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Effect of He implantation on the microstructure of zircaloy-4 studied using *in situ* TEM

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HIGHLIGHTS

- Differences in the evolution of α and βZr microstructures under 6 keV He ion implantation have been analysed using *in situ* TEM.
- Both thermal and irradiation stabilities of Zr hydrides particles were studied and were found to dissolve with increasing fluence.
- Two different mass-transport mechanisms for He in zircaloy-4 are believed to play a major rule in the Zr hydride irradiation-induced dissolution.
- He bubble lattices were observed to form during irradiation at 473 and 1148 K in α and βZr at around the same fluence of 1.7×10^{17} ions·cm^{-2}.

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ABSTRACT

Zirconium alloys are of great importance to the nuclear industry as they have been widely used as cladding materials in light-water reactors since the 1960s. This work examines the behaviour of these alloys under He ion implantation for the purposes of developing understanding of the fundamental processes behind their response to irradiation. Characterization of zircaloy-4 samples using TEM with *in situ* 6 keV He irradiation up to a fluence of 2.7×10^{17} ions·cm^{-2} in the temperature range of 298 to 1148 K has been performed. Ordered arrays of He bubbles were observed at 473 and 1148 K at a fluence of 1.7×10^{17} ions·cm^{-2} in αZr, the hexagonal compact (HCP) and in βZr, the body centred cubic (BCC) phases, respectively. In addition, the dissolution behaviour of cubic Zr hydrides under He irradiation has been investigated.

1. Introduction

Zirconium alloys have been widely used in the nuclear industry since the 1960s as nuclear fuel claddings because of their corrosion resistance, low thermal neutron absorption cross sections and their desirable mechanical properties [1–6].

In a nuclear reactor, neutron irradiation causes changes to the microstructure and properties of both structural and fuel materials. In the case of Zr alloys, it has been reported that dislocation loops are the most common type of damage observed which increase in size and decrease in density with increasing neutron irradiation temperature [7]. The formation and growth of vacancy-type dislocation loops [8] has been associated with the swelling of zircaloy-2 and -4 by Griffiths *et al.* [9]. Gilbert *et al.* observed in post-irradiated zircaloy-2 that (n,α) transmutation reactions, mainly from ^{10}B and O impurities, lead to the preferential nucleation of cavities on grain boundaries [7]. The low concentration of He, presence of dislocation loops, low energy for vacancy formation and relatively-high atomic volume of Zr have been connected with the absence of voids in neutron irradiated Zr and its alloys [4,7,10,11].

Ion beam irradiation has been applied as a powerful technique to test alloys and other materials prior to their use in nuclear reactors [12]. As well as avoiding the hazards associated with induced radioactivity, it is possible to reach the damage levels of a conventional light-water reactor (LWR) ($\approx$ 2 dpa[1]·year^{-1} [13]) in minutes to hours compared to rates in materials test reactors of between 10 and 20 dpa·year^{-1} [12]. By careful selection of the ion irradiation parameters such as damage rate and temperature, it is possible to simulate the conditions experienced in a nuclear reactor

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[1] Displacement-per-atom or dpa: at one dpa every atom has, on average, been displaced from its lattice site once.

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[12,14].

One area of particular interest has been the implantation of inert gases such He, Xe and Ar into metals [15] and much work has been done for many different systems including iron and its alloys [16], tungsten [17–19], copper [20], nickel [21], molybdenum [22,23] and carbon [24] which are important for both fission and fusion reactors.

There have been numerous studies looking into the effects of irradiation on Zr alloys [4–6,25,26]. Ran *et al.* [27] studied the effects of 800 keV Kr ions on the microstructure of the alloy Zr-Nb-Fe-Cu-Ni observed via transmission electron microscopy (TEM) during *in situ* annealing after irradiation at temperatures from 700 to 1225 K. The authors reported that the size of Kr bubbles was strongly dependent on the annealing temperature and time: bubbles were observed with diameters of around 2.1 nm at 700 K, 2.7 nm at 875 K and 8.9 nm at 1140 K after 180 min of annealing. An exponential empirical formula was proposed for the growth behaviour which was attributed to the increased mobility of Kr ions in the βZr phase.

Pagano *et al.* [28] performed 650 keV Kr irradiation *in situ* within a TEM on four different Zr alloys. Bubble formation was observed in all four alloys and at all irradiation temperatures. However, no clear relationship was found between the bubbles sizes and the irradiation temperature in the range from 573 to 973 K.

Some studies have addressed the effects of He implantation on the microstructure of Zr alloys. Zee *et al.* [29] reported the occurrence of blisters on the surface of Zr-2.5Nb (wt.%) alloy during 50 keV He implantation at temperatures from 100 to 773 K. They concluded that when the alloy is cold worked prior to irradiation, βNb precipitates could act as trapping sites resulting in the development of He bubbles at a fluence of 5×10^{17}ions$\cdot$cm^{-2}. Another *in situ* TEM annealing study was performed by Shen *et al.* [30] with the alloy Zr-Sn-Nb-Fe-Cr. They irradiated with 400 keV He ions and observed that the mean size of the He bubbles increased with irradiation temperature from 300 to 1173 K and with He fluence from 0.5×10^{17} to 5×10^{17}ions$\cdot$cm^{-2}.

In addition to studies of bubbles in Zr alloys, several papers have aimed to understand the behaviour of Zr hydrides (ZrH) which may lead to delayed fracture and embrittlement in Zr alloys under in-service conditions [31–35]. Hydrides are stable or metastable compounds of the ZrH system and are preferentially formed at grain boundaries during both cooling and corrosion processes [36]. Metallic hydrides are brittle, exhibiting high thermal conductivity, high electrical resistance, high hardness and are often associated with the embrittlement in Zr alloys [37]. Below 873 K, the stable phase of the ZrH system is δ which has a face-centred cubic (FCC) structure with a H content from 0 to 62 at.%. Two other phases are reported: the face-centred tetragonal (FCT, the γ-phase) which is a metastable phase observed below 873 K in the same H content range as the δ-phase, and the ε-phase which is also FCT and occurs when the H content is higher than 64 at.% at temperatures below 973 K [37,38].

Carpenter and Waters [39] performed an *in situ* TEM annealing study to explore the dissolution of γ hydrides up to 700 K. After annealing, the incomplete dissolution of hydrides was concluded to increase the dislocation density. The authors also performed *in situ* TEM electron irradiation of Zr to a dose of 0.065 dpa at room temperature showing that the irradiation can prevent dislocations from annihilating during thermal dissolution. The observed effect of dislocation pinning was associated with the formation of point defect clusters and jogs induced by the electron irradiation.

To date, there have been no studies which have used the technique of TEM with *in situ* He ion implantation to explore the microstructural evolution of Zr alloys. In this work, a TEM study with *in situ* ion irradiation has been performed on zircaloy-4 under 6 keV He bombardment. The irradiated samples have been examined at four temperatures in the range from 298 to 1148 K so as to match the temperatures of a LWR under normal operation and during loss of coolant scenarios and to investigate the differences in the damage microstructure of the αZr, βZr and δZrH phases.

2. Materials and methods

2.1. Samples studied

The material used in this work was zircaloy-4 with the composition Zr-1.45Sn-0.2Fe-0.1Cr (wt.%) and a melting point (T_m) of 2123 K. Prior to the TEM sample preparation, the alloy was chemically etched with a solution containing 5% of HF, 35% of HNO_3 and 60% of deionised water (vol.%). Optical micrographs after etching revealed the presence of equiaxed grains which may indicate that the alloy was cold worked and then annealed.

2.2. TEM sample preparation

Samples 3 mm in diameter were punched from a thin foil and mechanical polishing was performed using SiC paper from 120 to 1200 grit in order to reduce the thickness. The samples were electropolished using a Struers TenuPol-5. A recipe from Ref. [40] was adapted for use with this system: an electrolyte of 10% of $HClO_4$ and 90% of CH_3OH (vol.%) at a bath temperature of 233 K with a flow rate set to 30 (arbitrary units as indicated on the TenuPol-5 display). Electropolishing was performed to perforation and the samples were then washed in methanol and dried in air. Fig. 1 shows a high-resolution TEM image obtained after the sample preparation.

2.3. In situ irradiation and annealing within a TEM at the MIAMI-1 facility

Specimens were irradiated with 6 keV He ions *in situ* within a TEM at four temperatures: 298 (0.14T_m), 473 (0.22T_m), 973 (0.45T_m) and 1148 K (0.54T_m) using a double-tilt heating holder in a JEOL JEM-2000FX operating at 200 kV in the MIAMI-1 facility at the

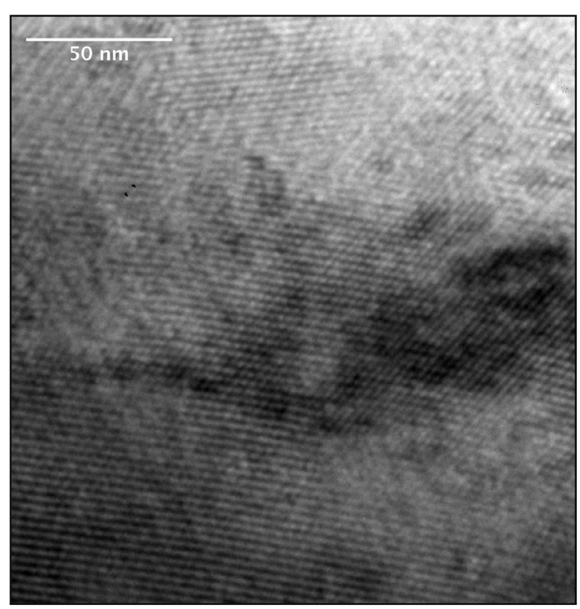

Fig. 1. High-resolution TEM image obtained at room temperature from an electropolished sample of zircaloy-4.