Journal of Nuclear Materials 383 (2008) 178–182

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Optimization of stress relief heat treatment of PHWR pressure tubes (Zr–2.5Nb alloy)

Gargi Choudhuri [a,*], D. Srivastava [b], K.R. Gurumurthy [a], B.K. Shah [a]

[a] Quality Assurance Division, Bhabha Atomic Research Centre, Mumbai 400085, India
[b] Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India

A B S T R A C T

The micro-structure of cold worked Zr–2.5%Nb pressure tube material consists of elongated grains of α-zirconium enclosed by a thin film of β-zirconium phase. This β-Zr phase is unstable and on heating, progressively decomposes to α-Zr phase and β-phase enriched with Nb and ultimately form β_{Nb}. Meta-stable ω-phase precipitates as an intermediate step during decomposition depending on the heat treatment schedule,

$$\beta_{Zr} \rightarrow \alpha + \beta_{enr} \rightarrow \alpha + \omega + \beta_{enr} \rightarrow \alpha + \beta_{enr} \rightarrow \alpha + \beta_{Nb}$$

Morphological changes occur in the β-zirconium phase during the decomposition. The continuous ligaments of β_{Zr} phase turn into a discontinuous array of particles followed by globulization of the β-phase. The morphological changes impose a significant effect on the creep rate and on the delayed hydride cracking velocity due to reduction in the hydrogen diffusion coefficient in α_{Zr}. If the continuity of β-phase is disrupted by heat treatment, the effective diffusion coefficient decreases with a concomitant reduction in DHC velocity. The pressure tubes for the Indian PHWRs are made by a process of hot extrusion followed by cold pilgering in two stages and an intermediate annealing. Autoclaving at 400 °C for 36 h ensures stress relieving of the finished tubes. In the present studies, autoclaving duration at 400 °C was varied from 24 h to 96 h at 12 h-steps and the micro-structural changes in the β-phase were observed by TEM. Dislocation density, hardness and the micro-structural features such as thickness of β-phase, inter-particle spacing and volume fraction of the phases were measured at each stage. Autoclaving for a longer duration was found to change the morphology of β-phase and increase the inter-particle spacing. Progressive changes in the aspect ratio of the β-phase and their size and distribution are documented and reported. These micro-structural modifications are expected to decrease DHC velocity during reactor operation.

1. Introduction

The current generation of CANDU pressure tubes are manufactured from Zr–2.5Nb alloy due to its higher strength, lower creep rate [1], improved corrosion behavior and lower deuterium pick up [2]. Further, the phenomena of accelerated corrosion and hydriding do not occur in Zr–2.5Nb pressure tubes [2]. The magnitude of critical stress for hydride reorientation to radial direction is higher for Zr–2.5Nb (180–220 MPa) as compared to Zircaloy-2 (80–110 MPa) [2]. Fabrication flow sheet of these Zr–2.5Nb pressure tubes mainly consists of vacuum arc melting, forging and extrusion at 800 °C followed by 2-stage cold-drawing to obtain 20–30% cold work in the final product. The finishing stage is autoclaving at 400 °C to produce a protective black lustrous oxide layer [3] and to relieve the internal stresses. The micro-structure of the tube consists of flat, elongated α-Zr grains containing about 1 at.% Nb and a high dislocation density with β-phase sandwiched between α lamellae having composition ~20 at.% Nb [4]. These β-phase are meta-stable at reactor operating temperature (260–300 °C), below the monotectoid temperature (610 °C). The β-phase decomposes first to the ω-phase and enriched β-phase and ultimately to the equilibrium α_{Zr} and β_{Nb} (85 wt%Nb) [5]. Upon thermal aging or irradiation, fine β_{Nb} particles precipitate which improves corrosion resistance of the pressure tube [6]. Generally, α grain size is 0.3–0.5 μm keeping the aspect ratio 1:5:50 (radial:transverse:axial direction). This grain morphology gives strength and prevents formation of radial hydrides during reactor

* Corresponding author. Tel.: +91 22 2559 4927; fax: +91 22 2550 5151.
E-mail address: gargi@barc.gov.in (G. Choudhuri).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.08.058

operation. These grains have a texture that has resolved basal pole components oriented approximately one third in radial, most of the remainder in transverse and only a small fraction in the longitudinal direction [6].

In place of extrusion and cold-drawing route, hot extrusion followed by a 2-stage cold-pilgering with intermediate annealing at 550 °C ± 10 °C for 6 h has also been established [7]. This route is being followed for pressure tube fabrication for the Indian PHWRs. Stress relieving of the finished tubes takes place during autoclaving (400 °C for 36 h). In the present study, duration of autoclaving at 400 °C was varied from 24 h to 96 h at 12 h-steps and the microstructural modifications in the β-phase were observed by TEM.

Pressure tube life is limited by hydrogen damage mechanisms, namely hydride embrittlement, delayed hydride cracking (DHC) [8,9] and hydride blistering. DHC requires hydrogen (H) migration under stress gradient and is responsible for growth of flaws. Breaking the continuity of beta (β) phase at α grain boundaries is expected to reduce H diffusivity and thereby DHC velocity. The objective of the present study is to standardize the parameters to be followed for stress relieving that brings about modification in the micro-structure to reduce the DHC velocity.

2. Experimental

Zr–2.5Nb pressure tubes manufactured by Nuclear Fuel Complex were used in this study. Coupons sliced from tubes just before autoclaving were used as starting material and are referred to as-received material. The β-phase morphology was analyzed in as-received and stress relieved conditions by carrying out the stress relieving at 400 °C, 10 kg/cm^2 pressure for 24, 36, 48, 72 and 96 h. One hundred micrometer thick discs of 3 mm diameter were cut from the longitudinal–radial (L–R) section of the autoclaved pressure tube. The disks were electro polished in a solution of 20% perchloric acid and 80% methanol at −50 °C using jet-thinning apparatus. These electron transparent foils were examined at 160 KV using JEOL transmission electron microscope. Elemental analysis was obtained using an energy dispersive spectrometer (EDS) attached with TEM.

Vickers hardness measurements using 300 g load were made on all the three principal planes for as-received and stress relieved specimens. Dislocation density measurement was carried out by X-ray line profile analysis on the coupons stress relieved in 2 different conditions, viz. (i) 400 °C/36 h and (ii) 400 °C/96 h. There are two basic techniques for measurement of dislocation density from X-ray line profile analysis: (i) Fourier space technique which involves Fourier analysis, (ii) real space techniques in which integral breadth analysis is most popular. In the integral breadth method the peaks that are affected by stacking fault are also included to give overall dislocation density including the stacking fault concentration. On the other hand, Fourier analysis gives separate estimation of stacking fault concentration in addition to dislocation density (ρ), coherent domain size (D), micro-strain (ε).The correction for instrumental broadening is the most important steps in estimation of material properties from line profile analysis.

Samples were taken from the outer surface of a pressure tube (L–T section). The autoclaved specimens were ground flat, polished mechanically and then etched. The specimens were irradiated using Phillips expert pro machine with Cu Kα radiation falling on this surface. Scan step size was 0.02° and scan rate 0.3°/min.

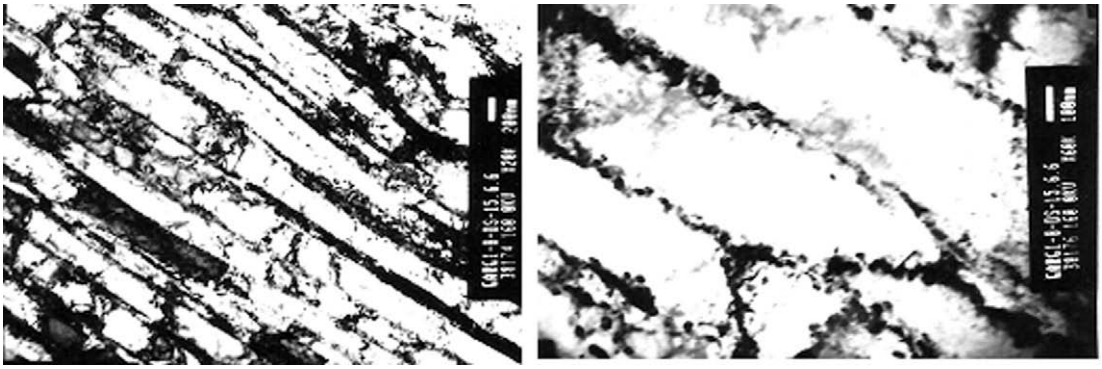

Fig. 1. Transmission electron micrographs showing elongated α-zirconium grains surrounded by a network of discontinuous β-phase in as-received indigenously made Zr–2.5Nb pressure tube material.

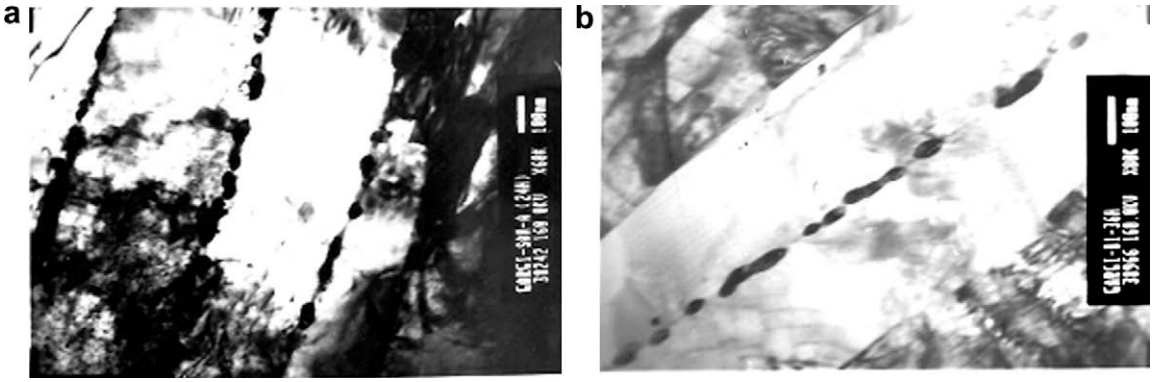

Fig. 2. TEM micrographs of pressure tube material autoclaved at 400 °C. (a) Stress relieved for 24 h showing a network of discontinuous β-phase in the grain-boundary of α. (b) Stress relieved for 36 h showing isolated dislocation distributed in the matrix of α.

Measurement of dislocation density was also carried out by counting the number of dislocation in the defined area of the TEM microphotographs.

3. Results

The bright field micrographs obtained in TEM of L–R section of as-received sample (25% cold pilgered) are shown in Fig. 1. The α-Zr matrix is surrounded by discontinuous β-Zr phase. The β-Zr phase is 32.5 nm thick and has a volume fraction of 8–15% and an aspect ratio of 2.6. Inter-particle distance of β in the longitudinal direction is in the range of 16.7–33 nm. The alpha grain is 0.28–0.36 μm thick in radial direction and has aspect ratio greater than 25. Matrix is heavily cold worked which restricts the measurement of dislocation density by TEM. Maximum hardness is observed in the L–R section and in the as-received specimen it is at HV 243.

The TEM micrographs of specimen that were stress relieved at 400 °C for 24 h are shown in Fig. 2(a). Matrix is still heavily cold worked. Volume fraction of β is reduced to be in the range of 4.7–5.5% and the aspect ratio of β has reduced to 1.67; the inter-particle spacing is increased to 36 nm. Nb content was 1 wt% in α_{Zr} and 11–14.6 wt% in β-phase. After 36 h of stress relieving, matrix dislocation density is decreased and isolated dislocations could be resolved as shown in Fig. 2(b). Measurement of dislocation density was carried out by measuring number of dislocation in the defined area of the microphotographs (it is around $7.6 \times 10^{14}/m^2$). Volume fraction of β is further reduced to be in the range of 2–3% and inter-particle spacing is increased to 63 nm.

Marginal reduction in dislocation density to $5 \times 10^{14}/m^2$ is observed after 48 h of stress relieving. Inter-particle spacing of β is further increased to 78.8 nm. The aspect ratio of β was found to be 1.5 which confirms that the β particles are progressively globulized and are more widely separated as shown in Fig. 3(a). After 72 h of stress relieving, no great change in micro-structure was observed, but the trend of globulization continues as shown in Fig. 3(b).

After 96 h stress relieving, dislocation density is around $3 \times 10^{14}/m^2$. Volume fraction of β is 2–3% and thickness of β is increased to 45 nm. Inter-particle spacing of β is further increased to 79.2 nm and they are widely separated as shown in Fig. 4, which is beneficial from hydrogen diffusion point of view. Aspect ratio of β is 1.14:1 which confirms that particles are more or less becomes globular.

Omega phase (ω) was not observed in the TEM micrograph of as-received as well as after 96 h stress relieving at 400 °C which is also confirmed by selected area diffraction pattern in TEM.

The micro-hardness value is slightly increased to HV255 after 24 h stress relieving and then it remains constant up to 36 h. The micro-structural changes observed during β-phase decomposition at 400 °C are summarized in Table 1 and Fig. 5.

Specimens stress relieved at 400 °C for 36 and 96 h were subjected to X-ray diffraction. Dislocation density was calculated by Line Profile Analysis of the XRD pattern using integral breadth technique. The results are presented in Table 2.

The dislocation densities calculated by this technique shows close agreement with those estimated from TEM micrographs. It can be seen from the results that a progressive increase in coherent domain size and decrease in dislocation density but no appreciable change in micro-strain occur during extended stress relieving.

4. Discussion

The indigenously made pressure tube is produced by extrusion and two stage pilgering with intermediate annealing route. Due to

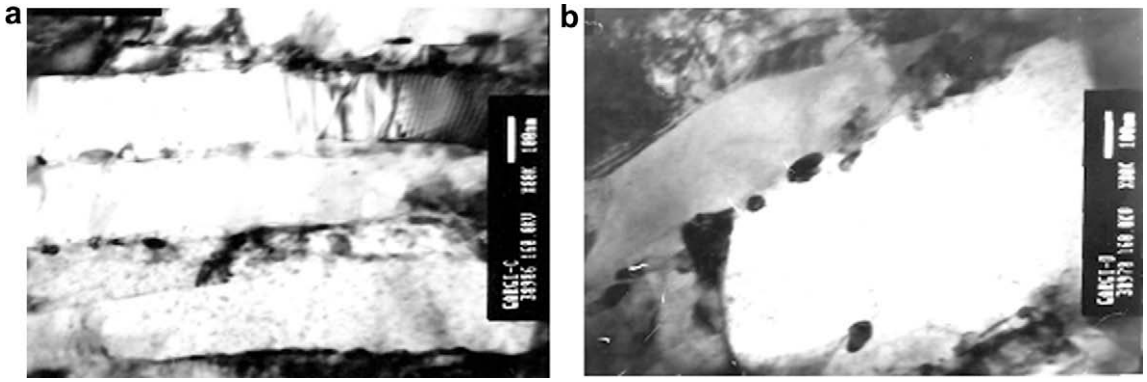

Fig. 3. TEM microphotographs of pressure tube material autoclaved at 400 °C. (a) Stress relieved for 48 h showing discontinuous β-particles in the α grain-boundary. (b) Stress relieved for 48 h showing a widely spaced globular β-particles in the grain-boundary of α phase.

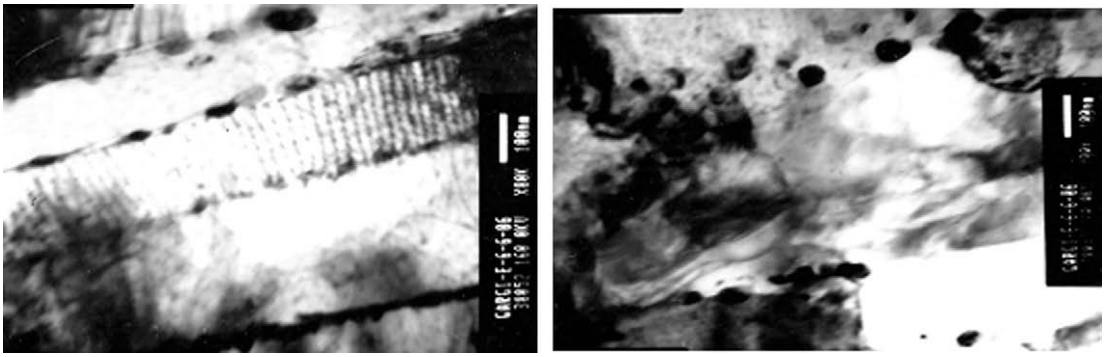

Fig. 4. Bright field transmission electron micrographs of indigenously made Zr–2.5Nb pressure tube material in 96 h autoclaved at 400 °C.

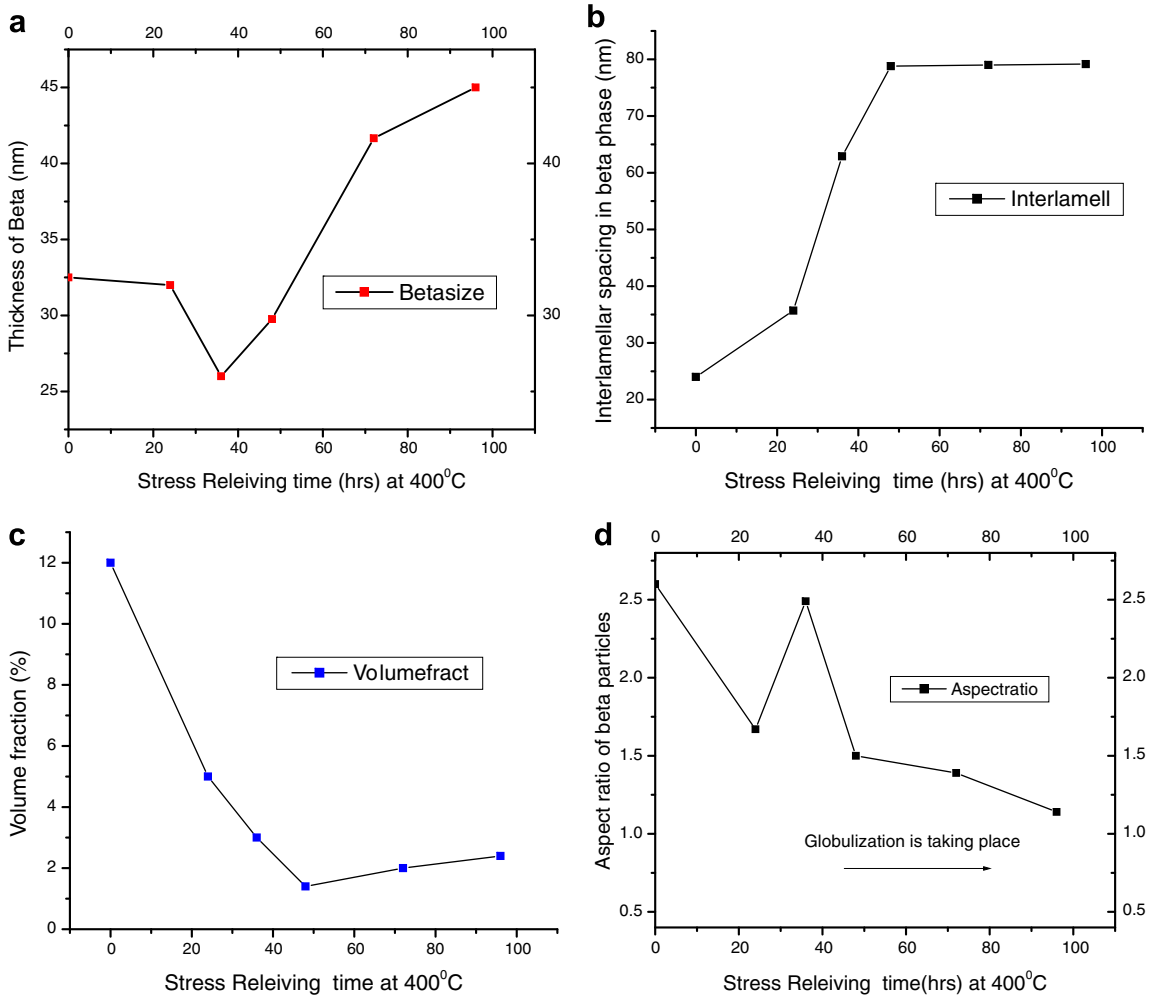

Fig. 5. Graphical representation of the effect of stress relieving at 400 °C on the dimensions of β-phase in indigenously produced Zr–2.5Nb pressure tube material. (a) Reduction in volume fraction of β-particles (%) during stress relieving. (b) Change in inter-particle spacing with stress relieving. (c) Variation of thickness of β-particles during stress relieving. (d) Globulization is taking place during stress relieving.

Table 1
The effect of stress relieving at 400 °C on the dimensions of β-phase in the L–R section of indigenously produced Zr–2.5Nb pressure tube material

Stress relieving condition	Dislocation density (TEM) per m^2	Hardness HV*	Thickness of β particles (nm)	Aspect ratio of β	Inter-particle spacing of β (nm)	β-Phase Volume fraction (%)	α-Aspect ratio	α-Thickness (μm)
As-received	Not able to measure	243.0	32.5	2.5–2.7	16.7–33	8–15	>25	0.28–0.36
24 h	–	255.0	32	1.67	35.7	4.66–5.30	>13	0.36
36 h	7.6×10^{14}	255.0	26	2.49	62.9	2.3–3.0	>9	0.28
48 h	5.4×10^{14}	245.7	29.76	1.5	78.8	1.4	>9	0.15
72 h	–	249.7	41.66	1.39	–	2.0	>12	0.16
96 h	2.9×10^{14}	254.6	45	1.14	79.2	2.4	>14	0.24

* Average of 5 measurements using 300 gm load.

Table 2
Results of line profile analysis using integral breadth technique

Sample description	Dislocation density by XRD (per m^2)	Dislocation density by TEM (m/m^3)	Coherent domain size (Å)	Micro-strain
Autoclaved at 400 °C/36 h	11.8×10^{14}	7.6×10^{14}	201.17	0.0014025
Autoclaved at 400 °C/96 h	2.9×10^{14}	2.9×10^{14}	350.8	0.0017443

this intermediate annealing at 585 °C for 6 h, the continuous thin boundary film of β-phase is decomposed into particles having thickness 32.5 nm in the radial direction with aspect ratio 2.6. With further stress relieving, these broken discontinuous particles start to globulize and the inter-particle spacing is increased. After 96 h of autoclaving, the particles are globular and widely separated. The inter-particle spacing is increased to 80 nm. As a result, the diffusion of hydrogen within the pressure tube is slowed down. The aim of this autoclaving step is to reduce the hydrogen diffusion velocity resulting in reduced DHC velocity.

CANDU pressure tubes are fabricated through extrusion followed by cold-drawing route. They are stress relieved at 400 °C for 24 h. As no intermediate annealing is involved, the micro-structure of non-autoclaved tube consists of α grain surrounded by continuous β-phase having length in the range of 5500 ± 3100 nm and thickness 300 ± 140 nm. After 24 h of stress relieving, their length becomes 4500 ± 1500 nm and thickness 240 ± 65 nm [5,10]. Higher reduction in particle size and larger increase in inter-particle spacing is achieved in the hot extrusion followed by pilgering with intermediate annealing as compared to cold-drawing route.

5. Conclusions

- Indian pressure tube in as-received condition has discontinuous β-phase which is expected for better performance of the tube from hydrogen intake and creep point of view.
- After 96 h autoclaving β-phase become globular and inter-particle spacing increased to 80 nm, i.e. they are widely separated compared to 36 h autoclaving.
- Adoption of modified stress relieving heat treatment will be based on evaluation of mechanical properties and ensuring the design requirement.

References

[1] J.W. Evans, P.A. Ross-Ross, J.E. Lesurf, H.E. Thexton, Atomic Energy Canada Limited, Report No. AECL-2982, 1971.
[2] D. Warr, V. Perovic, Y.P. Lin, A.C. Wallace, in: Zirconium in Nuclear Industry – 13th International Symposium, 2002, p. 313.
[3] D.O. Northwood, W.L. Fong, Metallography 13 (1980) 97.
[4] Glen M. Mc Dougall, Vincent F. Urbani, in: Zirconium in Nuclear Industry – 13th International Symposium, 2002, p. 247.
[5] M.T. Jovanovic, Y. Ma, R.L. Eadie, J. Nucl. Mater. 244 (1997) 141.
[6] V.F. Urbanic, M. Griffiths, in: Zirconium in Nuclear Industry – 12th International Symposium, ASTM STP 1354, 2000, p. 641.
[7] P. Pande, M. Narayana Rao, D.K. Wali, N. Saibaba, in: Conference Proceedings of "ZARC-91", Conducted by BARC during 12–13 December 1991, Mumbai, p. 155.
[8] Stefan Sagat, Christopher E. Coleman, Malcom Griffiths, Brian J.S. Wilkins, in: Zirconium in Nuclear Industry – 10th International Symposium, 1994, p. 35.
[9] M.T. Jovanovic, G.K. Shek, H. Seahra, R.L. Eadie, Mater. Charact. 40 (1998) 15.
[10] M.T. Jovanovic, R.L. Eadie, Y. Ma, M. Anderson, S. Sagat, V. Perovic, Mater. Character. 47 (2001) 259.