-enrich, Ni-depleted blocky regions, as shown in concentration profiles in Fig. 7, are retained [25]. The formation of blocky ferrite in the directionally solidified stainless steel is confirmed by means of X-ray diffraction patterns shown in Fig. 8, where only peaks corresponding to ferrite appear as the predominant phase besides austenite in the sample. Here, the ferrite should be referred to as \( \alpha \) ferrite because it forms during the solid-state transformation process rather than from the liquid during solidification.
5. Conclusions

We have revealed the detailed formation and evolution process of the blocky ferrite in AISI 304 austenitic stainless steel by the quenching technique under directional solidification. A two-phase microstructure consisting of the coupled growth between the thin lathy ferrite and austenite forms first from the melt and is surrounded by the liquid. As solidification develops, the rest of the liquid transforms into austenite gradually. On cooling, lathy ferrite disappears due to the solid-state transformation from ferrite to austenite, and plenty of fine ferrite colonies occur in the original austenite region. The formation of the ferrite colonies indicates that reverse solid-state transformation from austenite to ferrite takes place under low cooling rate due to the segregation and the instability of austenite during the growth of austenite. The fine ferrite colonies transform into blocky ferrite at room temperature.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (no. 50434040).

References