Solidification behavior in three-phase region of AISI 304 stainless steel

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1. Introduction

More and more attention is paid to microstructure formation and evolution of AISI 304 stainless steel because the mechanical properties and corrosion resistance are basically determined by the as-cast microstructures [1]. The typical solidified microstructure of Cr–Ni stainless steels is composed of ferrite and austenite. There are a variety of ferrite morphologies in the solidified microstructure due to complicated solidification and solid-state transformation behaviors [2–4].

Through extensive studies, it was confirmed that the morphology of ferrite has an important effect on the hot cracking susceptibility, corrosion resistance, and low temperature fracture toughness of Cr–Ni stainless steels [5–7]. According to the solidification path of Fe–Cr–Ni alloys, it is clear that ferrite can be generated by isomorphous transformation and eutectic transformation during solidification. The isomorphous transformation behavior is easy to be understood. However, it is difficult to obtain the phase transformation details of eutectic transformation due to complex solidification and subsequent solid-state transformation behaviors [8–11]. Quenching can freeze the microstructure and is considered as the most common method to observe the solidification details of metals and alloys [12]. Using the quenching technique, Frederiksson [13] found that skeletal ferrite precipitated from the melt first and the precipitation of ferrite was interrupted by the occurrence of austenite. Then, the rest of the melt transformed into austenite rather than ferrite on cooling. However, Frederiksson [13] pointed out that there was no obvious reason for the transformation from liquid to austenite.

Phase transformation details in the three-phase region after forming the two-phase microstructure are still not clear to date [3]. It is usually referred to as a eutectic/peritectic reaction. In the present letter, the solidification details of the three-phase reaction are revealed by quenching. The transformation of the retained liquid into austenite after forming the two-phase microstructure was examined in terms of solute diffusion and Gibbs free energy.

2. Experimental procedure

In the experiments, a commercial AISI 304 stainless steel was used. The nominal composition (wt%) of the alloy is Cr—17.93, Ni—8.76, Mn—0.77, Si—0.56, C—0.048, P—0.031, S—0.013, and Fe balance. The rods with dimensions of 7.0 mm diameter and 140 mm length were contained in an alumina tube. Directional solidification experiments were carried out under a controlled argon atmosphere. The temperature gradient in the liquid ahead of the solid/liquid interface was about 20 K/mm. After stabilizing at 1873 K, the samples were pulled down with a withdrawal velocity of 250 μm/s. After 50 mm steady growth, the alumina tubes were quenched into a brine-quenching bath to reveal the phase transformation details. The samples were electrolytically etched with 10% oxalic acid reagent. The solidified microstructures were analyzed by optical microscopy (OM). The concentrations of Cr and Ni were measured by EPMA.

3. Results and discussion

Fig. 1 shows the as-quenched microstructure at different solidification stages in the AISI 304 stainless steel. It can be seen...
that a two-phase microstructure, consisting of fine lathy ferrite and austenite, precipitates directly from the melt, as shown in Fig. 1(a). The two-phase microstructure is surrounded by the quenched liquid, as denoted by L. As solidification proceeds, the surrounding liquid transforms into austenite gradually. This transformation can be shown by Fig. 1(a), where the regions of austenite (A and B in Fig. 1(a)) originate from the initial liquid. Frederiksson [13] observed the transformation of the rest of the liquid into austenite as well. However, he could not give the reason for this transformation. On cooling, more liquid transforms into austenite, as shown in Fig. 1(b). When all the liquid is transformed into austenite, the solidification process is completed.

Under equilibrium solidification conditions, primary dendrite ferrite precipitates from the melt when the melt temperature is lower than the liquidus temperature. However, primary dendrite ferrite has not been found in the quenched microstructure. Instead, the two-phase microstructure forms directly, as shown in Fig. 1(a). It is well accepted that melt undercooling or cooling rate prior to solidification has a significant effect on the solidification behavior [14]. When the melt undercooling reaches a critical value, primary dendrite ferrite is restrained. Eutectic transformation will take place without the occurrence of primary dendrite ferrite.

Table 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cr (wt.%)</th>
<th>Ni (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta ferrite</td>
<td>19.60 ± 0.18</td>
<td>6.95 ± 0.25</td>
</tr>
<tr>
<td>Austenite</td>
<td>17.65 ± 0.11</td>
<td>9.75 ± 0.15</td>
</tr>
<tr>
<td>Quenched liquid</td>
<td>19.28 ± 0.21</td>
<td>11.13 ± 0.23</td>
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Fig. 4. (a) Relationship between Gibbs free energy and Cr content at 1725 K within the three-phase region and (b) magnification of the phase equilibrium between liquid and austenite.

Fig. 2 exhibits the concentration profile by EPMA. It is apparent that solute Ni is markedly enriched and Cr is slightly enriched in the quenched liquid. The Ni concentration in austenite in the two-phase microstructure is lower than that in austenite transformed from the liquid. The solute enrichment can also be shown from the line measurement by EPMA, as shown in Fig. 3. The measured concentration by EPMA is listed in Table 1. Fig. 2 and Table 1 indicate that Cr and Ni are both rejected into the liquid during the formation of the two-phase microstructure.

Solute redistribution in the liquid is determined by the magnitude of the solute partition coefficient. For Fe–Cr–Ni alloys, the partition coefficient of Ni ($k_{Ni}^d$) is about 0.85 while the partition coefficient of Cr ($k_{Cr}^g$) varies from 0.98 to 1.15 during solidification of ferrite [15]. In terms of austenite solidification, the solute partition coefficients for Ni ($k_{Ni}^g$) and Cr ($k_{Cr}^g$) are about 0.98 and 0.92, respectively. From the solute concentration in Table 1, the partition coefficient can also be obtained. For solidification of ferrite, $k_{Ni}^d$ is calculated as about 1.0, and $k_{Cr}^g$ is calculated as 0.62. For solidification of austenite, $k_{Ni}^g$ is calculated as 0.90, and $k_{Cr}^g$ is calculated as 0.88. It can be seen that the calculated partition coefficients from EPMA analyses fall into the values of Kerr and Kurz [15].

Therefore, during solidification of ferrite in the two-phase microstructure, the liquid becomes enriched in Ni since $k_{Ni}^d$ is much lesser than unity. The content of Cr approximately remains unchanged since $k_{Cr}^g$ approaches unit. During the formation of austenite, both Ni and Cr solutes will be segregated into the liquid since the partition coefficients for Ni ($k_{Ni}^g$) and Cr ($k_{Cr}^g$) are both lower than unity. Thus, Ni solute is rejected into the liquid for solidification of both ferrite and austenite. With the development of solidification, the segregation degree of Ni in the liquid becomes more severe compared with that of Cr solute. When this process repeats, Ni solute becomes extremely enriched in the liquid. Thus, the rest of the liquid finally transforms into austenite when Ni is an austenite-forming element. Ferrite cannot be formed any longer though Cr solute is slightly enriched in the liquid. Therefore, enrichment of Ni in the retained liquid after forming the coupled microstructure is the reason for the transformation from retained liquid into austenite.

To examine the transformation from the rest of the liquid to austenite from thermodynamic considerations, we calculate the Gibbs free energy for liquid, ferrite and austenite, as shown in Fig. 4. The calculated temperature is 1725 K which is within the three-phase region and approaches the final solidification temperature. Ni concentration is set as 11 wt.%, which is in agreement with the concentration (Table 1). From Fig. 4, it is apparent that only equilibrium between the liquid and austenite exists at 1725 K. The corresponding equilibrium content of Cr is about 16.5 wt.% for austenite and 19.4 wt.% for liquid. The results agree with the measured concentrations in Table 1. This means that when the retained liquid transforms into austenite, the Gibbs free energy of the system reaches a minimum at 1725 K. Therefore, it is inevitable that the retained liquid transforms into austenite after forming the two-phase microstructure.

4. Conclusion

We have revealed the solidification details of the three-phase region in AISI 304 stainless steel by quenching. A two-phase microstructure between thin lathy ferrite and austenite is formed directly from the melt. During the formation of the two-phase microstructure, Cr and Ni solutes are rejected into the liquid. After forming the two-phase microstructure, the retained liquid gradually transforms into austenite on cooling since Ni solute becomes extremely enriched in the liquid. This phase transformation has been examined by the consideration of Gibbs free energy.

Acknowledgment

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References