

The athermal $\alpha \rightarrow \omega$ transformation in Zr-2 at % Nb alloy

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The athermal $\alpha \rightarrow \omega$ transformation in Zr-2 at. % Nb alloy has been investigated by transmission electron microscopy. Analysis of the selected-area diffraction pattern has shown that the orientation relationships between the omega and the parent α -phase in quenched Zr-2 at. % Nb alloy are the same as have been previously observed for the $\alpha \rightarrow \omega$ reaction in pure zirconium. Thus it was deduced that the direct $\alpha \rightarrow \omega$ transition has taken place in the alloy during cooling. The α -originated ω -particles were visualized using the dark-field technique. The formation of the athermal omega in the α -region of β -stabilized Zr-Nb alloy is discussed in terms of the relative positions of the free energy equilibrium curves $T_0^{\beta \rightarrow \alpha}$, $T_0^{\beta \rightarrow \omega}$, $T_0^{\alpha \rightarrow \omega}$ and the corresponding $M_s^{\beta \rightarrow \alpha}$, $M_s^{\beta \rightarrow \omega}$ and $T_s^{\alpha \rightarrow \omega}$ start curves. It is concluded that the omega phase can occur over a much wider range of alloy compositions than is usually recognized on the basis of $\beta \rightarrow \omega$ transformation data.

1. Introduction

There have been many studies of omega transformation in β (bcc)-stabilized zirconium alloys. It was recognized [1, 2] that the ω -phase forms in β -metastable alloys over a limited concentration range either upon quenching ("athermal" omega) or during ageing. Cometto *et al.* [3] established that in Zr-Nb, "athermal" omega appears in β -metastable alloys containing 7-17.5 at.% Nb, but at lower solute content, in the α -martensitic region (hcp-structure), the ω -phase was not found.

In addition to its formation in β -stabilized alloys, the ω -phase has been observed in pure α -zirconium after the application of high pressure at room temperature [4, 5]. In addition, our very recent experiments [6] have shown that the omega also appears in pure zirconium at atmospheric pressure after cooling below 200 K.

While the mechanism of athermal $\beta \rightarrow \omega$ transformation has received extensive study (see, for example, [7]), very little has been done with regard to the $\alpha \rightarrow \omega$ reaction. In recent work [8], the atomistic description of the $\alpha \rightarrow \omega$ transition has been suggested and α/ω orientation relationships were inferred demonstrating three

variants of ω particles in the α -matrix, as being essentially different from those established for β/ω transformation (four variants). These results, in their turn, offered the possibility of determining unambiguously whether the observed ω -phase is a result of $\alpha \rightarrow \omega$ transformation (in this case the α/ω orientation relationships take place), or whether the ω -phase originates from the β -phase satisfying β/ω orientation relations to the parent phase [1, 2].

The question which arises now is as follows: if the omega appears upon cooling in pure Zr, why not make an attempt to observe the athermal omega in the α -region of Zr alloy with low solute content?

In this paper we will report our TEM observations of the omega which appears in α -parent phase in Zr-2 at.% Nb alloy upon quenching to room temperature. These results lead us to the conclusion that the ω -phase in Zr alloys can occur over a much wider composition range than was thought previously.

2. Experimental procedure

Zr and Nb metals of spectroscopic purity were

used to produce a 5 g button of Zr-2 at. % Nb alloy. The button was arc-melted five times under an argon atmosphere and then homogenized at 1000°C under a vacuum of 2×10^{-6} torr. Then the button was cut into slices and the slices were cold rolled to 150 μm thick foils. The foils were annealed for 3 h at 1000°C in vacuum of 2×10^{-6} torr and then drop-quenched in the vacuum into water-cooled DC704 diffusion pump oil.

Several TEM specimens were punched from the quenched foils and thinned in a "TENUPOL"-twin jet electropolishing unit under the conditions described in [8].

The structures were examined using a JEOL-200B electron microscope operating at 200 kV.

3. Experimental results

Fig. 1 shows a selected-area diffraction pattern (a) and its indexed schematic diagram (b) obtained for Zr-2 at. % Nb alloy which was quenched from the β -field to room temperature. The diffraction pattern contains both α -reflections, which are shown in Fig. 1b as open circles, and the ω -reflections, which are represented by black spots. Some ω -reflections are superimposed on α -reflections, for example, $000\bar{2}\omega_1$ coincides with $2\bar{1}0\alpha$ and $\bar{2}\bar{2}40\omega_3$ coincides with 20.2α . The reflections in the diffraction pattern which are due to double diffraction are not shown in Fig. 1b.

The orientation relationships between alpha and omega which can be deduced from Fig. 1 are consistent with those suggested for α/ω transformation [8], with three possible variants of ω -particle orientation with respect to the

α -matrix. Thus in Fig. 1b the subscript 1 refers to the ω -reflections which are indexed in terms of variant 1 ($[0001]\omega_1 \parallel [\bar{2}110]\alpha$, $(0001)\alpha \parallel (1\bar{2}10)\omega_1$) and subscript 3 refers to variant 3 ($[0001]\omega_3 \parallel [\bar{1}2\bar{1}0]\alpha$, $(0001)\alpha \parallel (1\bar{2}10)\omega_3$).

The crystallographic α/ω relation corresponding to variant 3 is illustrated in Fig. 2 where the $(0001)\alpha$ and $(1\bar{2}10)\omega$ stereographic projections have been superimposed so that $[0001]\omega \parallel [\bar{1}2\bar{1}0]\alpha$. The large circle drawn as a thick solid curve corresponds to the zone of α -reflections observed in the diffraction pattern. This large circle is very close to the zone of ω_3 -reflections (dashed curve) as must be expected for an ω_3 -variant.

Variant 1 can be obtained by rotating the ω -stereographic projection about the $(0001)\alpha$ pole so that positions of the $(0001)\omega$ pole and the $(\bar{2}110)\alpha$ pole will coincide. Thus the large circle drawn as a thin solid curve, which corresponds to the $0002, 0\bar{2}20, 0\bar{2}22$ omega planes, will lie close to the zone of α -reflections, leading to the appearance of $(000\bar{2})\omega_1$, $(0\bar{2}20)\omega_1$, $(0\bar{2}22)\omega_1$ reflections, as is observed in the diffraction pattern in Fig. 1.

Since the relations between omega and alpha are found to obey α/ω orientation relationships established in [8], it is reasonable to conclude that the direct $\alpha \rightarrow \omega$ transformation has taken place and the athermal α -originated omega has occurred in as-quenched Zr-2 at. % Nb alloy.

The ω -particles in the α -parent phase are clearly seen in the dark-field image (Fig. 3a) which was formed using an ω -reflection. The morphology of ω -particles appearing in Zr-2 at. % Nb alloy strongly resembles the morphology of omega obtained in pure zirconium [6]. A bright-field

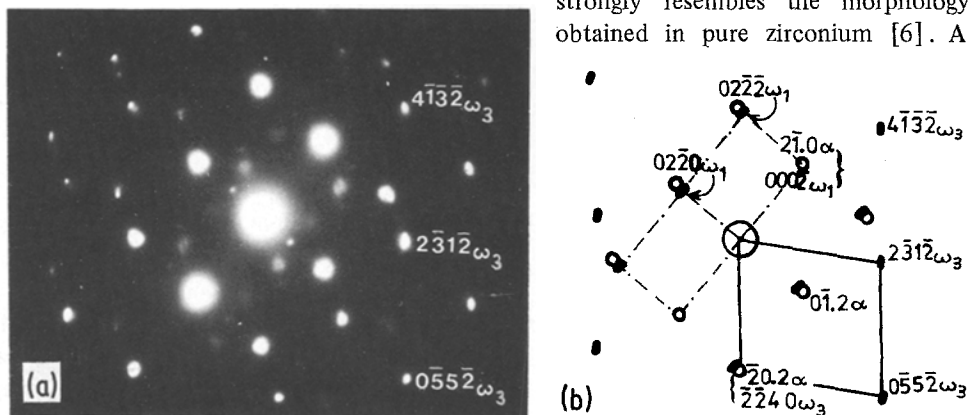


Figure 1 Zr-2 at. % Nb alloy quenched to room temperature. (a) Selected-area diffraction pattern showing two of the three possible variants of the ω -phase reflections which were indexed in terms of α/ω orientation relationships. (b) Key to (a). Open circles indicate α -reflections. Black spots refer to ω -reflections. Subscripts 1 and 3 refer to omega variant 1 and 3, respectively.

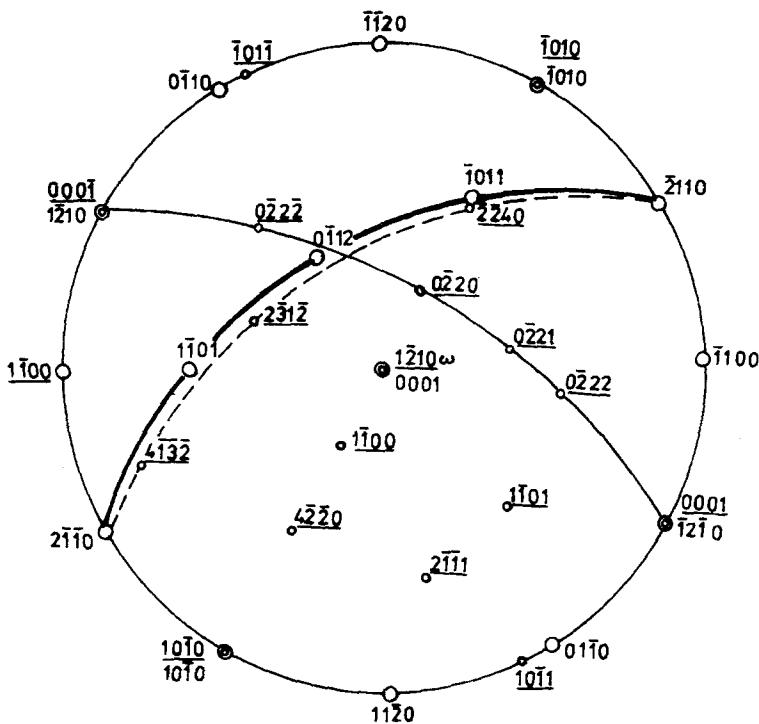


Figure 2 Superimposed stereogram illustrating the positions of diffraction zones for α -reflections (thick solid curve), ω_1 reflections (thin solid curve) and ω_3 reflections (dashed curve).

electron micrograph of as-quenched Zr-2 at.% Nb specimen is shown in Fig. 3b.

4. Discussion

The formation of the ω -phase due to the $\alpha \rightarrow \omega$ transformation in quenched alpha Zr-2 at.% Nb alloy can be closely correlated with the appearance of the ω -phase in pure α -Zr after cooling to temperatures less than 200 K [6]. A useful framework for discussing these results is the construction of a plot of $T_s^{\alpha \rightarrow \omega}$ against X which represents the variation of the start temperature T_s (at which the $\alpha \rightarrow \omega$ reaction begins on cooling) with solute

content X . Such a line for the Zr-Nb system can be derived in the following way.

In Fig. 4 one can see the experimental start temperature curves $M_s^{\beta \rightarrow \alpha}$ and $T_s^{\beta \rightarrow \omega}$ which were determined by Hatt *et al.* [9] and Cometto *et al.* [3], respectively. The point at 695°C for pure Zr was deduced from the data on $\beta \rightarrow \omega$ transition in pure zirconium at high pressures obtained by Jayaraman *et al.* [5]. The point at 865°C, which was taken from Hansen [10] represents the equilibrium temperature of the allotropic transformation $\beta \rightarrow \omega$ in zirconium. Comparing the position of this latter point with

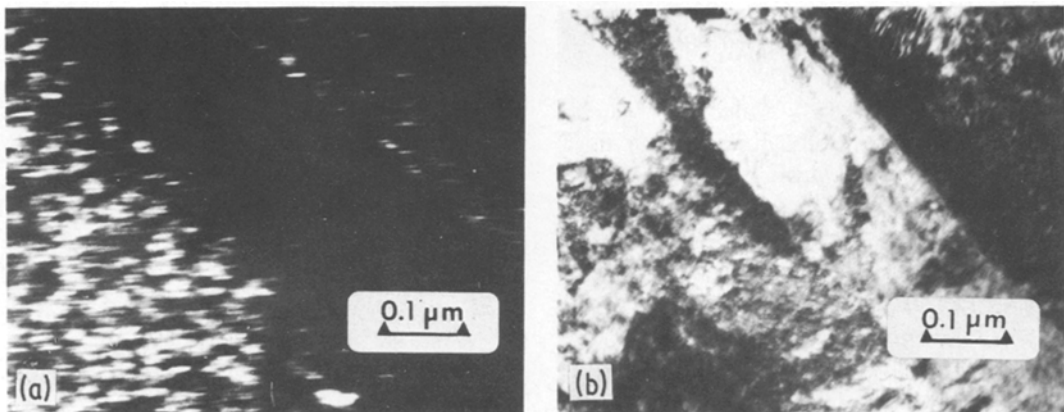


Figure 3 Electron micrographs for the Zr-2 at.% Nb as-quenched alloy. (a) Dark-field image formed in the ω -reflection. ω -particles appear as thin plates. (b) Bright-field image of the alloy.

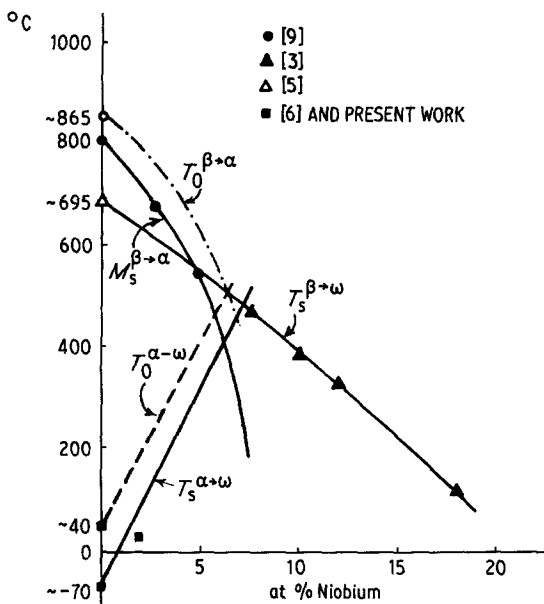


Figure 4 The relative positions of the free energy equilibrium curves $T_0^{i \rightarrow j}$ and the corresponding start temperature curves $T_s^{i \rightarrow j}$ for the Zr-Nb system.

the $M_s^{\beta \rightarrow \alpha}$ temperature for pure zirconium obtained in [9], we conclude that the curve $T_0^{\beta \rightarrow \alpha}$ against X (dash-dotted line designated $T_0^{\beta \rightarrow \alpha}$ in Fig. 4), which represents the variation of free energy equilibrium temperature $T_0^{\beta \rightarrow \alpha}$ with composition X , should lie slightly above the plot of $M_s^{\beta \rightarrow \alpha}$ against X and approximately parallel to it, with the difference ($T_0 - M_s$) being of the order of 70°C.

In the case of $\beta \rightarrow \omega$ transformation, the curve $T_s^{\beta \rightarrow \omega}$ against X and the free energy equilibrium curve $T_0^{\beta \rightarrow \omega}$ against X should be approximately superimposed, since the diffusionless $\beta \rightarrow \omega$ transformation was observed to be completely reversible with negligible hysteresis [3]. Therefore it may be concluded, that the strain energy involved in this transformation is small enough, thereby allowing the use of approximation $T_0^{\beta \rightarrow \omega} \simeq T_s^{\beta \rightarrow \omega}$.

The intersection of the $T_0^{\beta \rightarrow \alpha}$ and $T_0^{\beta \rightarrow \omega}$ curves yields the triple point through which the third line $T_0^{\alpha \rightarrow \omega}$ against X (which is where the free energy difference $\Delta F^{\alpha \rightarrow \omega}$ is zero) must pass. On the other hand, the curve $T_0^{\alpha \rightarrow \omega}$ against X must intersect the zirconium axis at the point of $\sim +40^\circ\text{C}$, as was determined in [6]. The combination of these factors allows to trace the position of the plot of $T_0^{\alpha \rightarrow \omega}$ against X as a straight line passing through the triple point and $+40^\circ\text{C}$ for pure zirconium, as illustrated in Fig. 4 (dashed line).

Since the $T_s^{\alpha \rightarrow \omega}$ temperature for pure Zr was found to be of the order of -70°C [6], it is reasonable to assume that the curve $T_s^{\alpha \rightarrow \omega}$ against X should be located below the $T_0^{\alpha \rightarrow \omega}$ against X curve and parallel to it with the difference ($T_0 - M_s$) being of the order of 110°C.

It is now possible to estimate the $T_s^{\alpha \rightarrow \omega}$ temperature, which turns out to be $\sim 90^\circ\text{C}$ for Zr-2 at.% Nb alloy. This implies that the ω -phase can virtually form by $\alpha \rightarrow \omega$ transformation in Zr-2 at.% Nb alloy on quenching to room temperature, as was experimentally observed in the present work.

The sequence of metastable phases which occur in Zr-2 at.% Nb alloy during quenching from the β -field should be as follows. In the course of cooling the $\beta \rightarrow \alpha$ reaction begins first, when the temperature drops below $M_s^{\beta \rightarrow \alpha}$. This reaction should be accomplished before the temperature becomes less than $T_s^{\beta \rightarrow \omega}$ (therefore β -originated omega was not observed in the quenched alloy). Then during cooling the line $T_s^{\alpha \rightarrow \omega}$ is crossed and $\alpha \rightarrow \omega$ transformation is initiated. Thus in the final structure we observe the α -phase and the alpha-originated ω -phase.

It is instructive now to correlate the occurrence of omega in pure zirconium and the emergence of this phase under suitable conditions in the alpha region of the zirconium-niobium alloy. Taking into account the result of the present work we can conclude that the omega phase can occur over a much wider range of alloy compositions than that which was recognized on the basis of the data on $\beta \rightarrow \omega$ transitions.

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