Precipitation of the Icosahedral Quasicrystalline Phase, R-phase and Laves Phase in Ferritic Alloys*

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1. Introduction

Improvement in mechanical properties has been made in several ferritic heat resistant steels being used in the power generating plants. There is a general trend in their compositional modifications toward decreasing carbon content as well as increasing contents of chromium and such refractory elements as Mo, Nb and W. These compositional modifications could improve high temperature creep strength and often lead to complex microstructural evolutions during creep. Fe2W Laves phase which precipitates during creep has recently drawn a growing interest as strengthening to improve the creep resistance of the ferritic heat resistant steels. In order to best utilize intermetallic phases, it becomes necessary to investigate the precipitation behavior in high Cr ferritic steels involving precipitation of some meta-stable and stable intermetallic phases as well as carbides and carbonitrides.

The present authors have made every effort to establish the basis of the development of carbon-free ferritic heat resistant alloys in which the Laves phase is solely the strengthener in the ferrite matrix in Fe-Cr-Nb-Ni and Fe-Cr-W-Co systems. It is found that the precipitates in Fe-Cr-W-Co system involve not only Laves phase but also R-phase both being TCP phase. In the present work, in order to further investigate the stability of these intermetallic phases, the alloys with and without a small amount of Si addition are employed. It is unexpectedly observed that selected area diffraction (SAD) patterns of the precipitates during aging at 873 K in the alloy containing Si exhibit nearly perfect five-fold symmetry similar to the one observed in the icosahedral quasicrystalline phase.

Since the icosahedral quasicrystal, hereafter denoted as I-phase, was first discovered in rapidly solidified Al-Mn alloys, stable icosahedral quasicrystals have discovered in many alloys such as Al, Zn, Cd and Cu-based alloys. In our experiments, there would be scientific interest in the precipitation of I-phase during isothermal aging in Fe-based alloys. To the authors’ knowledge, only a few reports on quasicrystalline precipitates during isothermal aging in conventional steels have been found in the literature. An example is on the quasicrystalline precipitates during isothermal aging at 748 K in a high strength maraging steel Fe-12Cr-9Ni-4Mo-2Cu-1Ti-0.15Si (mass%). It is also reported about I-phase formation in a duplex stainless steel aged at 823 K for 100 h.

The objectives of this work are to investigate the precipitation behavior of I-phase, R-phase and Laves phase during aging in Fe-10Cr-1.4W-4.5Co (at%) alloys with and without 0.3 at%Si and to compare the orientation relationship, precipitate morphology and phase stability of the I-phase with those of crystalline R- and Laves phases.

2. Experimental Procedure

Nominal compositions of the alloys used in the present study are Fe-10Cr-1.4W-4.5Co-0.3Si and Fe-10Cr-1.4W-4.5Co, in at%. The corresponding alloy compositions in mass% are Fe-9.1Cr-4.5W-4.6Co-0.15Si and Fe-9.1Cr-4.5W-4.6Co, respectively. Here the alloys are denoted as the Si alloy and Si-free alloy. They were prepared by induction melting in an alumina crucible and casting into a mold in an argon atmosphere. The ingots of about 300 g (30 mm in diameter and 50 mm in height) were then hot rolled at about 1373 K. The solid solution heat treatments were performed at 1553 K for 1 h under an Ar gas flow, and then quenched into water. The alloys were then aged at 873 and 973 K up to 1000 h respectively. Double aging was also carried out at 973 K/100 h + 873 K/120 h.

Microstructures of the alloys were observed by a transmission electron microscopy (TEM). 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. A JEOL JEM-2011 TEM and Philips CM200 TEM equipped with EDS were used at an accelerating voltage of 200 kV.

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3. Results and Discussion

3.1 Precipitation of the I-phase

The I-phase precipitates in the Si alloy aged at 873 K. Figures 1(a) and (b) show bright field images of the Si alloy aged at 873 K for 100 h and for 1000 h respectively. The precipitates of about a few tens of nm in size formed during aging are observed in the ferrite matrix, as shown in Fig. 1(a). In the solution treated condition, TEM observation of the unaged alloy showed no precipitates in the ferrite matrix. The I-phase precipitates are identified as plate-shaped by the trace analysis formed on the \{110\} planes of the \(\alpha\)-Fe matrix, as shown in Fig. 1(b). At this stage, the precipitates are about several hundreds of nm in size.

By tilting experiments a series of the selected area diffraction (SAD) patterns are obtained as shown in Fig. 2(a) through (c). The ratio between adjacent reciprocal vectors is found to be about 1.62, which is close to the golden section. Such a feature of SAD patterns is known to arise from so-called quasiperiodicity. Furthermore, the patterns reveal the two-, three- and five-fold symmetry respectively. These features of SAD patterns are expected from the icosahedral quasicrystal. Figure 2(c) shows the \(\{011\}\) diffracting plane of the \(\alpha\)-Fe matrix, where it is found that the 011 spot of the \(\alpha\)-Fe exactly coincides with one of the diffracting spots of the I-phase. The orientation relationship between the I-phase and \(\alpha\)-Fe matrix satisfying all the SAD patterns in Fig. 2 agrees well with what has been reported previously in a duplex stainless steel.

High-resolution electron microscope (HREM) image of the Si alloy aged at 873 K for 100 h and the Fourier transform of this image are shown in Fig. 3. The image is taken with the incident beam parallel to the five-symmetrical axis. Within the I-phase with darker contrast, the planes of five-fold symmetry are observed and one of the planes is parallel to the \(\{011\}\) plane of the \(\alpha\)-Fe. Presence of a typical five-fold symmetry and quasiperiodicity is confirmed by spots in the positions related to the golden section in the Fourier transform shown as an inset. In a HREM image, each bright-image point corresponds to an icosahedral chain or the tunnel inside a pentagonal atomic cluster. The distance between two neighboring icosahedra sharing a triangular face is about 0.2374 nm by using the calibration of the \(\{011\}\) plane of the \(\alpha\)-Fe matrix in the HREM image (\(a_{011} = 0.2027\) nm).

3.2 Precipitation of the R-phase

Bright and dark field images of the Si-free alloy aged at 873 K for 1000 h, the SAD pattern and the corresponding key diagram are shown in Fig. 4. The precipitates in the ferrite matrix are identified as R-phase from SAD patterns. The lattice parameters of R-phase identified by the present work...
are almost equal to the values of R-phase prototype Co$_5$Cr$_2$Mo$_3$, $a = 1.0903$ nm and $c = 1.9342$ nm in hexagonal ($a_0 = 0.9005$ nm, $\alpha = 74^\circ$31 in rhombohedral), which has been reported by Komura et al.$^{12}$ The strong streaks in the SAD pattern are found in Fig. 4(c), which are associated with planer faults of the plate-shaped precipitates as seen in the bright and dark field images of Figs. 4(a) and (b). The flat surfaces of plate-shaped R-phase are the {110} planes of the $\alpha$-Fe matrix. The same planes are reported for R-phase in the $\alpha$-Fe matrix of 25Cr-7Ni-0.14N-2.8Mo (mass%) stainless steel.$^{14}$ Since the flat surfaces of plate-shaped precipitates are perpendicular to the incident beam and planar faults are almost edge-on in Fig. 4(b), it is found that the flat surfaces are the (1450) planes (plane normal $[1450]$) and planar faults are the (0001) planes of R-phase as shown in Fig. 4(d). Comparing with the Si alloy, shown in Fig. 1, morphology of the precipitates resembles the I-phase.

The crystallographic orientation relationship between the R-phase and bcc $\alpha$-Fe matrix is established using SAD patterns as; $[1450]_{\text{R-phase}} \parallel [101]_{\text{Fe}}, \langle 3217 \rangle_{\text{R-phase}} \parallel (101)_{\alpha-\text{Fe}}, (0001)_{\text{R-phase}} \parallel (111)_{\alpha-\text{Fe}}$. Note that the orientation relationship obtained here is the same as that between the $\alpha$-Fe and R-phase reported in 25Cr-7Ni-0.14N-2.8Mo (mass%) stainless steel,$^{13}$ Fe-Cr-W alloy$^{14}$ and 0.11C-12Cr-6Mo-10Co (mass%) steel.$^{15}$

The chemical composition of the R-phase precipitates determined by TEM-EDS measurement is Fe 53.3, Cr 19.1, W 25.4, Co 2.2 in at% (Fe 34.0, Cr 11.3, W 53.2, Co 1.5 in mass%), which is close to the ratio of constituents for the R-phase Co$_5$Cr$_2$Mo$_3$ reported by Komura et al.$^{12}$

### 3.3 Two-dimensional structures of the R-phase and I-phase

A close resemblance of two-dimensional structures between the I-phase and R-phase is found based on the crystallographic features. The precipitate morphology of the I- and R-phases is the same plate-shape. The flat surfaces of plate-shaped I-phase are the five-fold symmetrical planes and R-phase (1450) planes. Figure 5 shows the (1450) projection of R-phase (space group $R_3$, $\alpha = 1.0903$ nm and $c = 1.9342$ nm in hexagonal), in which the minimum unit of repetition is shown by the parallelogram. This projection is obtained by computer software (Mac crystal kit) of structural analysis using the atomic parameters as given in the literature.$^{12}$ The figure depicts the arrangement of atoms within the layers with a width of 0.16 nm on the (1450) plane of R-phase. Since atomic sites of three elements in R-phase, $i.e.$ Fe, Cr and W, are not clearly determined, only two kinds of atoms, (Fe or Cr) and W, are shown. This projection consists of pentagon (dark contrast), triangle and diamond sheets. These pentagonal atomic clusters are chains of icosahedra of coordination number 12 (CN12). The crystal structure of R-phase has 159 atoms per hexagonal cell, in which the atoms of CN12 are 81, CN14 36atoms, CN15 18atoms and CN16 24atoms. The lines shown in Fig. 5 connect the center of the pentagonal atomic clusters. These bonding directions are satisfied with the five-fold symmetry, shown as an inset, which are defined as BOO (bond orientational order) with the characteristic of the quasicrystal.$^{16}$ The atomic arrangement in this plane is found to be very similar to that in the five-fold symmetrical plane of I-phase. Since it is reported that Si often plays an important role in I-phase formation,$^{17}$ it is suggested that the atomic arrangement of the R-phase becomes to have the quasiperiodicity by containing Si atoms.

### 3.4 Precipitation of the Laves phase

A bright field image of the Si alloy aged at 973 K for 1000h, the SAD pattern and the corresponding key diagram are shown in Fig. 6. The unusual blocky morphology of precipitates, a few hundreds nm in size, is frequently observed in the ferrite matrix as shown in Fig. 6(a). The analyses on the SAD patterns, shown in Figs. 6(b) and (c), reveal that the precipitate is not any more the I-phase but
3.5 Transformation from Laves phase to I-phase or R-phase

As described in the previous sections, it is found that the precipitates in the Si alloy aged at 873 K are the I-phase and those of the Si-free alloy are the R-phase. But in both alloys aged at 973 K, the precipitates are the Laves phase. In order to confirm whether I- and R-phases are stable or meta-stable at 873 K, the alloys were aged at 973 K for 100 h and subsequently aged at 873 K for 120 h. If the I- and R-phases are meta-stable and the Laves phase is stable at 873 K, the Laves phase precipitated at 973 K must remain during the aging at 873 K.

The precipitates in the Si alloy aged at 973 K/100 h+873 K/120 h are identified as I-phase from SAD patterns and the orientation relationship is the same as that in the Si alloy aged only at 873 K, shown in Fig. 2. It is also found that the precipitates in the Si-free alloy aged at 973 K/100 h+873 K/120 h are identified as R-phase and the orientation relationship is the same as that found after aging only at 873 K, shown in Fig. 4. It is concluded that I- and R-phases are stable at 873 K and Laves phase is stable at 973 K.

As described in the section 3.3, it is found that the structures among I-phase and crystalline R- and Laves phases with icosahedral of CN12 are closely similar based on the crystallographic features. Therefore, it is considered that I- and R-phases observed in the double-aged alloys have been formed by direct transformation from Laves phase rather than by dissolution, nucleation and growth. The transformation between quasicrystals and related crystalline phases has been observed in various alloy systems. It is known that this type of transformation is caused by the phason strain. In Al-Cu-Fe alloys, phason strain modes inducing rhombohedral-icosahedral structure transformation were found. In order to more understand the transformation between I-phase or R-phase and Laves phase, the further investigations including in-situ observation are necessary.

4. Conclusions

Precipitation behavior of I-phase, R-phase and Laves phase during aging in Fe-10Cr-1.4W-4.5Co alloys with and without 0.3 at%Si is investigated. The results on the crystallographic features of the I-phase are then compared with those of crystalline R-phase. The followings are the conclusions drawn from the present work.

1) By tilting experiments, a series of SAD patterns are taken from the Si alloy aged at 873 K. The two-, three- and five-fold symmetry and diffraction spots in the positions related to the golden section are found to originate from the icosahedral quasicrystal. The only one orientation relationship is established between the I-phase and α-Fe.

2) The precipitates of the Si alloy aged at 873 K are the I-phase but those of the Si-free alloy are the R-phase. However, the precipitates in both the Si and Si-free alloys aged at 973 K are the Laves phase. Through a double aging experiment at both temperatures, the transformation from the Laves phase to the I-phase or R-phase occurs between the two aging temperatures.

3) The flat surfaces of plate-shaped precipitates are the five-fold symmetrical planes of I-phase and the (1450) planes of R-phase, and are parallel to the {110} planes of the α-Fe. The bonding directions of the pentagonal atomic clusters in the (1450) R-phase projection are satisfied with BOO (bond orientational order) with the characteristic of the quasicrystal. A similarity in the structures among I-phase and crystalline R- and Laves phases rationalizes the transformation among these phases.

REFERENCES