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Investigation of elevated-temperature mechanical properties of δ-hydride precipitate in Zircaloy-4 fuel cladding tubes using nanoindentation

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ABSTRACT

Mechanical properties—Young's modulus and hardness—are measured for metal matrix of Zircaloy-4 cladding and δ-hydride embedded within its matrix using nanoindentation for the temperature range of 300 K–773 K. Yield strength and ultimate tensile strength values for each phase are also evaluated using their empirical relationships with hardness. At room temperature, the Young's modulus values are 99.24 GPa and 133.18 GPa, and the hardness values are 2 GPa and 4.58 GPa for Zircaloy-4 metal matrix and δ-hydride precipitate within its matrix, respectively. Hydrides have the higher hardness and the lower ductility than that of the surrounding matrix, which can result in embrittlement of the Zircaloy-4 cladding. Softening coefficient of the Zircaloy-4 metal matrix is greater than that of the δ-hydride phase precipitate. The mechanical properties of each phase determined from nanoindentation are in good agreement with values reported in the literature, and indicates that the nanoindentation technique can be used to study high temperature mechanical properties.

1. Introduction

Zircaloy-4 is widely used for nuclear fuel cladding tubes in water cooled nuclear power reactors because of its low thermal neutron absorption cross-section, suitable thermal conductivity, high dimensional stability, and corrosion resistance in the harsh environment of a reactor core. The cladding tubes encase radioactive uranium fuel pellets undergoing fission and their outer surfaces are exposed to pressurised coolant water which takes away heat generated due to fission for power generation [1,2]. Zircaloy-4 fuel cladding tubes undergo waterside corrosion during service and a fraction of hydrogen produced as a result of the corrosion diffuses into it [3].

Hydrogen remains in solid solution up to terminal solid solubility and it precipitates as hydride phase in the Zircaloy-4 metal matrix beyond this limiting concentration (about 80 ppm at 300 °C and about 200 ppm at 400 °C) [4–6]. Depending upon the hydrogen concentration in the zircaloy cladding and rate of heating or cooling, four different phases of hydride are observed: ζ-phase ($ZrH_{0.5}$), γ-phase (ZrH), δ-phase ($ZrH_{1.5-1.7}$), and ε-phase (ZrH_2) [7,8]. At reactor operating temperatures, the stable phases present are hexagonal closed packed zirconium with dissolved hydrogen and the face centered cubic δ-phase hydride. The hydrides observed in fuel cladding exposed to the reactor environment are most often of the δ-phase (ZrH_x where x~1.5 to 1.7) [9–11].

Precipitation of hydrides can degrade the mechanical properties of Zircaloy-4, primarily influencing its tensile strength, ductility, fracture toughness, and creep behaviour [12–15]. Degradation caused due to the presence of hydride precipitates can eventually affect the integrity of Zircaloy-4 fuel cladding during normal operation, accident conditions, and spent fuel storage period. The impact of hydrides on the mechanical properties of Zircaloy-4 has been sufficiently investigated at a macroscopic level to obtain its bulk behaviour [12–14,16,17]. However, compared with an embedded hydride precipitate, bulk zirconium hydride has a higher probability of containing defects such as voids and micro-cracks given the large volumetric expansion during its precipitation [18] — a volume expansion of approximately 17% is estimated for δ-hydride. Therefore, there are always some reservations about the exact effects of hydride formation on cladding bulk behaviour. That is why there has been a growing interest in studying the microscale

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properties of the co-existing individual phases. Moreover, progress in theoretical [19–21] and computational modellings of hydride related phenomena such as hydride embrittlement [22], hydride assisted cracking [23], alteration of creep performance by hydride precipitate [24] etc. has also driven the need of having more reliable experimental data on the mechanical properties of embedded hydride precipitates.

Puls et al. [18] hydrogenated the samples cut from Zr-2.5Nb pressure tube material to various hydrogen compositions ranging from $x = H/Zr$ of ~1.2–1.9. The Young's modulus value for the bulk δ-hydride specimen from the unconfined compression tests was calculated to be 97.5 GPa. They also performed micro-hardness tests using a diamond indenter and obtained similar trends. However, it was mentioned in their study that the specimens appear to contain small micro-cracks in their interior after hydrogenation, and this might have an impact on Young's modulus. Rico et al. [25] performed nanoindentation tests on pre-hydrided ZIRLO samples containing bulk of δ-hydride (16000 ppm of H). They reported that mechanical properties of the bulk zirconium hydrides and ZIRLO matrix are rather similar. Yamanaka et al. [26,27] fabricated bulk δ-phase ($ZrH_{1.5-1.7}$) zirconium hydride in the form of pellets from pure zirconium metal and investigated their thermal and mechanical properties. Using ultrasonic pulse-echo measurement technique, unlike Puls et al. [18] and Rico et al. [25], they found that zirconium hydride has higher elastic modulus values and much higher hardness values compared to the parent zirconium metal matrix. The elastic moduli slightly decreased with increase in hydrogen concentration whereas hardness decreased with increasing hydrogen concentration. Conventional uniaxial tensile tests were conducted on bulk δ-hydride sample by Kuroda et al. [28] and they obtained a Young's modulus of 135.9 GPa which corroborated the findings by Yamnaka et al. [26]. All these investigations were performed on bulk zirconium hydrides and a detailed description of the mechanical properties of the bulk zirconium hydrides is provided in Ref. [29]. Evans [30] determined Young's modulus and hardness of individual δ-hydride embedded in the Zircaloy-4 metal matrix using nanoindentation and they found that hydride has higher Young's modulus and hardness. Recently, Kese et al. [31] also conducted nanoindentation tests on individual δ-hydride embedded in the irradiated Zircaloy-2. They also reported higher value of hardness and Young's modulus for the precipitated individual δ-hydride. Theoretical studies [19–21] have been also performed using density functional theory to compute the mechanical properties of individual δ-hydride and all such studies have reported a larger Young's modulus for the δ-hydride precipitate.

Given the possible consequences as a result of degradation of mechanical properties of zircaloy fuel cladding due to hydrides precipitation, not only during normal reactor operation but also during spent fuel storage, there are limited experimental studies [18,25,26,28,30,31] conducted to determine mechanical properties of hydride. The objective of the present experimental investigation is to evaluate elevated-temperature (300–773 K) mechanical properties—elastic modulus and hardness—of δ-hydride precipitate embedded in Zircaloy-4 matrix material using nanoindentation technique.

2. Experimental procedures

2.1. Specimen preparation

The cold-worked stress-relieved unirradiated Zircaloy-4 cladding tube supplied by the Nuclear Fuel Complex, Hyderabad, India is used in the present work. It has an outer diameter of 13.08 mm and a thickness of 0.41 mm. The chemical composition of the Zircaloy-4 cladding material is provided in Table 1. The as-received material is hydrogenated to the concentrations of 600 ppm and 900 ppm using a gaseous hydrogen charging method. This gaseous charging facility, based on a modified Sievert's apparatus, consists of a cylindrical glass chamber placed inside the furnace. The clad specimen is weighed and then placed inside the chamber. The glass chamber is evacuated to create a vacuum of the order of 133.32×10^{-5} Pa. Subsequently the specimen chamber is heated to the temperature of 363 °C. Depending upon the weight of the sample, hydrogen is released into the specimen chamber up to a pre-computed pressure; a detailed description of the facility is given [32]. Hydrogen concentration in the cladding specimens is determined by an inert gas fusion technique using a LECO RH IE hydrogen determinator. The clad tubes—as-received, hydrogenated to 600 ppm and 900 ppm—are cut into 4 mm long samples for nanoindentation tests. The cross sectional surface of the samples is mechanically ground with SiC papers down to 1200 grit, and then etched to reveal their microstructure. Etching was a necessary step to precisely locate hydrides by in-situ imaging during nanoindentation tests. The optical microscopy confirms the presence of circumferentially oriented hydrides in these Zircaloy-4 samples, Fig. 1 shows precipitated hydrides at room temperature in one of the tested samples hydrogenated to 600 ppm.

2.2. Nanoindentation test

Nanoindenting has been widely used in recent years for characterising mechanical properties of materials on a nanoscale level [33–38]. The small size of the indenter makes it possible to obtain mechanical properties of embedded precipitates of different phases in the material. For hydride precipitates, it also eliminates the possible effects of voids and micro-cracks often found in bulk hydrides on its mechanical properties. In the present work, Young's modulus and indentation hardness of both hydride and Zircaloy-4 metal matrix phases are measured using a Hysitron TI 950 Triboindenter equipped with an in-situ scanning probe microscopy. This indenting machine incorporates a dual, independently-controlled resistive heating element architecture that heats from the top and bottom of the sample. The test probe is designed to maximise the thermal resistance of the shaft so that heat conduction through the shaft is negligible. The temperature is allowed to stabilise for 30 min before the indentation tests are started. This ensured that the indenter tip and the sample surface are maintained at a similar temperature, thereby minimizing the influence of heat flux and thermal drift on the measurements. Indentations are performed with a Berkovich indenter having a tip radius of 150 nm and tip total angle of 142.35° at the peak load of 500–1500 μN and the temperature in the range of 300–773 K. The displacement of the indenter for a given load and temperature is

Table 1
Chemical composition of zircaloy-4 fuel cladding.

Name of alloy	Alloy composition					
	tin	iron	chromium	carbon	oxygen	hydrogen
Zircaloy-4	1.25 wt%	0.24 wt%	0.09 wt%	225 ppm	1100 ppm	12 ppm