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Characterisation of β-quenched and thermally aged Zircaloy-2 by positron annihilation, hardness and ultrasonic velocity measurements

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Abstract

The evolution of microstructure and interfacial defects in β-quenched and thermally aged Zircaloy-2 is studied by positron annihilation, hardness and ultrasonic measurements. Defect-sensitive positron lifetime and *S*-parameter have shown an increase during isochronal aging treatment in the temperature range of 673–873 K, which indicates defect production as a consequence of intermetallic phase formation. Hardness measurements have revealed an increase beyond 473 K, a plateau between 673 and 873 K. At 973 K, the hardness value falls slightly below that of quenched sample, indicating the retention of as-quenched state. The hardness variation is qualitatively consistent with that of positron annihilation parameters. Ultrasonic velocity measurements have revealed complementary variations. Metallographic studies have shown evidence towards the existence of hard intermetallic phases between 673 and 873 K, based on which the observed experimental results are explained.

1. Introduction

Zircaloy-2 is an important structural material for pressurized heavy water reactors (PHWR) [1,2]. In Zircaloy-2, Sn, Fe, Cr and Ni are added as alloying elements for obtaining the desired mechanical properties, in addition to obtaining the required corrosion resistance in high temperature water. The solubility of these elements (except Sn) in low temperature β-Zr phase is limited because of the unfavourable size factor and/or crystal structure considerations [3]. However, the high-temperature β-phase can dissolve these elements to appreciable extent. Among the alloying elements used in Zircaloy-2, Sn is a β-stabiliser while the Fe, Ni, and Cr are α-stabilisers. The β-quenching treatment is given so as to homogenize the chemical composition and randomize the texture [3].

The β-quenching treatment results in a supersaturated solid solution in the form of a martensite structure. In order to obtain only the martensite structure without any secondary phases, optimal cooling rate should be employed. It has been reported that the hard intermetallic phases do not form above 1093 K. From the isothermal temperature–time transformation diagram given by

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Oestberg [4], one should have a cooling rate of atleast 120 K/s from 1223 K to 873 K, in order to avoid precipitation of hard intermetallics. The cooling rate can be less than 100 K/s below 873 K [4]. This clearly indicates the crucial role of the cooling rate to be maintained throughout the component volume to ensure that the hard intermetallic phases are not formed during β-quenching. Thus, it is important to characterise and detect the existence of intermetallic phases, so that suitable process optimisation can be done to avoid the occurrence of these.

In the present study, the formation and thermal stability of hard intermetallics in β-quenched state of the Zircaloy-2 is investigated using positron annihilation, hardness and ultrasonic velocity measurements and these are corroborated with metallographic studies. Ultrasonic measurements are an established tool to locate macroscopic defects in materials as well as for the characterisation of microstructures. Positron annihilation spectroscopy is a powerful technique for studying microscopic defects such as vacancies, vacancy clusters and dislocations [5].

2. Experimental

The chemical composition (in wt%) of the Zircaloy-2 samples is Sn – 1.62, Fe – 0.18, Cr – 0.1, Ni – 0.06, O – 1400 ppm and the balance is Zr. Samples of dimensions 10 mm × 10 mm and thickness 1 mm were heated at 1223 K for 2 h in vacuum-sealed quartz tube and water quenched to room temperature. These samples were subsequently subjected to isochronal aging treatments of 1 h at various temperatures between 473 K and 973 K. On the quenched and aged samples, positron annihilation, hardness and ultrasonic velocity studies were carried out. Positron lifetime experiments were carried out using a fast-fast coincident spectrometer having a time resolution (FWHM) of 260 ps. Positron Doppler broadening measurements were carried out using a high pure germanium detector having an energy resolution of 1.4 keV at annihilation gamma ray energy of 511 keV. A defect-sensitive line shape S-parameter viz. the ratio of central peak counts to total counts around 511 keV γ-ray is deduced from these measurements. The S-parameter signifies the positron annihilation events with low momentum electrons of the medium. The presence of defects viz., vacancies, vacancy clusters, dislocations and precipitate–matrix interfaces act as trapping centers for positrons, leading to an increase in the measured lifetime and S-parameter values [5]. Hardness of the specimens was obtained by Vicker's hardness tester using a 10 kg load. At least five measurements were made for each specimen. Ultrasonic velocity measurements were carried out using automated r.f. signal recording with a pulser-receiver (M/s Accu-Tron, USA), a 500 MHz Tektronix oscilloscope and a PC/AT 486. The ultrasonic velocity measurements were carried out over a range of frequencies (10 MHz, 16 MHz and 25 MHz) so as to record the response of the system over a wide dynamic range. A change in the ultrasonic velocity reflects the change in modulus or density due to the evolution of microstructural changes brought about by isochronal treatment. Metallography on these specimens was carried out to reveal the microstructures. The etchant used consists of 7% hydrogen fluoride, 42% nitric acid and 51% water.

3. Results and discussion

The variation of positron annihilation S-parameter as a function of annealing temperature is shown in Fig. 1. The measured value of as-quenched sample is taken as a reference. The observed S-parameter value for 473 K is comparable to that of the reference sample, thereafter it increases, exhibiting a plateau between 673 and 873 K and reduces to a value close to that of the reference at 973 K. The increase in the S-parameter above 573 K indicates an increase in positron trapping rate due to the presence of trapping sites. This indicates the production of positron trapping sites as a consequence of the formation of intermetallics in the matrix. The variation of mean positron lifetime as a function of aging temperature is shown in Fig. 2. The observed increase in lifetime is large, indicating the presence of large concentration of positron trapping sites viz., interfacial

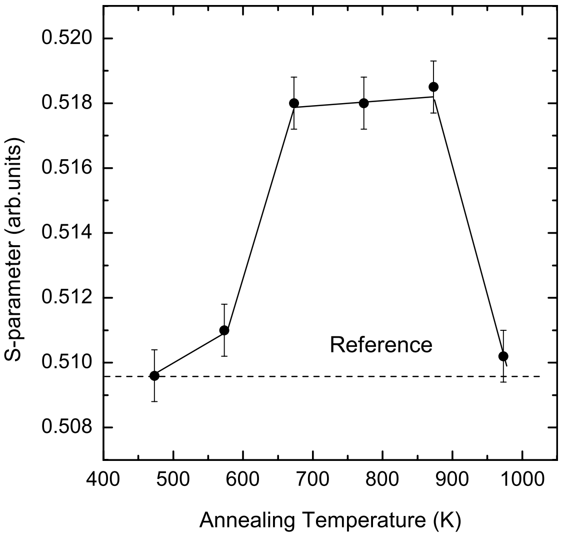

Fig. 1. Variation of Doppler S-parameter for samples annealed at different temperatures. The dashed line corresponds to reference value of β-quenched sample. The line drawn through the points is a guide to the eye.

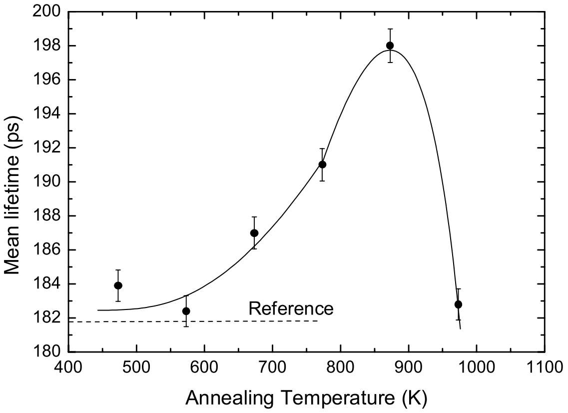

Fig. 2. Variation of mean lifetime with annealing temperature for β-quenched zircaloy-2. The dotted line corresponds to reference value of β-quenched sample. The line drawn through the points is a guide to the eye.

misfit dislocations between the matrix and the precipitates. The general variation of lifetime is slightly different than that of *S*-parameter in the initial temperature range, which is discussed below. The final decrease in positron annihilation parameters beyond 873 K could be ascribed to the reduction in the amount of intermetallic precipitates formed in the matrix.

In literature [5], both lifetime and *S*-parameter measurements have been reported for the investigation of the nature as well the evolution of the defect structures. It may be pointed out that positron annihilation measurements probe different aspects, due to positron trapping at defect sites. Angular correlation and Doppler broadening studies measure the changes in electron momentum, while positron lifetime values reflect the changes in local electron density. Based on the nature of defects, the sensitivity of each of these measurements may vary. For example, investigation of early stages of fatigue damage and the evolution of defect complexes has been reported in reactor alloys using lineshape *S*-parameter measurements [6]. In these studies, it is found that *S*-parameter is very sensitive to the variation of dislocation density in early stages but exhibits a saturation behaviour at later stages of fatigue life, due to the loss of sensitivity during the crack initiation and growth stages. In the present case, *S*-parameter exhibits early saturation, while positron lifetime shows more sensitivity to the evolution of the interfacial defects associated with intermetallic precipitates. The present *S*-parameter and lifetime results suggest that the onset of such intermetallic precipitation takes place beyond 573 K, leading to existence of large concentration of positron trapping sites during 673–873 K. Beyond 873 K, intermetallic precipitation is suppressed with positron annihilation parameters acquiring values close to that of reference sample. In fact, similar variation in positron lifetime was also observed in Ti-stablised SS316 [7], corresponding to the formation, growth and dissolution of TiC precipitates. The decrease in positron parameters above 873 K in the present case is attributed to reduced intermetallic precipitation, as the concentration of interstitial solute in quenched state could be well within the terminal solid solubility limit for precipitation at temperatures higher than 873 K. It is interesting to note that the observed precipitation temperature range is well below those reported earlier and discussed in a critical review by Arias [8]. Also the precipitation is seen to occur well below the $\alpha \rightarrow \alpha + \beta$ transformation [9]. However, one can not rule out the possibility of formation of precipitates during heating which ultimately dissolve at temperature above 873 K [4].

Hardness measurements, shown in Fig. 3, have revealed an increase from 573 K, a plateau between 673 K and 873 K, followed by a decrease to nearly original value of as-quenched sample at 973 K. The variation of macroscopic parameter like hardness is fully consistent with defect evolution as sensed by positron annihilation measurements. As a consequence of the presence of defect species, the observed hardness values exhibit large values during 673–873 K. Microstructural features revealed by metallographic observations are shown in Fig. 4. As-quenched sample consisted of martensitic structure as shown in Fig. 4(a), while aging at elevated temperatures up to 873 K resulted in the formation of hard intermetallic phases as seen in Fig. 4(b). Aging at 973 K resulted in the reduction of the amount of intermetallics and the formation of α-Zr in a few isolated places as revealed in Fig. 4(c). Due to the formation of hard intermetallic precipitates, matrix–precipitate interfaces act as positron trapping sites, giving rise to observed changes seen in *S*-parameter and lifetime values, as shown in Figs. 1 and 2 and hardness variation seen in Fig. 3.

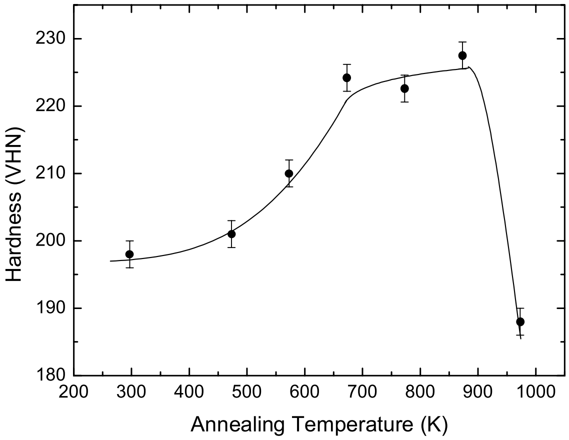

Fig. 3. Variation of hardness with annealing temperature. The line is a guide to the eye.

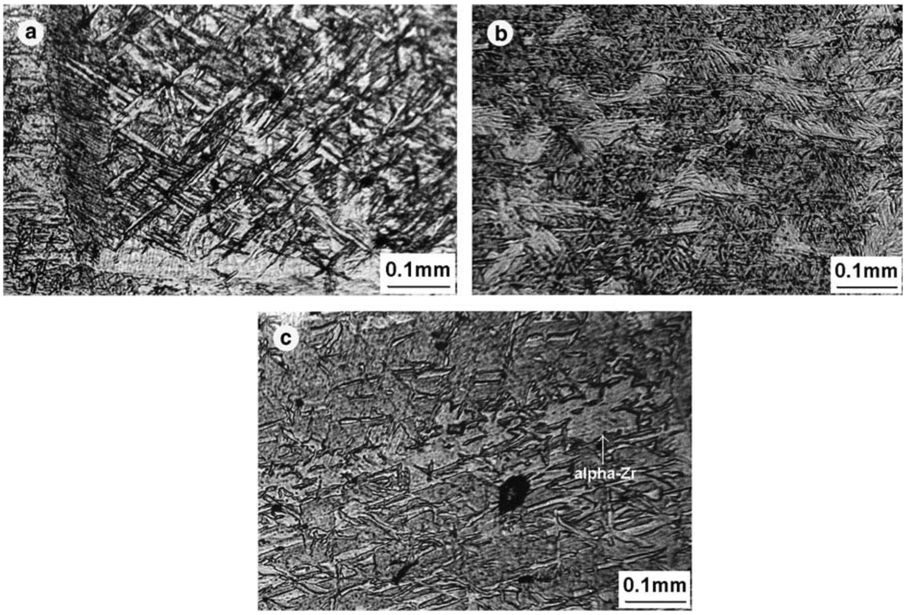

Fig. 4. Optical micrographs of β-quenched and thermally annealed Zircaloy-2. (a) β-quenched, (b) annealed at 773 K and (c) annealed at 973 K.

For comparison, the ultrasonic velocity measurements carried out on the same samples [10] are shown in Fig. 5 for three frequencies viz., 10 MHz, 16 MHz and 25 MHz. The observed ultrasonic velocity variation is complementary to that of hardness and positron annihilation results. The observed variation is found to be maximum for 25 MHz waves, indicating stronger coupling of the waves with the medium, as compared to lower frequencies. The longitudinal velocity decreases initially as a function of aging temperature, exhibiting a broad minimum around 800 K and there after it increases attaining values close to the reference value. The observed reduction in ultrasonic velocity can be attributed to the change in the mean modulus brought about by the precipitates of hard intermetallic phase. At 973 K, because of presence of only a small amount of intermetallics, the ultrasonic velocity increases close to that of the as-quenched sample. The changes seen in ultrasonic velocity are complementary to that of positron lifetime variation i.e., exhibiting a continuous change rather than saturation behaviour seen in *S*-parameter and hardness variations. While positron lifetime probes the local electron density changes, the ultrasonic velocity probes the microstructural modulus or density changes. When the modulus of the matrix decreases, locally the electron density decreases giving rise to a reduction in measured ultrasonic velocity and an increase in positron lifetime values. These changes can be ascribed due to the production and growth of intermetallic precipitates in the matrix.

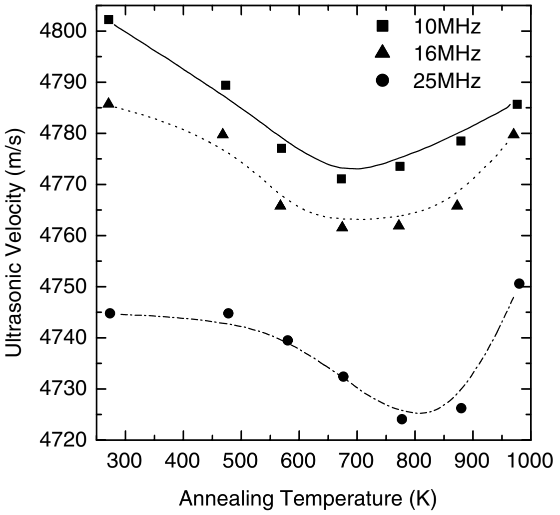

Fig. 5. The variation of longitudinal velocity with annealing temperature for 10 MHz, 16 MHz and 25 MHz ultrasonic frequencies.

The observed features in the experimentally measured parameters viz., positron lifetime and Doppler lineshape, hardness, and ultrasonic velocity are mutually consistent and are in accordance with the microstructural observations. The observed variation of the experimental parameters can be explained based on the following. At lower aging temperatures up to 573 K, lower kinetics restricts the formation of intermetallics. At higher temperatures, even though the kinetics is favourable, the amount of intermetallic formed is less because of higher solubility of the elements, forming the intermetallics, in the matrix. But aging at intermediate temperatures viz., 673–873 K, results in appreciable formation of intermetallics as revealed by changes observed in hardness, positron annihilation parameters and ultrasonic velocity. Metallography observations provide corroborative evidence towards this.

4. Conclusions

Formation of intermetallic precipitates in β-quenched Zicaloy-2 samples were investigated by positron annihilation, hardness and ultrasonic velocity measurements. The positron annihilation parameters exhibit an increasing trend during 673–873 K temperature range, indicating the formation of misfit dislocations due to the occurrence of intermetallic phases. Complementary changes are observed in hardness, ultrasonic velocity and metallographic measurements. While positron annihilation studies provided information about atomistic interfacial defects associated with intermetallic precipitates, the ultrasonic velocity measurements were probing the changes in mean modulus. Hardness and metallography measurements provided macroscopic evidence towards the changes brought about by the intermetallic precipitates.

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