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An SEM study of β-phase decomposition during the annealing of Zr–2.5% Nb alloy

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Abstract

The effect of annealing on the decomposition of the β-phase in Zr–2.5% Nb pressure tube material was studied by SEM (scanning electron microscopy). Annealing was carried out at 400°C for 0, 24 and 1000 h. Previous to annealing, the specimens were electrolytically hydrided, the final hydrogen amount being about 60 $\mu g/g$. Long time annealing causes the β-phase ligaments to decompose into smaller particles. Hydrides are formed along the β-phase ligaments and they become shorter as the lengths of the ligaments decrease with annealing. The SEM technique proved to be useful in studying the decomposition of the β-phase ligaments.

1. Introduction

The current generation of pressure tubes for CANDU nuclear reactors are manufactured from Zr–2.5% Nb alloy by extrusion, cold drawing and autoclaving processes [1] that develop the desired combination of strength, corrosion resistance and neutron economy required for in situ reactor operation. Extrusion is done at approximately 850°C in the two phase ($\alpha + \beta$) region of the phase diagram. Prior to service all commercial Zr–2.5% Nb pressure tubes are cold worked about 30% after extrusion and are then steamed in an autoclave at 400°C for 24 h (to produce a protective oxide layer and relieve internal stresses). On cooling to room temperature, the extruded alloy has an elongated grain structure and contains approximately 10% of retained β_{Zr} ($\sim$ 20 wt% Nb). TEM (transmission electron microscopy) studies [2] show that in the as-extruded condition, β_{Zr} appears as a nearly continuous film of varying width between the α-grains. The retained β_{Zr} phase is metastable below the monotectoid temperature (610°C) and at the operating temperatures of the CANDU reactors (260–300°C) this phase will eventually decompose, first to the ω-phase and ultimately to the equilibrium β_{Nb}-phase containing $\sim$ 85 wt% Nb [3].

A marked decomposition of the β_{Zr}-phase was observed after prolonged annealing [4]. In most cases the reaction path involves the precipitation of the metastable ω-phase as an intermediate step in the β-phase decomposition:

$$\beta \rightarrow \omega + \beta_{Zr} \rightarrow \alpha + \omega + \beta_{Zr} \rightarrow \alpha + \beta_{Zr} \rightarrow \alpha + \beta_{Zr} + \beta_{Nb} \rightarrow \alpha + \beta_{Nb} \tag{1}$$

TEM study revealed that the previously continuous β-phase film was decomposed into individual particles after 10 days of annealing at 400°C [5]. The composition of these particles was found to be consistent with the niobium-rich (70 wt% Nb) phase [6]. Skinner and Dutton [7] also reported the decomposition of the β-phase using TEM. In the case of the pressure tube, decomposition commences during the first 24 h at 400°C in the autoclave treatment and continues during in-reactor operation. Annealing at higher temperatures produces a complete break-up of the β-phase (i.e. the continuity of the β-phase ligaments is completely lost [8,9]).

Though the resolution of SEM (scanning electron microscopy) is inferior to that of TEM, the SEM can provide

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a high-magnification image of the surface of the material. The topography of this image is very similar to optical microscopy but at a resolution which is an order of magnitude better. This feature helps to simplify the interpretation of images. In this paper, the effect of annealing time on the decomposition of the β-phase ligaments using SEM will be reported.

2. Experimental

2.1. Material

The material used in this investigation was Zr–2.5% Nb pressure tube (Darlington tube H 737) manufactured by the standard technological process, except that the stress relief (autoclaving at 400°C for 24 h) has not been performed (denoted as-manufactured). The as-manufactured material was hydrided in sulphuric acid at 90°C for 30 h. After hydriding a diffusion anneal at 300°C for 48 h was performed. The inert gas fusion technique (Leco RH-3 Hydrogen Determinator) was used for hydrogen analysis. The concentration of hydrogen after hydriding was approximately 60 μg/g. The β-phase morphology was investigated in as-manufactured, but non-autoclaved specimens (defined as non-annealed specimens) and in specimens annealed for 24 h and 1000 h at 400°C. The three standard conditions for testing were: 0, 24 and 1000 h of annealing.

2.2. Metallography

Specimens for SEM examinations were prepared by grinding, using SiC papers, down to 800 grit, after which mechanical polishing was applied using 6 μm diamond paste. The attack polishing which was used as a final polishing procedure, may be regarded as a preparation technique in which there is simultaneous chemical attack and mechanical abrasion. A mixture of Cr_2O_3 and 0.5% HF was used. The Cr_2O_3 was freshly prepared by igniting $(NH_4)_2Cr_2O_7$. Since the useful life of the freshly prepared Cr_2O_3 is approximately 3 h, commercially available Cr_2O_3 is not suitable. Attack polishing was done manually on a rotating polishing wheel which was charged with a small amount of Cr_2O_3 and 0.5% HF solution in sufficient amounts to form a moderately viscous slurry. After approximately 30 s, a gray to black film develops on the surface of the specimen. After the film has appeared, distilled water is added to the polishing slurry along with a small amount of abrasive. Polishing is continued, along with distilled water additions, until the film is removed and a bright, shiny surface is produced. The major advantages of the attack polishing technique are: the flatness of the surface, the optical activity of the surface which allows features such as cracks to be related to the grain structure and the short etching time required to reveal phases such as hydrides. Full details on attack polishing have been previously described [10].

The next step in metallographic preparation was chemical etching. The aim of chemical etching was to enhance phase contrast of the β-phase ligaments. For chemical etching a mixture of 20 parts (by volume) lactic acid, 10 parts HNO_3 and 1.2 part HF was prepared. Etching was performed by swabbing for 5–10 s.

Metallographic observations using a Model S-2700-C Hitachi SEM were performed on three planes, i.e. axial–radial (A–R), radial–tangential (R–T) and axial–tangential (A–T). A sketch of the pressure tube depicting the orientation of the crystal grains is shown in Fig. 1. It was found that the secondary electron mode gave superior contrast when studying β-phase morphology.

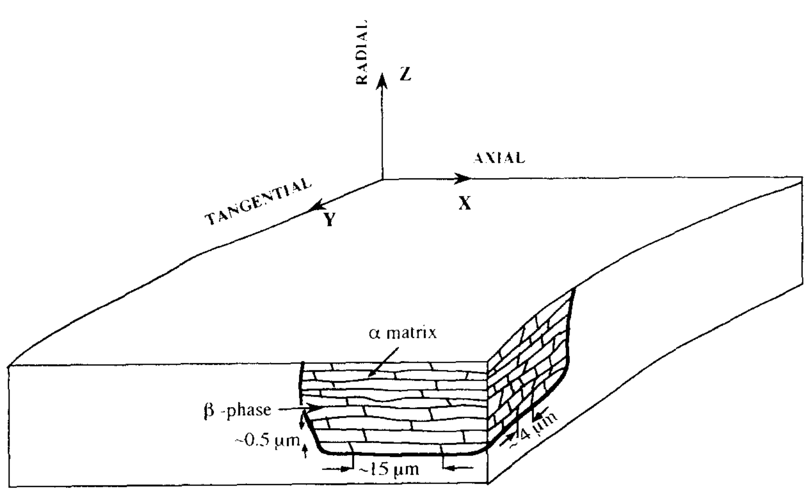


Fig. 1. Sketch of a section of the pressure tube showing α grain orientation and approximate grain size.

2.3. Hardness measurements

Vickers hardness measurements (load 5 kg) were performed on all three planes. The specimens were attack polished before testing. Hardness was measured after 0, 10, 24, 100 and 1000 h of annealing at 400°C.

3. Results and discussion

3.1. Morphology of the β-phase

The microstructure of non-annealed specimens is shown in Fig. 2a–c. In the A–R plane (Fig. 2a) long β-phase ligaments may be seen in the axial direction. The matrix is α-zirconium. The thickness of the β-phase is about 300 nm. The shape of the interface between the β-phase and the α-matrix is quite irregular and the approximate length of the β-phase ligaments is $5{,}500 \pm 3{,}100$ nm. The appearance of the β-phase as long ligaments is a result of the extrusion and cold drawing processes during the fabrication of Zr–2.5% Nb pressure tubes. In the R–T plane the β ligaments are partially curved and their length is $2{,}900 \pm 900$ nm. The β-phase observed in the A–T plane (Fig. 2c) is quite different from those in the two other planes. The β-phase appears as sheets possibly with perforations, although these may result from the wavy nature of the sheet and the planar polishing technique.

The microstructure of specimens annealed at 400°C for 24 h is shown in Fig. 3a–c. The α/β interface becomes smoother and the length of the β ligaments is $4{,}500 \pm 1{,}500$ nm in the A–R plane (Fig. 3a). Compared to non-annealed material, the β ligaments are somewhat thinner i.e. 240 ± 65 nm. In the R–T plane (Fig. 3b), the average width of the β-phase is between $1{,}500 \pm 700$ nm, which is roughly half of the width of the β-phase in the non-annealed condition. The decrease of all β-phase dimensions is the result of its decomposition during 24 h of annealing. No significant changes in the β-phase morphology were observed in the A–T plane (Fig. 3c).

The decomposition of the β-phase is more remarkable after 1000 h of annealing (Fig. 4a–c). The ligaments of the β-phase become less continuous and are now composed of discrete particles whose length in the A–R plane ($1{,}800 \pm 600$ nm) is three times less than in the non-annealed condition. The higher magnification clearly shows the

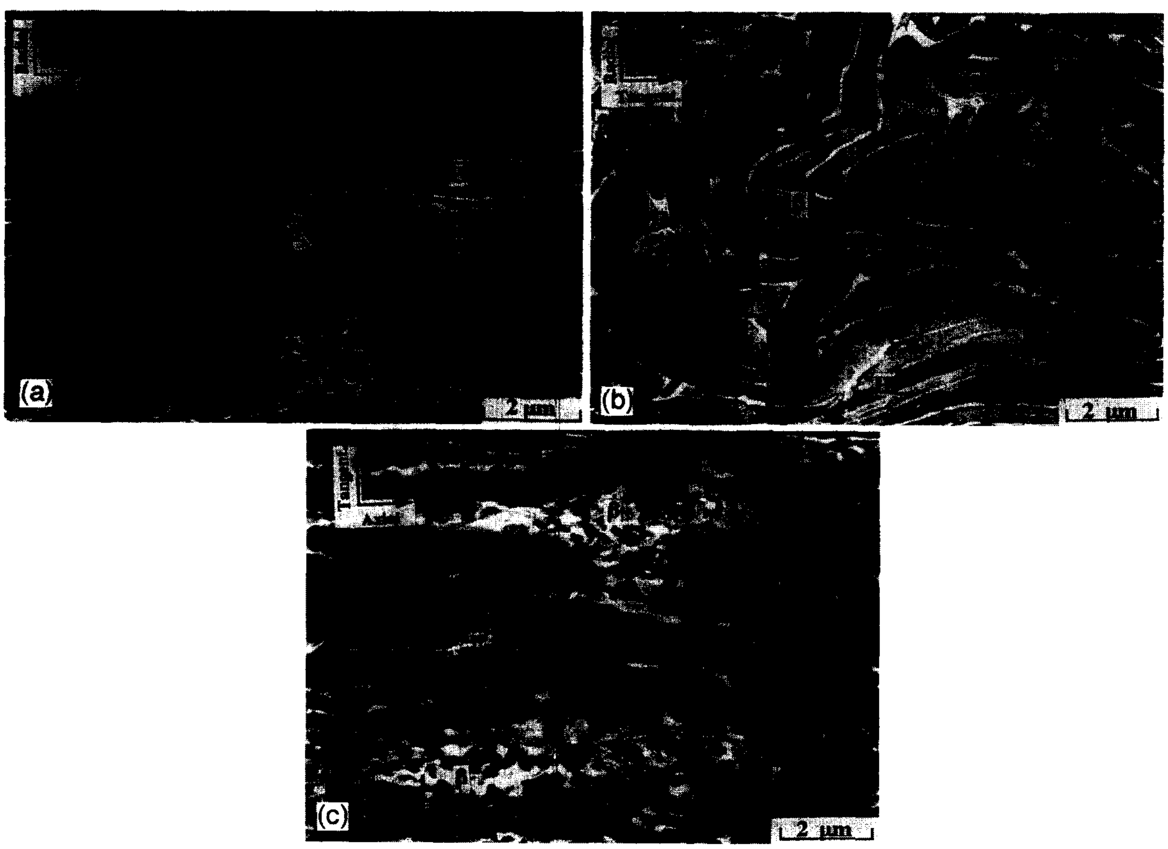


Fig. 2. SEM micrograph of non-annealed specimens. (a) A–R plane; (b) R–T plane and (c) A–T plane. H-hydride.

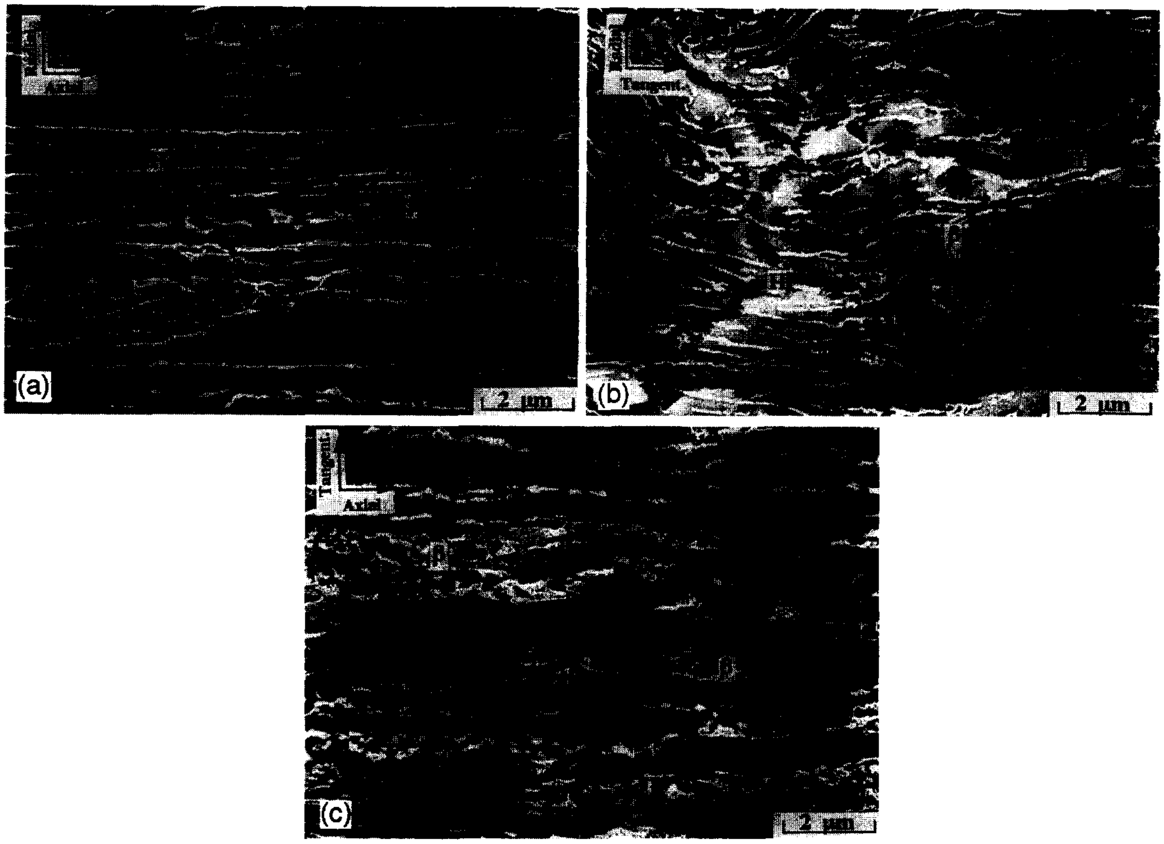
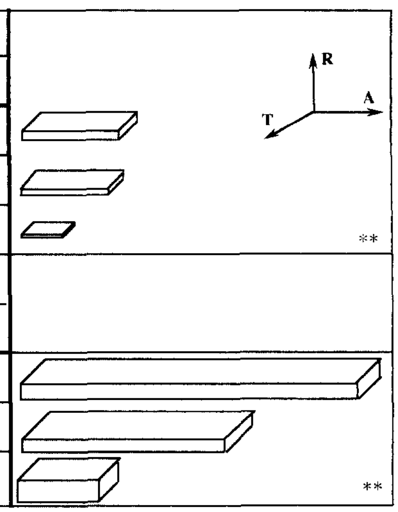


Fig. 3. SEM micrograph of specimens annealed for 24 h at 400°C. (a) A–R plane; (b) R–T plane and (c) A–T plane. H-hydride.

Table 1
The effect of annealing temperature on dimensions of the β-phase and hydrides

Dimensions of the β-Phase			
Time of annealing (h)	**Length-axial (nm)**	**Width-tangent. (nm)**	**Thickness-radial (nm)**
0	5,500±3,100	2,900±900	300±140
24	4,500±1,500	1,500±700	240±65
1000	1,800±600	950±700	170±60
Dimensions of Hydrides			
Time of annealing (h)	**Length-axial (nm)**	**Width-tangent. (nm)**	**Thickness-radial (nm)**
0	50,000±20,000	5,400±2,000	650±200
24	32,000±5,000	5,200±1,800	600±250
1000	8,000±4,000	5,000±2,500	1200±300



** The real β phase and hydrides vary in dimensions and are more or less curved. the schematic drawings show only the relative maximum dimensions in the straight form.

significant decomposition of the β-phase ligaments (Fig. 4a). The decomposition of the β-phase in the R–T (Fig. 4b) and A–T planes (Fig. 4c) is also visible.

3.2. Morphology of the hydrides

Hydrides which are precipitated during cooling from 300°C may be seen in all specimens. In most cases these hydrides are formed on the β-phase ligaments, especially when a narrow 'channel' between the two parallel ligaments exists (see for e.g. Fig. 2a, Fig. 3a and Fig. 4a). The length of hydrides decreases at all annealing temperatures, which implies that the 'shrinking' of hydrides strongly depends on the length of 'chain' of the β-phase ligaments. The width and thickness of hydrides remain practically unchanged after 24 h of annealing, but the thickness is nearly doubled after 1000 h (Fig. 4b). This increase in thickness is likely related to the rebalancing of nucleation and growth with the change of the phase morphology and also is affected by some recovery and recrystallization processes in the α-phase.

All the data on the size of the β-phase and hydrides are summarized in Table 1.

Our SEM results proved that the annealing treatments have produced a significant microstructural change in the grain boundary β-phase. Long time annealing at 400°C has caused the β-phase to decompose and break up. The microstructural evolution of the β-phase during annealing is quite complex. Our SEM micrographs clearly show that after 1000 h of annealing the final structure consists of β_{Nb} discrete particles embedded in the continuous α-matrix. In our case it is not clear whether the β_{Nb} is completely formed, or some amount of the ω-phase still exists in the microstructure. Our previous results [11] indicate that the amount of niobium in specimens annealed for 1000 h is only about 50%, but this value should be regarded as approximate due to the rather large diameter of the EDS electron beam. At the same time the ω-phase was not detected.

The age hardening of Zr–2.5% Nb alloy has been attributed to the increase in strength of the β-phase when the ω plates form during the early stage of aging. The grain boundary $\omega + \beta_{Zr}$ phase then behaves as a fiber strengthening phase [4]. The effect of annealing time on hardness (Fig. 5), however, shows that hardness decreases from the very beginning of annealing. Since annealing

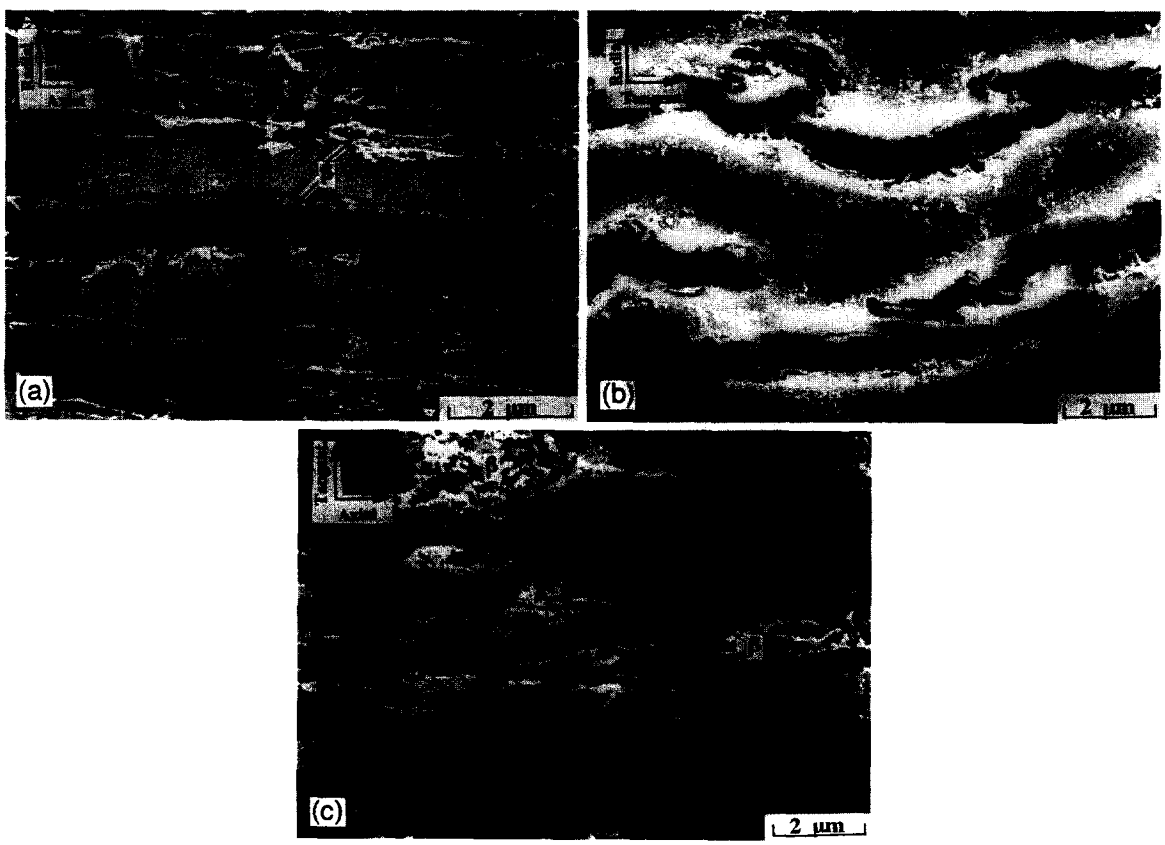


Fig. 4. SEM micrograph of specimens annealed for 1000 h at 400°C. (a) A–R plane; (b) R–T plane and (c) A–T plane. H-hydride.

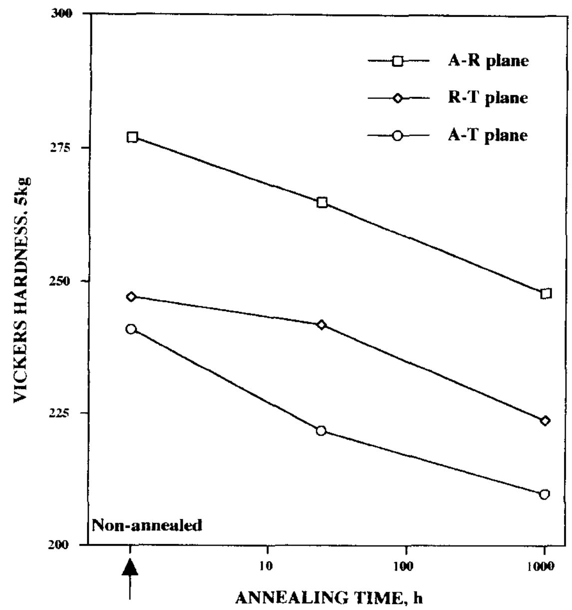


Fig. 5. The effect of annealing time on hardness.

times applied in this study were only 24 and 1000 h it was not possible to detect any hardening effects in the early stage of aging. The changes in the α-phase (recovery of cold work and even recrystallization at 400°C), together with disappearance of the ω-phase and the loss of the β-phase continuity during annealing may cause the decrease of hardness.

4. Conclusions

(1) Annealing at 400°C produces significant microstructural changes in the grain boundary β-phase. Long time annealing for 1000 h at 400°C causes the β-phase ligaments to decompose into smaller particles.

(2) Hydrides are precipitated mainly along the β-phase ligaments. The length of hydrides decreases together with the decreasing length of the β-phase ligaments, as a consequence of the β-phase decomposition.

(3) This SEM technique reported here for the first time proved to be very useful in studying the β-phase decomposition in Zr–2.5% Nb pressure tube material revealing details of the structural changes which are inaccessible by either optical microscopy or TEM.

Acknowledgements

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