The Precipitation Behavior of a Zr-2.5 Wt Pct Nb Alloy

C. P. LUO and G. C. WEATHERLY

The morphology, crystallography, and nature of precipitates in a quenched and aged Zr-2.5 wt pct Nb alloy has been studied by transmission electron microscopy. The needle-shaped matrix precipitates and equiaxed twin boundary nucleated precipitates produced by aging at 500 °C were the equilibrium Nb-rich β1 phase. On aging at 600 °C, the matrix precipitation was a mixture of β2 needles and coarse metastable Zr-rich β1 particles, while only β1 particles were found at twin boundaries. The growth direction of the needle-shaped particles, 6.6 deg to 8.2 deg from (1100)h, and their orientation relationship can be predicted by an invariant line strain model. The β1 precipitates have the Burgers orientation relationship. The formation of metastable β1 and stable β2 particles is considered from the free energy approach of Menon, Banerjee, and Krishnan.

I. INTRODUCTION

The Zr-2.5 wt pct Nb alloy finds extensive use in pressure tube applications in the nuclear power industry because of its low neutron absorption cross section, high corrosion resistance, and excellent creep properties. When the alloy is quenched from the β phase field and aged below the monotectoid temperature of 610 °C, precipitation hardening occurs. The as-quenched alloy, α' martensite, contains acicular plates with (1010)h internal twins. Upon aging the martensite at 500 °C for 240 hours, Williams and Gilbert observed both needle-like and spherical precipitates in the matrix and at twin boundaries. The precipitates being a Nb-rich bcc phase with a lattice parameter of 0.331 nm. These observations were confirmed in a later study by Sabol, who used aging temperatures from 400 to 600 °C to study the precipitation behavior.

However, Banerjee et al. found that at 550 and 600 °C, only the Zr-rich β1 phase (bcc) with a = 0.352 nm formed, while at 500 °C the Nb-rich β2 phase, a = 0.334 nm, was observed. Banerjee et al. also reported that both the matrix and twin-nucleated precipitates had an identical orientation relationship—the Burgers relationship.

In this study the results of a detailed investigation of the morphology, orientation relationship, and nature of the precipitates formed in a quenched and aged commercial Zr-2.5 wt pct Nb alloy are presented. Two types of precipitates are found, in agreement with the study of Banerjee et al. The β2 precipitates are needle-shaped and an invariant line strain model proposed by Dahmen is used to predict both the growth direction and crystallographic orientation of the particles. The coarser β1 precipitates have a more equiaxed morphology, and have the Burgers orientation relationship.

II. EXPERIMENTAL PROCEDURE

Small sections were removed from a commercially produced Zr-2.5 wt pct Nb pressure tube* and cold rolled to 0.5 mm thick strips with intermediate anneals at 900 °C for 1 hour in vacuum. The strips were then sealed in evacuated quartz tubes, back-filled with argon, solution treated at 1000 °C for 20 minutes, and water quenched, followed by aging in vacuum for up to 240 hours at 500 °C or 60 hours at 600 °C. The aged samples were chemically thinned in a solution containing 5 parts HF, 45 parts HNO3, and 50 parts water. TEM foils were prepared from the strips using a twin-jet thinning device with a solution of 6 vol pct perchloric acid, 35 vol pct butanol, and 59 vol pct methanol at −30 °C and a current density of 4.8 A/cm².

All TEM observations were carried out on a Hitachi H800 200 kV transmission electron microscope equipped with a double-tilt specimen holder.

III. RESULTS

A. As-Quenched Microstructures

In the as-quenched condition, the alloy consisted of α' martensite plates (HCP), many of which were internally twinned (Figure 1a). A selected area diffraction pattern taken from the twinned area (Figure 1b) shows the twinning plane to be {1011}h in agreement with previous reports. The twinning angle, i.e., the angle between the reciprocal lattice vectors (1011) and (1100), in the [1120]h zone depended on the c/a ratio, being, respectively, 56.8 deg, 57.1 deg, and 57.2 deg for the c/a values of 1.603, 1.591, and 1.590 measured in this study (Table I). A cross-check on the c/a measurement obtained by conventional methods is therefore possible by measuring this twinning angle.

B. 500 °C Aged Microstructures

Figure 2 shows the precipitate morphologies obtained by aging at 500 °C for 240 hours. In those α' plates without internal twins, needle-like Nb-rich precipitates, denoted β2 by Banerjee et al., were observed (Figure 2a). On tilting the foil to a position with the common vectors (0002)h/(1100),

*The major impurities in the commercial alloy are O (1000 to 1300 ppm by weight) and Fe (300 to 700 ppm). All other impurities are present at a level of 100 ppm or less.

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tion to the needle-like precipitates formed both within the matrix and twins, more equiaxed precipitates were found to be precipitated at the twin boundaries (Figure 2(c)). Although some of the twin-boundary nucleated precipitates appear to be growing into the matrix in directions parallel to the needle planes (Figure 2(c)), on tilting to the (0002)h position (e.g., Figure 2(b)), no unique growth direction could be detected for these precipitates. In Figure 2(c) the twin boundaries lie almost parallel to the electron beam, but on tilting so that the twin boundaries are nearly normal to the beam, the twin boundary-nucleated precipitates appear to be evenly distributed within the matrix. At this orientation these might be misinterpreted as spherical matrix precipitates. This is more clearly shown in Figure 2(d) where the twin planes are lying at ~60 deg to the electron beam, giving the appearance of "ghost" twin boundaries. Banerjee et al. explained these as being the traces of twins which have dissolved as the precipitates grew. However, an image such as Figure 2(d) could always be restored to one such as Figure 2(c) by tilting the foil so that the twin planes lay parallel to the electron beam, with the equiaxed precipitates always lying at the twin boundaries. This observation suggests that there are only two distinct precipitate morphologies in the 500 °C aged microstructure, a needle-like precipitate in the matrix and an equiaxed precipitate lying at the twin boundaries.

C. 600 °C Aged Microstructures

Needle-like matrix precipitates were again found within both the untwinned and twinned α' plates (Figures 3(a) and (c)), with coarser twin boundary precipitates (Figure 3(c)). In addition, a third precipitate morphology, a more massive matrix precipitate, was observed either to coexist with the other two precipitate types or on its own. In the vicinity of the coarse matrix precipitates few, if any, needle-like precipitates were observed, but in the majority of the untwinned α' plates, the needle-shaped particles were dominant. These observations suggest that the formation of these two types of precipitates are competitive reactions at the 600 °C aging temperature. This was confirmed by lattice parameter measurements (see Table I and the next section) which demonstrated that the coarse matrix and twin nucleated precipitates were the Zr-rich phase (denoted β1 by Banerjee et al.), whereas the needle-shaped precipitates were the Nb-rich β2. The β2 precipitates again showed strain field

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Table I. Summary of Crystallographic Information Obtained from Bcc Precipitates

<table>
<thead>
<tr>
<th>Heat Treatment Condition</th>
<th>Aged 240 Hours/500 °C</th>
<th>Aged 60 Hours/600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-Quenched</td>
<td>Needles</td>
</tr>
<tr>
<td>(c/a)_h</td>
<td>1.603</td>
<td>1.591</td>
</tr>
<tr>
<td>a (nm)</td>
<td>0.321 ± 0.01</td>
<td>0.322 ± 0.002</td>
</tr>
<tr>
<td>ab (nm)</td>
<td>0.331 ± 0.0015</td>
<td>0.331 ± 0.0015</td>
</tr>
<tr>
<td>θ/θ*</td>
<td>1.028 ± 0.003</td>
<td>1.028 ± 0.003</td>
</tr>
<tr>
<td>O. R. (γ °)**</td>
<td>3.8 ± 0.1</td>
<td>4.5 ± 0.1</td>
</tr>
<tr>
<td>Growth</td>
<td>8.2 ± 1.0</td>
<td>6.6 ± 0.8</td>
</tr>
</tbody>
</table>

*As measured directly from patterns containing reflections from both phases.
**As defined in Section III-E.