Orientation Relationships of Icosahedral Quasicrystalline Phase and Laves Phase Precipitates in a Ferritic Alloy*

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The precipitation behavior and orientation relationships of icosahedral quasicrystalline phase (I-phase) and Laves phase precipitates in ferrite matrix have been investigated by transmission electron microscopy (TEM) in an Fe-10Cr-1.4W-4.5Co-0.3Si (at%) alloy. It is found that the precipitates of the alloy aged at 873 K are the I-phase but those of the alloy aged at 973 K are the Laves phase. Through a double aging experiment at both temperatures, it is shown that the transformation between the I-phase and the Laves phase occurs. Although a single orientation relationship is established between the I-phase and the ferrite matrix, three different types of the orientation relationships between the Laves phase and the ferrite matrix are obtained by the analysis of SAD patterns. The results can be explained by the coincidence between the five-fold symmetrical plane of the I-phase and the (1120) plane of the Laves phase on the phase transformation between them.

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1. Introduction

High Cr ferritic heat resistant steels containing W have been developed for the power generating plants. These steels are composed generally of the tempered martensite matrix and the precipitates of MX carbonitride, M(C,N) carbide and intermetallic compounds such as the Laves phase, μ phase and z phase, etc. 1) It is suggested that fine precipitation of the Fe3W Laves phase under the service condition improves the creep resistance of the ferritic heat resistant steels. 2) On the other hand, the coarsening of the Laves phase reduces the creep strength and toughness of the steels particularly at ambient temperature. Then it is important to make it clear the precipitation behavior of the Laves phase in order to best utilize the Laves phase.

The present authors have investigated the precipitation behavior of the intermetallic phases by transmission electron microscopy (TEM) in Fe-10Cr-1.4W-4.5Co alloys with and without 0.3 at%Si. 3) From a series of SAD patterns taken from the precipitates of the Si-containing alloy aged at 873 K, the two-, three- and five-fold symmetry and diffraction spots at the positions related to the golden section have been found to originate from the icosahedral quasicrystal, hereafter denoted as I-phase. It has been also found that the precipitates of the Si-containing alloy aged at 873 K are the I-phase but those of the Si-free alloy are the crystalline R-phase. However, the precipitates in both the Si-containing and Si-free alloys aged at 973 K have been found to be the Laves phase. Furthermore, it is interesting that the transformation between the Laves phase and the I-phase (or R-phase) occurs between the two aging temperatures.

The objective of this work is to investigate the orientation relationships among the I-phase, the Laves phase and the α-Fe matrix which are related to the transformation between the I-phase and the Laves phase precipitates in an Fe-10Cr-1.4W-4.5Co-0.3Si (at%) alloy.

2. Experimental Procedure

Nominal composition of the alloy used in the present study is Fe-10Cr-1.4W-4.5Co-0.3Si in at%. The corresponding alloy composition in wt% is Fe-9.1Cr-4.5W-4.6Co-0.15Si. The alloy was prepared by induction melting in an alumina crucible and casting into a mold in an argon atmosphere. The ingot of about 300 g in weight, 30 mm in diameter and 50 mm in height was then hot rolled at about 1373 K. Solid solution heat treatment was performed at 1553 K for 1 h under an argon gas flow, and then quenched into water. The alloy was then aged at 873 and 973 K up to 1000 h. Double aging was also carried out at 973 K for 100 h followed by at 873 K for 120 h. Microstructure of the alloy was observed by transmission electron microscopy (TEM) using a JEOL JEM-2011 at an accelerating voltage of 200 kV. Thin foils for TEM observation were prepared by twin-jet electropolishing using a solution of 10% perchloric acid and 90% methanol at below 223 K.

3. Results and Discussion

3.1 Orientation relationship between I-phase and α-Fe

It has been shown that the I-phase precipitates in the ferrite matrix during aging at 873 K. 3) Figure 1(a) shows a bright field image of the alloy aged at 873 K for 1000 h. By the trace analysis, plate-shaped precipitates are formed on the [110] planes of the α-Fe matrix. At this stage, the precipitates are about several hundreds of nm in size. A SAD pattern taken along the plane normal of the plate-shaped precipitates and the corresponding key diagram are shown in Fig. 1(b). The plane normal of the plate-shaped precipitates is the five-fold symmetrical axis of the I-phase, and is parallel to the (011) direction of the α-Fe. It is found that 011 spot of the α-Fe exactly coincides with one of the diffracting spots of the I-phase.

By tilting experiments, a series of SAD patterns have been taken from the alloy aged at 873 K. 3) Figure 2 shows the stereographic projection giving the orientation relationship

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The I-phase has six five-, ten three- and fifteen two-fold symmetrical planes. One of the five-fold symmetrical planes of the I-phase agrees with a two-fold symmetrical plane of the α-Fe traces and two of the five-fold symmetrical planes are very close to two-fold symmetrical planes of the α-Fe.

3.2 Orientation relationship between Laves phase and α-Fe

It has been found that the precipitates in the alloy aged at 973 K are not any more the I-phase but Laves phase. The blocky morphology of the precipitates, a few hundreds nm in size, is frequently observed in the ferrite matrix. It is found that three types of the orientation relationships between the Laves phase and the α-Fe (OR-L/α) exist as a result of analysis on various SAD patterns in the alloy aged at 973 K. The SAD patterns and the corresponding key diagrams are shown in Fig. 3(a) (OR1-L/α), Fig. 3(b) (OR2-L/α) and Fig. 3(c) (OR 3-L/α).

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\begin{align*}
\text{OR1-L/α:} & \quad [10\bar{1}]_{\text{Ib-Fe}} \parallel [12\bar{1}]_{\text{Laves}}, \\
& \quad (111)_{\text{Ib-Fe}} \parallel (110)_{\text{Laves}}, (011)_{\text{Ib-Fe}} \parallel (0001)_{\text{Laves}} \\
\text{OR2-L/α:} & \quad [\bar{1}1\bar{3}]_{\text{Ib-Fe}} \parallel [\bar{2}\bar{1}\bar{1}0]_{\text{Laves}}, \\
& \quad (1\bar{1}0)_{\text{Ib-Fe}} \parallel (011)_{\text{Laves}}, (4\bar{1}1)_{\text{Ib-Fe}} \parallel (0001)_{\text{Laves}} \\
\text{OR 3-L/α:} & \quad [011]_{\text{Ib-Fe}} \parallel [2\bar{1}\bar{1}0]_{\text{Laves}}, \\
& \quad (100)_{\text{Ib-Fe}} \parallel (02\bar{2}3)_{\text{Laves}}, (1\bar{1}\bar{1})_{\text{Ib-Fe}} \parallel (0001)_{\text{Laves}}
\end{align*}
\]

It is noted that these orientation relationships are different from the following orientation relationship obtained for the C14 Fe2Nb Laves phase and the α-Fe in an Fe-10Cr-1Nb (at%) alloy reported by the present authors and for the C14 Fe2W and the α-Fe in the Cr-W heat resistant steels reported by Abe et al. and Murata et al.:\(^{6,7}\)

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\begin{align*}
[\bar{1}1\bar{1}]_{\text{Fe}} & \parallel [01\bar{1}0]_{\text{Fe2Nb}}, (011)_{\text{Fe}} \parallel (2\bar{1}10)_{\text{Fe2Nb}}, \\
(211)_{\text{Fe}} & \parallel (0001)_{\text{Fe2Nb}}
\end{align*}
\]

A detailed discussion on the three types of the OR-L/α will be made later in section 3.4.

3.3 Transformation between I-phase and Laves phase

As described in the previous sections, it is found that the precipitates in the alloy aged at 873 K are the I-phase. But during aging at 973 K, the precipitates are the Laves phase. The precipitates in the alloy double-aged for 973 K/100 h+873 K/120 h are identified as the I-phase from SAD patterns, and the orientation relationship is the same as that in the alloy aged only at 873 K as shown in Fig. 2. It is concluded that the I-phase observed in the double-aged alloys has been formed by direct transformation from the Laves phase rather than by dissolution, renucleation and growth. Hereafter the transformation between the I-phase and the Laves phase is denoted as the I/Laves phase transformation. In order to better understand the I/Laves phase transformation, in-situ observation was carried out by using a TEM heating stage up to about 973 K, however the I/Laves phase transformation has not been observed as the change in diffraction patterns.

The I/Laves phase transformation is considered here in based on a similarity in the structures between I-phase and Laves phase. Figure 4 shows the (1120) projection of C14 Laves phase with a unit cell shown by rectangle (PbS/mmc, Fe2W \( a = 0.427 \ c = 0.7704 \) nm). The C14 structure is arranged in the hexagonal ABAB... sequence in the [0001] direction and consists of pentagon-triangle sheets. These pentagonal atomic clusters are chains of icosahedra of coordination number 12 (CN=12). Furthermore, it is ob-
served that the strong spots in the SAD pattern taken along zone axis $h_{11}/C22220$ of the Laves phase are apparently aligned in a pseudo-five-fold symmetry as shown in Fig. 3(b). However, this SAD pattern is for a crystalline phase because all the spots are completely periodic. It is suggested then that the icosahedral unit exists in the crystal structure of the Laves phase. It is found that the atomic arrangement in the $(11/C22220)$ plane of the Laves phase is very similar to that in the five-fold symmetrical plane of the I-phase. Therefore, it is considered that the five-fold symmetrical plane of the I-phase coincides with the $(11/C22220)$ plane of the Laves phase on the I/Laves phase transformation.

3.4 Orientation relationships among I-phase, Laves phase and $\alpha$-Fe.

By the present work, the single orientation relationship is established between the I-phase and the $\alpha$-Fe. However, there are three types of the orientation relationships between the Laves phase and the $\alpha$-Fe. This section demonstrates the reason of the orientation relationships among them based on the I/Laves phase transformation.

Three different types of the OR-L/$\alpha$ obtained by the analysis of SAD patterns in section 3.2 can be explained by the coincidence between the five-fold symmetrical plane of the I-phase and the $(1120)$ plane of the Laves phase on the I/Laves phase transformation. The stereographic projection of the OR-I/L along the five-fold symmetrical plane of the I-phase is shown in Fig. 5(a). When the $(1120)$ plane of the Laves phase is superimposed, by a proper rotation it is found that the $(1210)$ plane of the Laves phase almost coincides with another five-fold symmetrical plane.
Figures 5(b), (c) and (d) show three types of the OR-L/α obtained by the experiments as shown in Fig. 3. In the OR1-L/α shown in Fig. 5(b), the basal plane of the Laves phase is parallel to the (011) plane of the α-Fe. It is found in Fig. 5(a) that repeated rotations of the Laves phase against the I-phase by 72 degrees yield the same OR, in which two of the {1120} planes of the Laves phase almost coincide with the five-fold symmetrical planes. However, the OR-L/α is not the same when the Laves phase rotates 72 degrees toward the α-Fe matrix. By the rotation of the Laves phase against the α-Fe, the OR1-L/α shown in Fig. 5(b) develops into the OR2-L/α in which the basal plane of the Laves phase is parallel to the (411) plane of the α-Fe as shown in Fig. 5(c). By another rotation of the same angle, the OR2-L/α shown in Fig. 5(c) develops into the OR3-L/α in which the basal plane of the Laves phase is parallel to the (111) plane of the α-Fe as shown in Fig. 5(d). It should be noted that three types of the OR-L/α by these rotations are coincident with the results obtained by experiments as shown in Fig. 3.

The three types of the OR-L/α are different from the orientation relationship between the Fe₂Nb Laves phase and the α-Fe, OR-Fe₂Nb/α, reported by the present authors. The OR-Fe₂Nb/α, shown in section 3.2, is in agreement with none of the three types of the OR-L/α obtained in the present work. It is noted that the OR-Fe₂Nb/α is the same as that of the C14 Fe₂W and the α-Fe in the Cr-W heat resistant steels reported by Abe et al. and Murata et al. It is considered that, as these steels contain many other alloying elements, the phase stability of the I-phase may be modified so as not to precede the precipitation of the Fe₂W Laves phase. Because it is important that the three types of the OR-L/α obtained in the present work are related to the OR-I/α, they are different from the orientation relationship between the Fe₂W Laves phase and the α-Fe reported in the literature.

4. Conclusions

The orientation relationships among the I-phase, the α-Fe and the α-Fe are investigated by TEM in an Fe-10Cr-1.4W-4.5Co-0.3Si (at%) alloy. It is found that the precipitates of the alloy aged at 873 K are the I-phase but those of the alloy aged at 973 K are the Laves phase. It is shown that the I/Laves phase transformation occurs through double aging between both temperatures. The single orientation relationship is established between the I-phase and the α-Fe. Three different types of the orientation relationships between the Laves phase and the α-Fe are obtained by the analysis of SAD patterns, which can be explained by the coincidence between the five-fold symmetrical plane of the I-phase and the (1120) plane of the Laves phase on the I-Laves phase transformation.

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