



Observation of kinetics of γ zirconium hydride formation in Zr–2.5Nb by neutron diffraction

W.M. Small^a, J.H. Root^b, D. Khatamian^{c,*}

^a Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

^b Neutron Program for Materials Research, National Research Council of Canada, Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0

^c Reactor Materials Research Branch, Atomic Energy of Canada Ltd., Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0

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Abstract

Neutron diffraction was employed to observe an isothermal transformation among zirconium hydrides in a commercial zirconium alloy. A specimen of Zr–2.5Nb, which contained about 200 mg deuterium/kg of alloy, was heated to 450°C for almost 17 h, then cooled directly to 17°C and held at this temperature for an extended time. A series of neutron diffraction patterns was collected during this thermal cycle. The diffraction patterns show that a small amount of the tetragonal γ -phase zirconium hydride appears soon after cooling, along with a predominant quantity of the cubic δ -phase hydride. Over three subsequent days at 17°C, the amount of γ -phase hydride increases while there is a corresponding reduction in the amount of δ -phase hydride. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The zirconium alloy Zr–2.5Nb (Zr–2.5 wt% Nb) is used to fabricate pressure tubes for CANDU¹ nuclear reactors. A recent publication by Root and Fong [1] demonstrated that neutron diffraction is a powerful tool to investigate the dissolution and precipitation of zirconium hydrides as a minority phase in Zr–2.5Nb pressure tube material. Zirconium hydrides appear in Zr–2.5Nb in two main forms: a cubic δ -phase zirconium hydride (ZrH_{1.6}) and a tetragonal γ -phase zirconium hydride (ZrH) [2]. In Ref. [1], it was also shown that a conversion of the γ -hydride phase into the δ -hydride phase occurs upon heating above 180°C. Further heating of the alloy was performed to a soaking temperature above 400°C, where all the hydrogen existed as dissolved at-

oms. Upon subsequent cooling, hydrides precipitated again, with the δ -phase being the dominant hydride in the alloy.

A suggestion has been made [1] that there might be a slow transformation of the δ -phase to γ -phase after cooling from high temperature. This phenomenon is expected to span a time interval on the order of days or weeks at room temperature. Slow conversion of one hydride phase to another may have some technological importance because the volume per zirconium atom in the δ -phase crystal lattice is about 4% larger than in the γ -phase. The stresses on the matrix material in the vicinity of a hydride precipitate are therefore expected to be reduced in the δ -to- γ conversion.

This paper presents results from a study to determine whether a slow δ -phase to γ -phase transformation occurs, and whether this change can be detected using neutron diffraction. It provides experimental evidence that there is a gradual conversion of δ -phase zirconium hydride to γ -phase zirconium hydride after cooling from a temperature where all hydrogen is dissolved in the Zr–2.5Nb matrix.

* Corresponding author. Tel.: +1-613 584 3311 ext 3662; fax: +1-613 584 3250; e-mail: khatamiand@aecl.ca.

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2. Experimental

2.1. Specimen

The specimen was a piece of Zr–2.5Nb pressure tube with dimensions 30 mm high, 4 mm thick and 8 mm wide. The as-received alloy is a two-phase material, 90% of which is hexagonal close-packed α -zirconium with very little dissolved niobium and 10% of which is body-centered cubic β -zirconium that contains at least 20% niobium. When the alloy is heat treated below 600°C for a week, the β -phase gradually decomposes into isolated precipitates containing over 95% niobium. These observations are consistent with the microstructural behavior of this alloy as predicted from the recently published Zr–Nb phase diagram [3].

Deuterium was introduced to the specimen from the gas phase at 400°C. Annealing was performed at 450°C for 72 h to diffuse the deuterium into the bulk of the specimen. Subsequently, the specimen was cleansed of excess surface deuteride and held at 750°C for one week. This heat treatment was designed to ensure a homogeneous deuterium content along the specimen length. The heat treatment also changes the microstructure of the specimen from one of highly elongated α -Zr grains into one with more equiaxed α -Zr grains interspersed with β -Zr particles. The β -phase exists either at triple points or along the long axis of the α grains [4]. Following all the intended neutron diffraction measurements, three small coupons (~200 mg each) were sliced from the top, middle and bottom sections of the specimen and examined by differential scanning calorimetry

(DSC) [5]. The DSC examination indicated that the top and mid-sections of the specimen had almost identical deuterium concentrations of ~200 mg/kg (mg deuterium/kg of alloy), while the bottom section had ~216 mg/kg. These results show that the specimen was homogeneous with respect to deuterium concentration, except for the bottom portion, which was masked during the neutron diffraction measurements.

2.2. Neutron diffraction

Neutron diffraction measurements were made on the E3 neutron diffractometer at the Nuclear Reactor Universal (NRU) research facility at Chalk River Laboratories. A sketch of the experimental arrangement is shown in Fig. 1. The thermal neutron beam from the reactor was diffracted from a squeezed single-crystal germanium monochromator to select a neutron wavelength $\lambda = 0.237$ nm. The monochromatic beam passed through a low-efficiency monitor. This monitor serves as the method to normalize measurements to a common reference intensity. After emerging from the monitor, the remaining neutron beam passed through a graphite filter to suppress the 'higher order' contamination by neutrons with wavelengths $\lambda/2$ and $\lambda/3$, which may also be diffracted by the monochromator. The filtered neutron beam then penetrated the walls of a vacuum furnace, the graphite heater element and then the specimen itself. (Note that neutrons penetrate through many millimeters of most engineering materials, so it is straightforward to examine specimens inside equipment that holds them at realistic conditions of temperature and load.) The whole volume

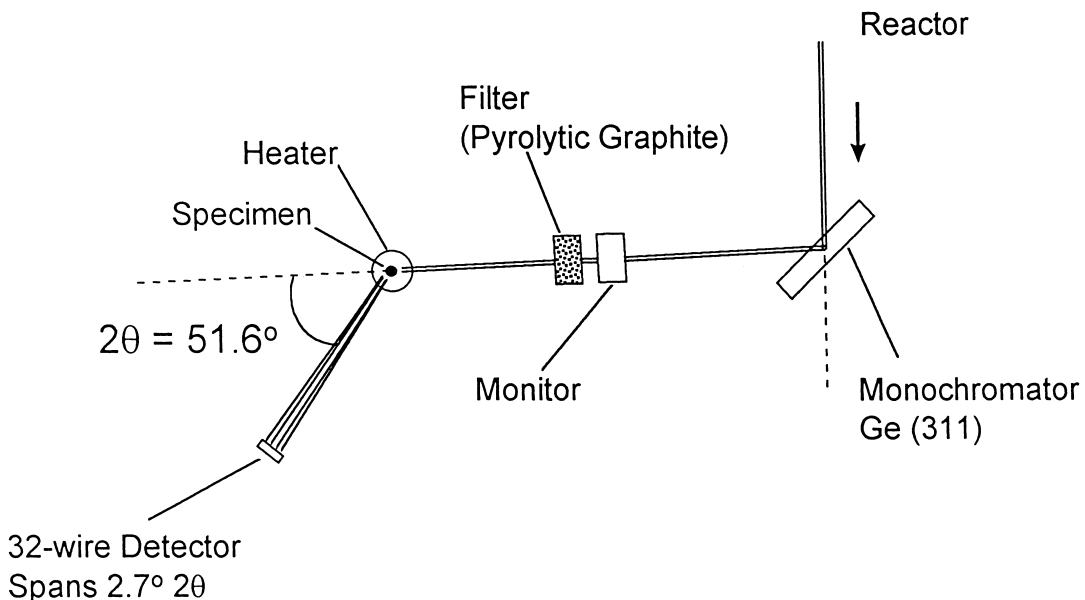


Fig. 1. Schematic of layout for neutron diffraction experiments.

of the specimen was bathed in the neutron beam. The (1 1 1) diffraction peaks of both hydride phases were examined simultaneously in a 32-channel multi-wire detector that spanned 2.7° of scattering angle, 2θ . The mean angle of the detector was centered at 51.6° of 2θ , midway between the γ and δ hydride peaks. Diffraction patterns were collected every 15 min at early times after cool-down, when the greatest rate of change was expected. At longer times after cool-down, the data acquisition time was increased, up to about 4 h per pattern after a day had elapsed, but the monitor was used to re-normalize all diffraction patterns for direct comparisons. Any changes in diffraction peak intensities could then be ascribed to either growth or disappearance of hydride precipitates within the metal matrix.

2.3. Thermal cycle

The temperature was monitored by a type-K thermocouple imbedded in a hole at mid-height of the specimen. The furnace vacuum was better than 1×10^{-6} Torr (0.1 mPa) during data acquisition. The specimen was first heated to a soak temperature of 450°C and was held there for about 17 h. Several neutron diffraction patterns were collected at this temperature to verify that no hydride peaks were present. Power to the furnace was then shut off. The interior of this chamber was temporarily back-filled with helium to improve the cooling rate of the specimen. Fig. 2 illustrates the cooling curve for the specimen. Within the first 20 min, the specimen temperature dropped below the threshold of 180°C where the γ -phase hydride starts to form. Vacuum was re-established and data collection was started as

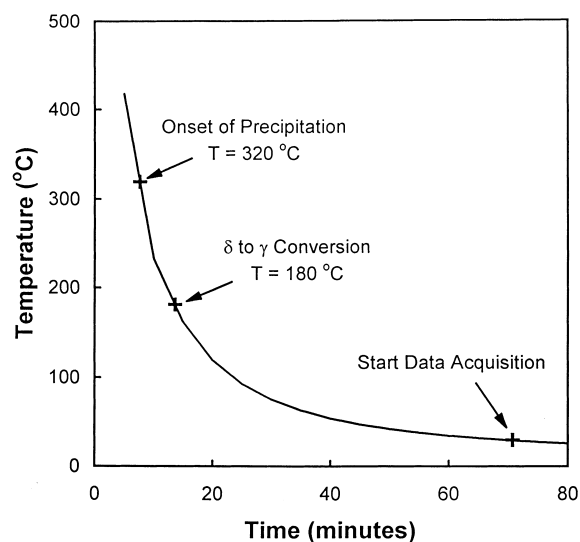


Fig. 2. Cooling curve for the specimen in this neutron diffraction experiment.

soon as the specimen temperature fell below 23°C . For most of the diffraction patterns, the specimen temperature was 17°C .

3. Results

When the specimen temperature was 450°C , all of the hydrides were dissolved and no hydride peaks were observed in the neutron diffraction pattern. An example of a diffraction pattern obtained at 450°C is shown in Fig. 3. The result is simply a sloping background of neutrons counted in each detector channel, with statistical fluctuations that fall within normal limits.

After cool-down, diffraction peaks from the specimen are observed for both the δ - and γ -zirconium hydrides. In Fig. 4, a comparison is shown of the diffraction patterns at early and late times following cool-down. After 55 h, there are clearly two well-defined hydride peaks, the lower angle peak being $\delta(1\ 1\ 1)$ and the higher one being $\gamma(1\ 1\ 1)$. At the early time, the γ -phase peak is relatively weak and the δ -phase peak is the dominant one. Assuming that all other factors are equal, the integrated intensity of a diffraction peak is directly proportional to the volume of material in the neutron beam [6]. With a specimen of fixed dimensions, completely bathed in the neutron beam, the intensity of the hydride diffraction peak is proportional to the volume fraction of precipitates in the specimen. However, there may be a fixed scaling factor that is distinct for each peak, related to the preferred orientations of hydride crystallites within the matrix. This scale factor might be quite different

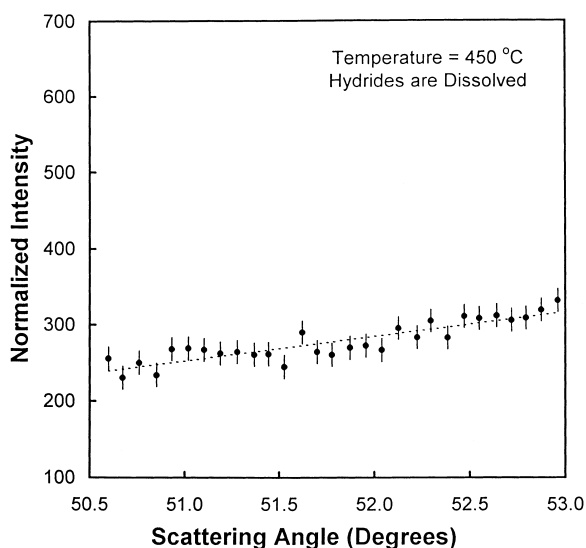


Fig. 3. Neutron diffraction pattern for Zr-2.5Nb with deuterium concentration of ~ 200 mg/kg obtained at 450°C . The error bars represent the uncertainty in counting random events.

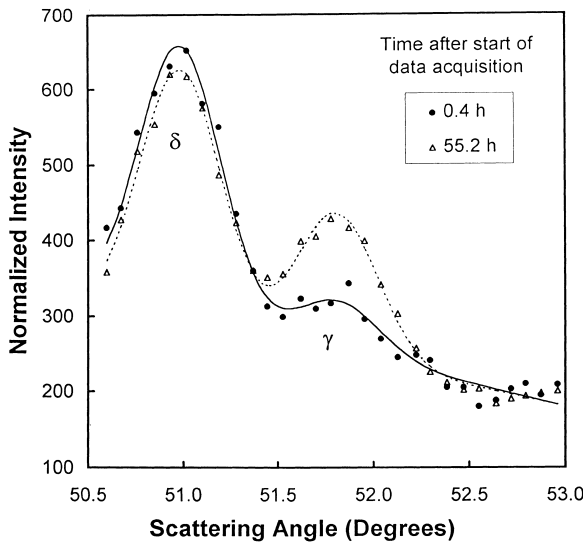


Fig. 4. Neutron diffraction patterns for Zr-2.5Nb with deuterium concentration of ~ 200 mg/kg obtained at 17°C , 0.4 and 55.2 h after cooling from 450°C . The continuous curves are the result of fitting the data to a function consisting of two Gaussians plus a linearly sloping background.

for each hydride and would vary with specimen orientation. Therefore, one cannot generally expect a one-to-one correspondence between loss of intensity in the $\delta(1\ 1\ 1)$ peak and increase of intensity in the $\gamma(1\ 1\ 1)$ peak. However, as the specimen orientation was held constant during the experiment, it is reasonable to evaluate the kinetics of growth or disappearance of each phase separately. To help make this evaluation, a model function was fitted to each diffraction pattern; two Gaussians plus a linearly sloping background. Fitted functions are shown in Fig. 4, and they appear to represent the raw data reasonably well.

The integrated intensities of the fitted gaussian functions are plotted as functions of time after cool-down in Fig. 5. These trends show a decline in intensity of the δ -hydride as the signal from the γ -hydride grows. Several mechanisms such as lattice shear, order-disorder transition and diffusion may play a role in the transformation of δ -phase into γ -phase.

4. Discussion

Many investigators have studied the formation and stability of the Zr hydride phases under a variety of conditions. Bailey [7], using X-ray and electron diffraction, showed that needle like γ -hydride precipitates form in Zr foils containing < 500 mg H/kg of Zr when they are fast cooled or quenched into iced brine after annealing at 800°C . He also observed the γ -hydride in furnace

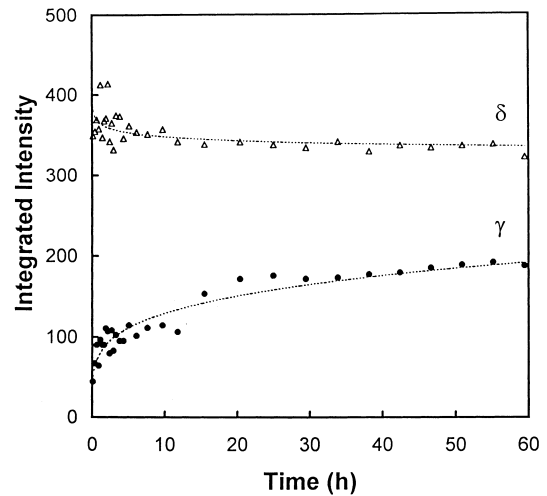


Fig. 5. Kinetics of δ to γ hydride transformation in Zr-2.5Nb at 17°C after being cooled from 450°C . Note that the lines are only guides to the eye.

cooled foils, but found no evidence for presence of the δ -hydride. Sidhu et al. [2] also found no δ -hydride in specimens of low hydrogen content. In a later measurement, Bailey [8] showed that the formation of δ - and γ -hydrides was favored by slow and fast cooling, respectively. Under slow cooling, X-ray diffraction patterns obtained from specimens containing > 100 mg H/kg of Zr by Gill et al. [9] showed the hydride phase to be predominantly δ , but traces of the γ -phase were also identified. Nath et al. [10], by varying both the hydrogen concentration and the cooling rate, showed that ratio of δ/γ hydride increases with increasing the H concentration and decreasing the cooling rate. More recent studies by Cann et al. [11,12] have shown that only γ hydride appears if the concentration of hydrogen in the specimen is less than about 20 mg/kg and that, at higher hydrogen concentrations, the amount of γ and δ hydride formation depends on the cooling rate and the amount of impurities such as oxygen in the specimen.

The specimen in the present experiment contains about 200 mg deuterium (the heavy isotope of hydrogen)/kg of alloy. This level is equivalent to a hydrogen concentration of about 100 mg/kg. A specimen of Zr-2.5Nb with a similar concentration of hydrogen was previously studied by Root and Fong [1]. In the as-received condition, the specimen contained precipitates, with a predominance of the γ -phase and a lesser amount of the δ -phase hydrides. This specimen was heated to dissolve the precipitates. Upon exceeding a temperature of 180°C , a large fraction of the γ -phase hydrides disappeared, coincidentally as there was an increase in the amount of the δ -phase hydride. Clearly, there is a crystal-structure transition near 180°C , with the δ -phase preferred at high temperature and the γ -phase preferred at

lower temperature. At a temperature of 320°C, all of the hydrides were dissolved. On subsequent cooling of the specimen, the δ -phase appeared first. Upon passing the 180°C boundary, the γ -phase did not appear abruptly. Instead, it gradually appeared with decreasing temperature during a cooling sequence that lasted for more than a day. The suggestion of Ref. [1] that there may be a slow process at conversion between the δ and γ phases has been confirmed in the present work and it has also been shown that γ hydride is the more stable phase at ambient temperatures. This is in agreement with the specific heat measurements of Bashkin et al. [13] which indicated that γ hydride is thermodynamically stable at room temperature.

In the present experiment, the concentration of hydrogen is about 100 mg/kg and the cooling rate cannot be classed as a 'quench'. About 6 min elapse between the time the temperature drops below the critical temperature for onset of precipitation and the time that the δ -to- γ phase transition is passed. During this initial period, precipitates nucleate and grow in the δ hydride phase. By cooling past the 180°C boundary, one expects that the remaining hydrogen in the α -phase would further precipitate and form new hydrides in the γ -phase. Note that, as discussed earlier, the amount of hydrogen remaining in the α -phase depends on the cooling rate and would be within the range from ~ 20 mg/kg (the solubility limit for precipitation of H in Zr at 180°C [14]) up to the total hydrogen concentration of the specimen.

Now consider the hydrogen that is already bound into δ -phase precipitates before the temperature drops below the 180°C boundary. In the δ -phase, the zirconium atoms form a face-centered cubic lattice. An average of 1.6 hydrogen atoms per zirconium occupies a subset of tetrahedral interstitial sites, at random. The δ -hydride precipitates are in a state of hydrostatic compression because the volume per zirconium atom is 17% higher in this state than in the host crystal lattice. If this hydride transforms to the γ -phase, there will be a partial relief of this precipitate-matrix stress because the volume per zirconium atom is 4% less in the γ -hydride than in the δ -hydride. Thus, the δ -to- γ transformation is energetically favorable [13]. In addition, the γ -hydride is more ordered than the δ -phase. There is only one hydrogen atom per zirconium atom, and the occupancy of the tetrahedral interstitial sites is restricted to only one of the two (1 1 0) planes in the face-centered tetragonal zirconium lattice [2].

For a large precipitate of δ -hydride to transform to the γ -phase, about 40% of the hydrogen atoms must migrate from the original precipitate into the surrounding host material. The hydrogen that remains within the original precipitate boundaries must find 'ordered' positions in the zirconium lattice. This migration and ordering is expected to be very sluggish and to require a long time to occur. In the present experiment, at a tempera-

ture of 17°C, the ordering process may require many days to complete and even the core section of the hydride may never have a possibility to transform. According to this picture, one would expect to find precipitates with a predominance of δ -phase hydride in the core region and γ -phase close to the interface between the precipitate and the host metal. Such a microstructure has been observed by metallography and electron microscopy in the works of Barraclough and Beevers [15] and Cann and Atrens [11], respectively.

The transformation from δ - to γ -hydride phase is analogous to the disorder-order transition that occurs during cooling of some binary alloys, such as Cu₃Au and Ni₃Mn. The kinetics of such transitions are often characterized by noting that the volume fraction, V , of the ordered phase increases as time, t , raised to some exponent, n . Since the intensity, I , of the γ -phase diffraction peak is proportional to the volume fraction of the γ -hydrides present in the specimen [6], one may write the general power expression as

$$I = at^n,$$

where a is a proportionality constant. Fig. 6 is a full-logarithmic plot of all the integrated intensities for the γ -hydride in Zr-2.5Nb for various times at 17°C. A least-squares fit of these data yields a value for the exponent of 0.22 (± 0.011). This exponent is intriguing, as a value of 0.25 has been interpreted by Furakawa [16] in the context of scaling theory to correspond to a phase transformation that is controlled by mobility near the surface of the transforming object. In the δ -to- γ hydride transition, hydrogen must diffuse beyond the surface of an existing precipitate. This concept of the mechanism for the δ -to- γ transformation seems to conform to that scaling class.

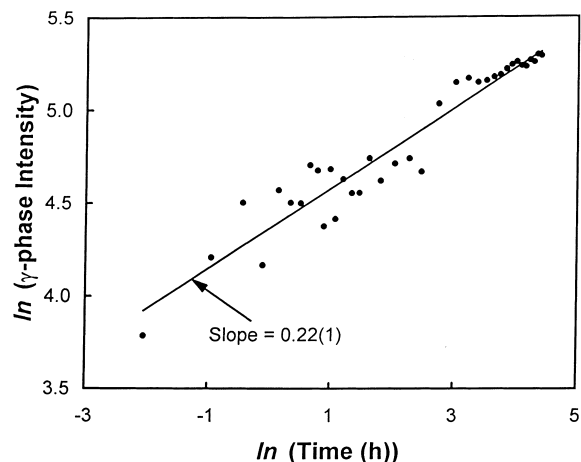


Fig. 6. Logarithmic plot of the integrated intensities for the γ -hydride in Zr-2.5Nb obtained after various times at 17°C. The line is a least squares fit to the data.

5. Conclusions

Neutron diffraction has provided unambiguous evidence of hydride precipitation kinetics in Zr–2.5Nb pressure tube material. Cooling the alloy from a temperature, where all hydrides are dissolved to about 17°C, causes a fraction of the δ -phase hydride to convert into the γ -phase over several days.

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References

- [1] J.H. Root, R.W.L. Fong, *J. Nucl. Mater.* 232 (1996) 75.
- [2] S.S. Sidhu, N.S. Satya Murthy, F.P. Campos, D.D. Zaubers, *Adv. Chem. Series* 39 (1963) 87.
- [3] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak (Eds.), *Binary Alloy Phase Diagrams*, 2nd ed., ASM International, Materials Park, OH, 1990.
- [4] R.A. Holt, M. Griffiths, R.W. Gilbert, *J. Nucl. Mater.* 149 (1987) 51.
- [5] D. Khatamian, V.C. Ling, *J. Alloys Comp.* 253 (1997) 162.
- [6] G.E. Bacon, *Neutron Diffraction*, 3rd ed., Clarendon, Oxford, 1975.
- [7] J.E. Bailey, *Acta Metall* 11 (1963) 267.
- [8] J.E. Bailey, *J. Inst. Met.* 97 (1969) 60.
- [9] B.J. Gill, P. Cotterill, J.E. Bailey, *J. Less-Common Met.* 39 (1975) 189.
- [10] B. Nath, G.W. Lorimer, N. Ridley, *J. Nucl. Mater.* 58 (1975) 153.
- [11] C.D. Cann, A. Atrens, *J. Nucl. Mater.* 88 (1980) 42.
- [12] C.D. Cann, M.P. Puls, E.E. Sexton, W.G. Hutchings, *J. Nucl. Mater.* 126 (1984) 197.
- [13] I.O. Bashkin, V.Yu. Malyshev, M.M. Myshlyayev, *Sov. Phys. Solid State* 44 (1992) 1182.
- [14] G.F. Slattery, *J. Inst. Met.* 95 (1967) 43.
- [15] K.G. Barraclough, C.J. Beevers, *J. Less-Common Met.* 35 (1974) 177.
- [16] H. Furakawa, *Adv. Phys.* 34 (1986) 703.