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Accroissement de la précipitation dans l'alliage Zr-2,5Nb par irradiation aux protons

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Whiteshell Laboratories
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RÉSUMÉ

On a irradié aux protons de 3,6 MeV l'alliage Zr-2,5Nb recuit pour savoir si l'irradiation aux protons accroîtra la précipitation de la phase β riche en Nb dans les grains α. L'examen au microscope électronique à transmission d'une feuille mince, après irradiation à 770 K pendant 18 h et à 720 K pendant 264,5 h ayant causé une détérioration totale de 0,94 dpa, a révélé une dispersion fine de précipités dans les grains α. L'analyse par diffraction des neutrons des précipités a révélé qu'ils comportent des espacements de plans réticulaires correspondant à la phase β riche en Nb. Ce résultat concorde avec la précipitation de la phase β observée après l'irradiation aux neutrons et appuie donc l'application de l'irradiation par les protons pour simuler les effets de l'irradiation par les neutrons dans l'alliage Zr-2,5Nb.

On a présenté cette communication à la Conférence intitulée «Evolution of Microstructure in Metals During Irradiation» (Évolution de la microstructure dans les métaux au cours de l'irradiation) qui a eu lieu à Muskoka, en Ontario, du 29 septembre au 2 octobre 1992; celle-ci sera publiée dans la revue "Journal of Nuclear Materials".

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ABSTRACT

A 3.6 MeV proton irradiation of annealed Zr-2.5Nb has been performed to determine whether proton irradiation will enhance the precipitation of Nb-rich β-phase precipitates within the α-grains. A transmission electron microscope examination of a foil after irradiation at 770 K for 18 h and at 720 K for 264.5 h to a total damage of 0.94 dpa revealed a fine dispersion of precipitates within the α-grains. Electron diffraction analysis of the precipitates found they have lattice plane spacings consistent with the Nb-rich β-phase. This result is in agreement with the β-phase precipitation observed following neutron irradiation, and thus it supports the use of proton irradiation to simulate neutron-irradiation effects in Zr-2.5Nb.

This paper was presented at the Evolution of Microstructure in Metals During Irradiation Conference held in Muskoka, Ontario, 1992 September 29 to October 2 and will be published in the Journal of Nuclear Materials.

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VALUE AND IMPLICATIONS

Proton irradiation has the potential to accelerate experiments to study the effects of irradiation on the annulus gas corrosion of Zr-2.5Nb pressure tube material. For proton irradiation to be a valid simulation of neutron irradiation, it is necessary that the proton irradiation cause precipitation of Nb-rich particles in the α-phase as observed under neutron irradiation. The results described in this report confirm that proton irradiation does enhance the precipitation of Nb particles within the α-phase.

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CONTENTS

1. INTRODUCTION

Pressure tubes in CANDU (CANada Deuterium Uranium; registered trademark) reactors are made from the alloy Zr-2.5Nb. Its resistance to corrosion and oxidation in water or moist air is greatest when the α-phase contains the maximum amount of Nb in solution without being supersaturated. In laboratory experiments below 870 K, the α-phase of cold-worked or annealed material remains supersaturated with Nb. In contrast, during neutron irradiation in CANDU reactors β-Nb precipitates are observed in the α-grains after 1 to 2 years for irradiation temperatures of 570 K (Griffiths et al. 1992). This results in the composition of the α-phase decreasing towards the equilibrium value. Consequently, the corrosion and oxidation rates are reduced by neutron irradiation (Urbanic and Gilbert 1990). If corrosion experiments are to be done using protons to simulate neutrons, for a valid simulation the proton irradiation should generate similar microstructural changes to those produced by neutron irradiation. The objective of this experiment was to test whether β-Nb precipitates were produced in the α-phase of Zr-2.5Nb by proton irradiation in a repeat of a similar experiment using neutrons (Coleman et al. 1980).

2. EXPERIMENTAL PROCEDURE

To provide a simple starting microstructure, material from the same pressure tube as used for the neutron irradiation (Coleman et al. 1980) was annealed at 970 K for one hour, to produce equiaxed α-grains with a low dislocation density and with the β-phase confined to the α-grain boundaries. Foils 170 μm thick were cut from the annealed tube with a continuous wire spark machine. The thickness of these foils was further reduced to 50 μm by lapping, and standard pickling and electropolishing techniques. Specimens with an area for proton irradiation of 4 mm wide by 25 mm long were then cut from these foils. The 50 μm foil thickness was required so that the 3.6 MeV protons would pass completely through the foils. Should the protons be stopped within the foils, they might result in the precipitation of small zirconium hydrides, which could confuse the identification of any irradiation-enhanced precipitation of the β-Nb phase.

The high-energy proton beam was obtained using a Van de Graaff accelerator to energize the protons to 3.6 MeV. The energy spread in the beam was limited to $\pm$ 0.2 MeV by the use of a combination of quadrupole focusing magnets and slits. To ensure even irradiation over the whole specimen, the beam was scanned over an area slightly larger than the specimen at a vertical scan rate of 112 Hz and a horizontal scan rate of 4 kHz. During the irradiation, the specimen was maintained at the required temperature by a combination of proton beam heating and direct current heating controlled by an infrared pyrometer.

Initially, we planned to perform the irradiation at 770 K to minimize obscuring irradiation damage and maximize the nucleation and growth of identifiable precipitates. To minimize specimen oxidation during the proton irradiation, the specimen was maintained in a He gas atmosphere at a pressure 7.0 kPa above atmospheric pressure. The He was first purified by passing it over uranium turnings at 490 K to remove residual O_2 and H_2O. Further reduction of these residual gases was achieved by heating two pieces of Zr foil to dull red (~ 820 K) within the specimen chamber. However, after 18 h at 770 K, the specimen was oxidizing at a rate sufficient to completely oxidize the specimen during the irradiation. To prevent this, the specimen's temperature was lowered to 720 K after 18 h, and the irradiation continued for an additional 264.5 h, to accumulate a total damage of 0.94 dpa based on calculations using the E-DEP-1 computer code (Manning and Mueller 1974). As a control experiment, foils with the identical specimen fabrication route were either sealed in evacuated glass capsules or placed in a similar He atmosphere and then given the same heat treatment as the proton-irradiated specimen. These different control specimens were prepared to determine whether the oxide layer and the associated increased oxygen concentration in the metal matrix might have an effect on the precipitation in the α-Zr phase.

A series of 3-mm diameter discs for preparation as transmission electron microscope (TEM) specimens were punched from the proton-irradiated and unirradiated foils. To remove the oxide surface layer on the foils exposed to the He atmosphere, the discs were given a preliminary ion thinning until the underlying metal matrix was exposed. These discs and those from the foil in the evacuated capsule were then thinned by electropolishing to produce electron transparent areas for examination at 200 kV in an JEOL 200B TEM.

3. RESULTS

The microstructure of the starting 50-μm foil material is shown in Fig. 1. It consisted of equiaxed α-grains, 3 to 4 μm in diameter, with β-phase occurring at triple points and as ribbons between the α-grains. The β-phase appeared homogeneous, with no ω-phase particles visible. Some small (0.02 to 0.2 μm in diameter) globular β-phase particles were found within a few of the α-grains. These may be remnants of the β-phase ligaments in the original pressure tube material after grain growth during the annealing heat treatment.

The α-grains in the foils heat treated the same as the proton-irradiated specimen were similar in appearance to those in the starting foil (see Fig. 2). However, the β-phase ribbons and grains at the α-grain boundaries in these heat-treated foils were found to have decomposed into arrays of individual β-phase particles. The β-phase lattice parameters determined from electron diffraction analysis of these particles showed them to be Nb-rich [4,5], with Nb concentrations ranging from 72 to 88 at.%. The microscope camera constants used for determining the β-phase parameters were found from measurements of the lattice parameters in adjacent α-phase grains. The α-grains in the foils heat treated in the He atmosphere and in the evacuated glass capsules were both found to be generally free of β-phase precipitates.

The β-phase particles resulting from decomposition of the grain-boundary ribbon and triple-point β-phase in the proton-irradiated foil were similar in appearance to those in the heat-treated foils. Lattice parameters determined from electron diffraction patterns gave Nb concentrations ranging from 82 to 90 at.%. Within the α-grains of this specimen, small platelet, or needle-like precipitates, were observed, often under the same diffracting conditions used to image the β-phase particles at the α-grain boundaries. Corresponding bright-field and dark-field electron images of these platelets are shown in Fig. 3. These platelets were found to vary in size from 5 to 40 nm in length. Dark-field stereo images confirmed that the platelets were within the foil and not surface artifacts. The crystallographic planar spacings calculated from the electron diffraction spots used for dark-field imaging of the platelets in different α-grains were all consistent with those predicted lattice plane spacings in high Nb concentration β-Nb phase in Zr-2.5Nb (Berghout 1962, Knapton 1960).

4. DISCUSSION

The TEM examination of the foils from before and after heat treatment and after irradiation revealed that the continuous β-phase initially present at α-grain boundaries had decomposed into individual Nb-rich β-phase particles in the irradiated and the heat-treated specimens, in agreement with the predictions of Cheadle and Aldridge (1973). The similar Nb enrichments of the β-phase particles at the grain boundaries in the heat-treated and the proton-irradiated foils show that a similar degree of β-phase decomposition had occurred in both foils.

During the irradiation, the surface oxides on this foil increased in thickness, due to oxygen pickup from the surrounding He gas. Based on the electropolishing time required during the subsequent TEM specimen preparation, it was estimated that the metal thickness remaining after the irradiation was approximately 25 μm. Metallography of the cross section of the control specimen heat treated in the He atmosphere showed that the oxide layer on each surface of this foil was a quarter of the foil thickness, thus also leaving a 25 μm thick metal layer. As shown in Fig. 2, the TEM examination of this layer in the control specimen revealed no precipitates in the α-grains. This result shows that neither the stresses within the metal due to surface oxide layers, nor the increase of oxygen within the metal due to diffusion in from the oxide layers, is causing the formation of the precipitates in the α-grains. Calculations, assuming oxygen diffusion in from the plane surfaces of the foil (Crank 1956) and grain-boundary oxygen diffusion rates in α-Zr (Ritchie and Atrens 1977) predict an oxygen concentration increase from 0.6 to 2.1 at.% at the centre of the metal layer after the irradiation heat treatments.

The small platelet precipitates were only observed in the proton-irradiated foil. These precipitates are similar in morphology to the "sword-shaped" precipitates reported by Coleman et al. (1980) following neutron irradiation of similar material. The precipitates observed after neutron irradiation at 770 K were 250 to 1000 nm in length, while those at 670 K were 5 to 30 nm long (Coleman et al. 1980). In comparison, the precipitates in the proton-irradiated samples were 5 to 40 nm in length. Based on an interpolation of the neutron-irradiation results to 720 K, larger precipitates than observed after the proton irradiation would be expected at this temperature. However, the smaller size of the precipitates after proton irradiation may be due to the different irradiation times: 1350 h and 282.5 h for the neutron and proton irradiations, respectively. Since the calculated irradiation damage for the neutron irradiation, 0.62 to 0.74 dpa, is less than that for the proton irradiation, 0.94 dpa, total damage is not likely a factor in the size difference.

The identification of the platelets as the Nb-rich β-phase is based on the measurement of the spacings of diffraction spots used for imaging the platelets in the dark-field images. These spots were found to have planar spacings consistent with those expected from (110) planes in the Nb-rich body-centred cubic (bcc) β-phase. In addition, in some cases, the Nb-rich β-phase particles at the α-grain boundaries were also in contrast during imaging with these spots. The diffraction spot spacings are also close to those predicted for {200} reflections in δ- and γ-zirconium hydride. However, during examination of the diffraction patterns from the precipitates, no lowest-order hydride reflections, {111}, were found. The absence of these reflections strongly suggests that the precipitates are not hydrides. The small size of these precipitates prevented two-dimensional electron diffraction patterns from being obtained to confirm the bcc structure. Their small size, and the fact that they are embedded in an α-Zr matrix, has also prevented confirmation of Nb enrichment by chemical analysis using energy-dispersive X-ray spectrometry.

5. CONCLUSION

A fine dispersion of precipitates was observed within the α-grains in annealed Zr-2.5Nb alloy following 3.6 MeV proton irradiation for 18 h at 770 K and for 264.5 h at 720 K to a total damage of 0.94 dpa. Electron diffraction analysis of these precipitates found they were consistent with the bcc Nb-rich β-phase. These β-phase precipitates are similar to those observed following neutron irradiation [1,2]. This result shows that proton irradiation is a valid simulation of neutron irradiation with respect to the enhanced precipitation of β-phase precipitates in α-grains in Zr-2.5Nb.

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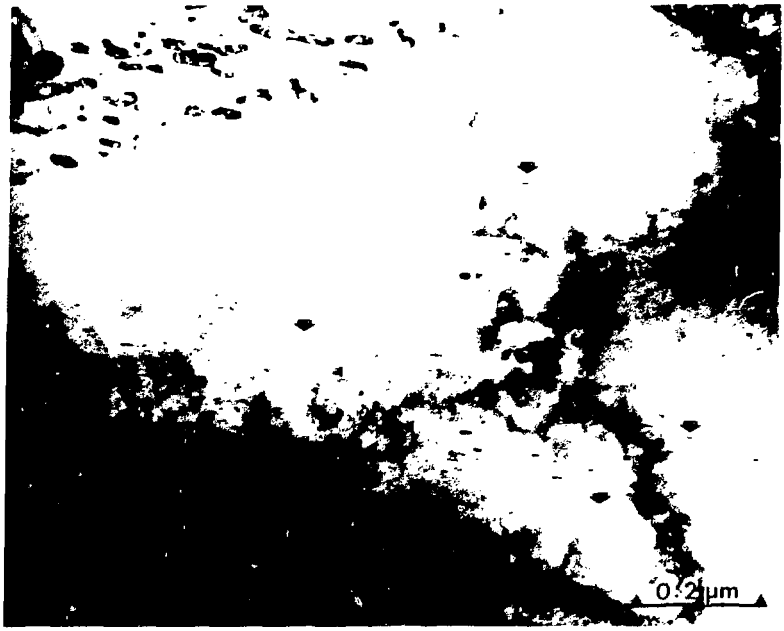
FIGURE 1: A bright-field TEM image showing the microstructure of the annealed Zr-2.5Nb foil material before proton irradiation. The light grains are α-Zr with approximately 1 at.% Nb in solution, while the dark grains at the α-grain boundaries are β-phase bcc Zr-20 at% Nb.

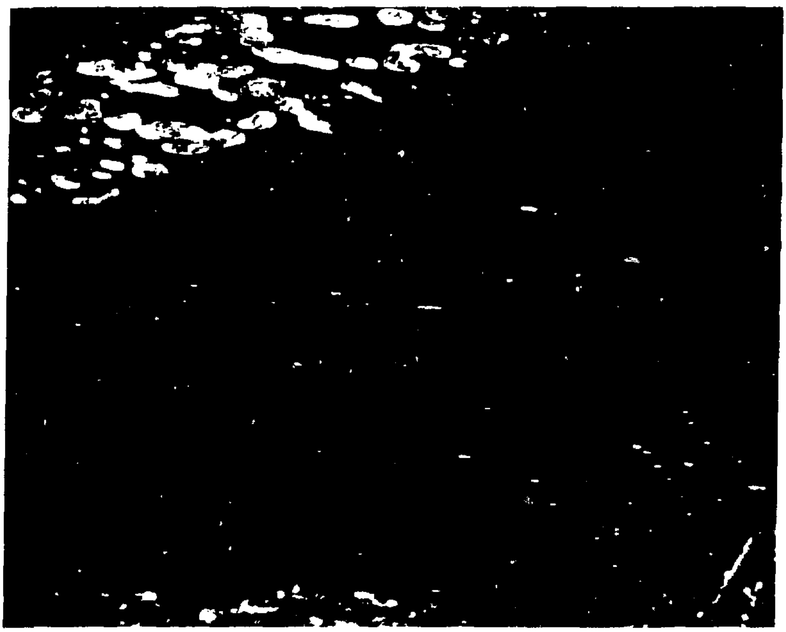
(a)

(b)

FIGURE 2: Bright-field (a) and (200) β-phase dark-field (b) TEM images showing the microstructure of an annealed Zr-2.5Nb foil after heat treating for 18 h at 770 K and 264.5 h at 720 K, in a flowing He atmosphere similar to that experienced by the proton-irradiated sample. The light-grey regions in (a) are the α-Zr phase, while the dark globular particles near the α-grain boundaries are the Nb-rich bcc β-phase.



(a)



(b)

FIGURE 3: Bright-field (a) and (200) β-phase dark-field (b) TEM images showing the platelets (typical ones arrowed in (a)) observed in the α-grains in Zr-2.5Nb irradiated with 3.6 MeV protons for 18 h at 500°C and 264.5 h at 450°C. Nb-rich particles from the decomposition of the Zr-20 at.% Nb are also visible at the left top and bottom of these images.

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