Growth Behaviour of Athermal ω -Phase Crystals in a Ti-15mass%Mo Alloy Studied by *In-situ* Dark Field and High Resolution Electron Microscopy

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The formation of athermal ω -phase crystals in β -Ti alloys has been postulated based on the negative temperature dependence of electrical resistivity. However, no direct evidence has been reported. In order to clarify the formation and morphology of athermal ω -phase crystals in Ti-15mass%Mo alloys cooled to and held at 131 K, *in-situ* dark field image observations and high resolution electron microscope (HREM) observations were carried out using a TV-VTR system. It was found that athermal ω -phase crystals with spherical shape and a size of approximately 20 nm were formed by cooling to 131 K in areas that were not irradiated by electrons, but, no formation was observed in areas irradiated by electrons. HREM images of the athermal ω -phase crystals revealed the atomic structure of ω -phase crystals. Athermal ω -phase crystals formed by cooling were annihilated by electron irradiation, and the stability depended on the holding period at 131 K, that is, the longer the period, the more stable the crystals became. The annihilation caused by the temperature rise from 131 to 200 K was a function of time. The annihilation was noticed at 1680 s, but not at 780 s. This fact suggests that an incubation time exists in the case of the $\omega \rightleftharpoons \beta$ transformations. It seems that the $\beta \rightleftharpoons \omega$ phase transformations indicate hysteresis.

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I. Introduction

Since Ames *et al.* found a negative temperature dependence of electrical resistivity in Ti-Nb alloys in 1954⁽¹⁾, a similar dependence in metastable β -Ti alloys such as Ti-Nb, Ti-V and Ti-Mo has been found by many authors⁽²⁾⁻⁽⁵⁾. Williams *et al.* considered that the phenomenon resulted from the appearance of athermal ω -phase crystals, which were formed by a covalent bond mechanism⁽²⁾. They also identified the formation temperature of athermal ω -phase crystals from electron diffraction pattern observations with a specimen cooling holder at 102 K, but did not describe the direct relationship between the occurrence of the negative temperature dependence and the formation of the crystals. Recently, Ikeda *et al.* performed a detailed analysis of the negative temperature dependence of electrical resistivity for Ti-V⁽⁴⁾ and Ti-Mo⁽⁵⁾ alloys. From the results, they identified both the starting and finishing temperatures of the formation of athermal ω -phase crystals and attempted to confirm both temperatures using an electron diffraction pattern analysis of the specimen as it cooled⁽⁴⁾. Moreover, they demonstrated that if athermal ω -phase crystals consisted of linear defects, the negative temperature dependence did not occur⁽⁵⁾. However, be-

cause the dependence has been observed in many alloy systems, it seems that the morphology of athermal ω -phase crystals is not linear. On the other hand, although electron diffraction pattern analyses can be used to identify the atomic structures of precipitates and crystals, it is difficult to know their detailed morphology from the analyses only. Moreover, because electron irradiation affects phase transformations in thin foil specimens⁽⁶⁾, it is necessary to observe directly the morphology of athermal ω -phase crystals formed by cooling. This is particularly important when considering the origin of the anomalous temperature dependence of electrical resistivity, and also to obtain knowledge about the mechanism of the β - ω transformation.

In the present study, direct observations on the formation and morphology of athermal ω -phase crystals in as-quenched Ti-15mass%Mo alloys cooled to and held at 131 K were carried out using an *in-situ* dark field imaging technique and high resolution electron microscopy with a double tilt cooling stage. The formation and growth behaviour of the crystals and their annihilation due to electron irradiation and temperature rise were also discussed.

II. Experimental Procedure

A Ti-15mass%Mo (abbreviated as Ti-15Mo) alloy button ingot was prepared by an arc furnace in a high purity argon atmosphere and then hot-rolled. Plates with approximately 15 mm length and 0.5 mm thickness were

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cut out and solution-treated at 1073 K for 3.6 ks in a vacuum. These were then rapidly cooled by ice water injected into a quartz glass tube without breaking the vacuum. Thin foil specimens for electron microscope observations were prepared by electropolishing. A JEM 2010F electron microscope operated at 200 kV and 160 kV was used. Specimens were cooled to and held at 131 K using a double tilt cooling stage, EM-31100. It was confirmed that the lowest temperature of specimens attained by this holder was 131 K. Variations in electron diffraction patterns from room temperature to 131 K allowed by incident beams parallel to $\langle 110 \rangle$ and $\langle 113 \rangle$ directions were continuously recorded using a TV-VTR system. *In-situ* dark field image observations of the formation and growth of athermal ω -phase crystals were also carried out from room temperature to 131 K. The images were recorded by a TV-VTR system and were processed by a Vizituniversal-system. Images were also taken using photographic films. High resolution electron microscope (HREM) images at 131 K were also recorded using the same system, and were image-processed.

III. Results and Discussion

Figure 1 shows dark field images of ω -phase crystals from an identical specimen. These images were taken using the same one diffraction spot from one variant of

ω -phase crystals⁽⁷⁾. Figure 1(a) shows as-quenched ω -phase crystals with a high density. The size is 1.5–3 nm, which is almost the same as that of Ti-14mass%Mo⁽⁸⁾ and Ti-11.5Mo-4.5Sn-6Zr⁽⁹⁾ (mass%) alloys. The specimen was cooled to 131 K, and the as-quenched ω -phase crystals were *in-situ* observed under electron irradiation. Figure 1(b) shows a result of the observation, and it is noted that their sizes and density are almost the same as those in the as-quenched state. Figure 1(c) shows an image from an area of the specimen held at 131 K for 1.8 ks, which was at approximately 1 μm from the area shown in Figs. 1(a) and (b). ω -phase crystals with a diameter of approximately 20 nm can be seen, but the density has decreased. Figure 1(d) shows an image from another area, which was also held at 131 K for 10.8 ks without electron irradiation. It is noted that an ω -phase crystal has grown to over 40 nm in diameter. Figures 1(c) and (d) clearly reveal that athermal ω -phase crystals are formed by cooling to and holding at 131 K without electron irradiation. It is also found that the shape of the crystals formed at 131 K is cuboidal or spherical (hereafter, described as spherical), and not linear. Therefore, it seems that the negative temperature dependence of electrical resistivity in a Ti-15Mo alloy results from the appearance of spherical athermal ω -phase crystals, as described in the introduction.

HREM observations of athermal ω -phase crystals

Fig. 1 Dark field images of athermal ω -phase crystals taken using the same diffraction spot of one ω -phase variant crystals in the same specimen: (a) as-quenched, (b) cooled to 131 K under electron irradiation, (c) cooled at 131 K for 1.8 ks without electron irradiation, and (d) cooled at 131 K for 10.8 ks without electron irradiation.

Fig. 2 An HREM image of an athermal ω -phase crystal formed by cooling at 131 K for 14.4 ks: (a) an original image recorded by a TV-VTR system, (b) a corresponding diffraction pattern, (c) a FFT diffraction pattern from (a), and (d) a processed image formed using 000 and intensities denoted by arrows in (c). Suffix M of a lattice spacing 0.23 nm indicates the matrix.

have been carried out to investigate the structure image using a TV-VTR system to reduce the effects of the incident beams, because athermal ω -phase crystals formed by cooling disappear due to electron irradiation, which will be described below, and moreover, electron beams are concentrated into a small area of specimens to take HREM images. **Figure 2(a)** shows an original HREM image of an athermal ω -phase crystal formed by cooling at 131 K for 14.4 ks with a diffraction pattern in $\langle 113 \rangle$ orientation as shown in Fig. 2(b). Figures 2(c) and (d) show the Fast Fourier Transformed (FFT) diffraction pattern and the processed lattice image, respectively. The processed image was formed using 000 and intensities denoted by arrows in Fig. 2(c). Lattice fringes of 0.40 nm and 0.23 nm which correspond to planar spacings of $\{\bar{1}010\}$ and $\{\bar{1}013\}$ planes, respectively, of the athermal ω -phase crystal can be revealed in the lattice fringe of 0.23 nm which corresponds to the planar spacing of the matrix $\{110\}$ plane.

In order to identify the starting temperature of the formation and growth of athermal ω -phase crystals, first, a thin foil specimen was cooled to 163 K. However, no formation of athermal ω -phase crystals was observed. Then, the specimen was cooled to 131 K, and a dark field image observation was carried out immediately. It is noted that athermal ω -phase crystals with a size of 10–20 nm were formed. The results of *in-situ* observations at 131 K are shown in **Fig. 3**. Figures 3(a)–(i) are dark field images and Figs. 3(j)–(r) are bright field images. All images were continuously recorded using a TV-VTR system. An ω -phase crystal denoted by an arrow in Fig. 3(a) becomes brighter after 1 s, but after 2 s is not recognized. In the same way, an ω -phase crystal denoted by an arrow in Fig. 3(c) appears, but the brightness gradually decreases as seen in Fig. 3(d) and the particle disappears in Fig. 3(e). Similar phenomena are also observed in the series of bright field images; in Fig. 3(o), three ω -phase crystals denoted by arrows are

Fig. 3 *In-situ* dark field and bright field images at 131 K immediately after the specimen was cooled to 131 K. The time intervals between images is 1 s, except 2 s between images (b) and (c), (h) and (i), and (l) and (m). Images (a)–(i) are dark field images taken using one spot of one ω -phase variant crystals. Images (j)–(r) are bright field images.

Fig. 4 *In-situ* dark field images showing the effect of electron irradiation on the stability of athermal ω -phase crystals formed by cooling at 131 K for 10.8 ks. Images were taken at (a) 0 s, (b) 8 s, (c) 22 s, (d) 45 s, (e) 70 s and (f) 124 s from the onset of the electron irradiation.

visible, although they are not observed 3–5 s earlier. After 1 s, these also disappear. Therefore, athermal ω -phase crystals formed in a specimen cooled at 131 K for a short time are not stable, and it seems that their life times are 1–2 s under electron irradiation. After observation for approximately 60 s, all ω -phase crystals disappeared.

One reason for the formation of ω -phase crystals due to cooling to 131 K is considered as follows: in the literature, it has been reported that ω -phase crystals in a Ti-20 mass%Mo alloy are formed by hydrostatic pressures over 0.7 GPa⁽¹⁰⁾. They are also formed by a compressive stress at the boundaries of the $\{11\bar{2}\}\langle 111\rangle$ twin band in a Ti-15Mo-5Zr (mass%) alloy⁽¹¹⁾, where the atomic distances are smaller than the nearest neighbour distance. In the former case, the stored elastic strain energy per unit volume due to a hydrostatic pressure of 0.7 GPa has been estimated as 0.022×10^{-10} Nnm/nm³⁽¹²⁾. In the present case, as the specimen is cooled from room temperature to 131 K, the specimen contracts. If the coefficient of thermal expansion is assumed to be the principal strain, it is possible to calculate the volume strain due to cooling based on the theory of elasticity. Consequently, the principal stress can be calculated. Using the coefficient of thermal expansion of a Ti-15V-3Al-3Cr-3Sn (mass%) alloy (8.41×10^{-6} K⁻¹)⁽¹³⁾, Young's modulus (90.0 GPa) and Poisson's ratio (0.343) of a Ti-20mass%Mo alloy⁽¹⁴⁾, the principal stress per 1 K can be calculated as approximately 0.72 MPa. Since the specimen was cooled from room temperature to 131 K, the calculated stress becomes approximately 0.12 GPa. Although we do not know the coefficient of thermal expansion, Young's modulus or Poisson's ratio of a Ti-15Mo alloy, a stress of 0.12 GPa is much smaller than the critical hydrostatic pressure of 0.7 GPa mentioned above. Therefore, it is

difficult to explain the origin of the formation and growth of athermal ω -phase crystals by considering only the volume contraction due to cooling.

Figure 4 shows a result of an *in-situ* dark field image observation at 131 K of ω -phase crystals, formed by holding the specimen at 131 K for 10.8 ks. These images were also taken using the same one diffraction spot from one variant of ω -phase crystals as in Figs. 1 and 3. The images indicate the effect of electron irradiation on the stability of the ω -phase crystals. The time intervals between images (a) to (f) are shown in each image. In Fig. 4(a), a large ω -phase crystal (approximately 50 nm in diameter) can be seen together with some small ω -phase crystals. It is noted that the size of the large ω -phase crystal does not change for 22 s, but, both the brightness and size decrease after 45 s. In Fig. 4(f), the ω -phase crystal has almost disappeared, and after 148 s has disappeared completely. The small ω -phase crystals can also be seen to disappear gradually. These results suggest that athermal ω -phase crystals formed by cooling to and holding at 131 K are rather weak to electron irradiation. Figure 5 shows another result of the same *in-situ* observation of athermal ω -phase crystals formed by cooling at 131 K for 1.8 ks. During the observation, an ω -phase crystal denoted by an arrow in Fig. 5(a) disappears in Fig. 5(c). Another ω -phase crystals denoted by arrows in Figs. 5(c) and (e) appear. It is also noted that their life times (6–15 s) are longer than those in Fig. 3, but shorter than that in Fig. 4.

It is known that during electron microscope observations, electron irradiation causes temperature rise and radiation damage of specimens. In order to investigate only the effect of temperature rise, the behaviour of ω -phase crystals formed by cooling to 131 K were observed with rising temperature, and each observation was

Fig. 5 *In-situ* dark field images of athermal ω -phase crystals formed by cooling at 131 K for 1.8 ks showing their annihilation and formation. It is noted that their life times are longer than those in Fig. 3, but shorter than that in Fig. 4.

carried out for only 5 s at each temperature to reduce the effect of electron irradiation as much as possible. The acceleration voltage of the electron microscope 160 kV was also adopted for the same purpose. **Figure 6** shows the result. In Fig. 6(a), athermal ω -phase crystals formed by cooling at 131 K for 5.4 ks are visible. As the temperature rises from 131 K to 200 K in 1680 s (heating rate: 0.041 K/s), these ω -phase crystals disappear as shown in Fig. 6(b), and only small ω -phase crystals such as those in as-quenched crystals can be seen. **Figure 7** shows another result. In Fig. 7(a), athermal ω -phase crystals formed under the same conditions as those in Fig. 6(a) are visible. However, the same temperature difference was generated in 780 s (heating rate: 0.088 K/s), and ω -phase crystals with almost the same size are visible in Fig. 7(b). These results clearly show that the effect of temperature rise on the annihilation of athermal ω -phase crystals formed by cooling under electron irradiation depends on the rate of the temperature rise.

It is known that martensitic transformations occur after incubation periods, and it is understood that the incubation periods depend inversely on the probability for particles such as atoms and electrons to go over the potential barrier, that exists between the matrix and martensitic phases⁽¹⁵⁾. Since the β to ω -phase transformation has a martensitic component⁽¹⁶⁾, it is also con-

sidered that the ω to β -phase transformation as shown in Figs. 6 and 7 includes the same component, that is, an incubation behaviour. Therefore, it is understood that the phenomena as shown in Figs. 6 and 7 result from the relationship between the incubation period and the period of temperature rise, that is, 1680 s exceeds the incubation period (Fig. 6), but 780 s does not (Fig. 7).

It is not easy to separate both the effects of temperature rise and radiation damage due to electron irradiation. However, it is interesting to compare the result of Fig. 4 with Fig. 7 although athermal ω -phase crystals in Fig. 7 were formed at 131 K for 5.4 ks. Figure 7(c) shows that athermal ω -phase crystals are annihilated due to electron irradiation at 200 K for 11 s even if the acceleration voltage and beam current are lower than those in the case of Fig. 4. Therefore, it seems that under electron irradiation, athermal ω -phase crystals observed at 200 K were annihilated earlier than those observed at 131 K as shown in Fig. 4. That is, in the former case, the annihilation takes 11 s, but in the latter case, 124 s. This fact suggests that the higher the specimen temperature the earlier the annihilation of athermal ω -phase crystals under electron irradiation occurs.

In addition, during the temperature lowering, the formation of athermal ω -phase crystals at 163 K was not observed as mentioned above (cooling rate: 0.067 K/s),

Fig. 6 Effect of temperature rising from 131 K to 200 K in 1680 s on the stability of athermal ω -phase crystals formed by cooling at 131 K for 5.4 ks. (a) athermal ω -phase crystals at 131 K, (b) annihilation of athermal ω -phase crystals after the specimen temperature rose to 200 K for 1680 s (the heating rate is 0.041 K/s).

Fig. 7 An effect of temperature rising from 131 K to 200 K for 780 s on the stability of athermal ω -phase crystals formed by cooling at 131 K for 5.4 ks. (a) athermal ω -phase crystals at 131 K, (b) remaining athermal ω -phase crystals after the specimen temperature rose to 200 K for 780 s (the heating rate is 0.088 K/s), and (c) After electron irradiation for 11 s, athermal ω -phase crystals disappeared.

but, during the temperature rising, athermal ω -phase crystals formed by cooling at 131 K was still observed at 165 K (heating rate: 0.04 K/s). These results suggest that the $\beta \rightleftharpoons \omega$ phase transformations indicate hysteresis.

IV. Summary

In order to clarify the formation and morphology of athermal ω -phase crystals in Ti-15mass%Mo alloys cooled to and held at 131 K, *in-situ* dark field image observations and HREM observations were carried out. The formation and growth of athermal ω -phase crystals were confirmed. Their annihilation due to electron irradiation and temperature rise are discussed. The results obtained are as follows:

(1) Athermal ω -phase crystals with spherical shape and a size of 20–30 nm were formed by the cooling in areas that were not irradiated by electrons. HREM images of the athermal ω -phase crystals revealed clearly the structure image of ω -phase crystals. It seems that the formation of the athermal ω -phase crystals accounts for the negative temperature dependence of electrical resistivity. However, no formation of athermal ω -phase crystal was observed in areas irradiated by electrons.

(2) Athermal ω -phase crystals formed by the cooling were annihilated by electron irradiation, and the stability depended on the holding period at 131 K; the longer

the period, the more stable the crystals became.

(3) It seems that the annihilation behaviour of athermal ω -phase crystals due to electron irradiation was remarkable in a specimen held at a temperature higher than 131 K.

(4) The annihilation caused by the temperature rise from 131 K to 200 K is a function of time. The annihilation was noticed at 1680 s, but not at 780 s. This fact suggests that an incubation time exists in the case of the ω to β transformation.

(5) It seems that the $\beta \rightleftharpoons \omega$ phase transformations indicate hysteresis.

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