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Energetic particle irradiation study of TiN coatings: are these films appropriate for accident tolerant fuels?

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HIGHLIGHTS

- Nanocrystalline TiN thin films were produced via magnetron sputtering.
- The films were irradiated with heavy ions *in situ* within a TEM.
- TEM and STEM characterisation indicates that the TiN dissociates under irradiation.
- EFTEM and STEM-EDX showed Ti segregation at grain boundaries and in Xe bubbles.
- Ti-rich zones will experience same oxidation reaction as Zr alloys.

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ABSTRACT

Coating nuclear fuel cladding alloys with hard thin films has been considered as an innovative solution to increase the safety of nuclear reactors, in particular during a of loss-of-coolant accident (LOCA). In this context, and due to its suitable mechanical properties and high corrosion resistance, titanium nitride thin films have been proposed as candidate coatings for zirconium alloys in new accident tolerant fuels for light water reactors. Although the properties of TiN hard coatings are known to be adequate for such applications, the understanding of how the exposure to energetic particle irradiation changes the microstructure and properties of these thin films is still not fully understood. Herein, we report on heavy ion irradiation *in situ* within a Transmission Electron Microscopy (TEM) of magnetron-sputtered TiN thin films. The coatings were irradiated with 134 keV Xe^+ ions at 473 K to a fluence of 6.7×10^{15} ions·cm^{-2} corresponding to 6.2 displacements-per-atom where significative microstructural alterations have been observed. Post-irradiation analytic characterisation with Energy Filtered TEM and Energy-Dispersive X-ray spectroscopy carried out in a Scanning Transmission Electron Microscope indicates that TiN thin films are subjected to radiation-induced segregation. Additionally, the nucleation and growth of Xe bubbles appears to play a major role in the dissociation of the TiN thin film.

1. Introduction

The Fukushima-Daiichi nuclear accident in 2011 has established new challenges for research and development towards the consolidation of Accident Tolerant Fuels (ATF) [1,2]. Zirconium is currently the major constituent of fuel assembly alloys used in the nuclear industry worldwide; however, at high temperatures and during LOCA events, these alloys suffer from oxidation by steam which increases the hydrogen gas generation rate [3–6]. This dangerous accumulation of hydrogen gas could be mitigated or

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even avoided if the zirconium-based alloys were coated with a protective thin film.

Among the variety of commercially available thin films that could serve this purpose, titanium nitride (TiN) is widely used in several industries such as mechanical tools, medical implants and aerospace engineering [7]. TiN thin films have recently been proposed as hard coatings for zirconium-based alloys in Light-Water Reactors (LWRs) [8,9] mainly due to their desirable properties of high mechanical strength [10], suitable corrosion resistance [11] and tribological behaviour [12]. However, with prolonged exposure to the extreme environment of a nuclear reactor these properties will be modified (often degraded) [13]. Therefore, it is important to evaluate the performance of these candidate materials when exposed to displacing irradiation, prior to their use in reactors.

To date, the radiation resistance of TiN thin films has been studied in a wide variety of conditions. The microstructure of polycrystalline TiN thin films was studied at room temperature and under light ion irradiation by Wang et al. and Wan et al. up to fluences of 1×10^{17} ions·cm^{-2}. These authors observed that the grain boundaries, which are abundant in nanocrystals, acted as sinks for radiation-induced Frenkel pairs, providing pathways for diffusion and annihilation, thus suggesting a certain degree of radiation tolerance [14,15]. The radiation performance of TiN films under Ar ion irradiation at room temperature has also been studied by Popovic et al. [16]. These authors observed that the 120 keV Ar irradiation caused a decrease of the lattice parameter of TiN crystals from 0.427 to 0.423 nm which resulted in an increase of the strain in the film layer at fluences of 1×10^{16} ions·cm^{-2}. At higher fluences, 2×10^{17} ions·cm^{-2} and higher irradiation energies, 200 keV Ar^{+}, the increase of the electrical resistivity of the irradiated TiN thin films was attributed to the formation of smaller grains as a result of the ion collisions with the film microstructure [17]. In a later work the same authors carried out irradiation with heavy ions – 400 keV Xe up to 2×10^{16} ions·cm^{-2} at room temperature – and observed that in the irradiated film, XRD measurements exhibited the split of the (111) reflection which indicated both phase transformations as well as contraction of the TiN lattice [18] as opposed to Xue et al. who observed expansion of the TiN lattice under 100 keV Ar irradiation at 873 K [19]. Uglov et al. reported that small Zr additions into the TiN may increase its structural stability under heavy ion irradiation [20], but no post-irradiation microstructural analysis was performed by the authors.

The different microstructural changes induced by ion irradiation in TiN thin films suggested that this material is strongly sensitive to the conditions of the experiment such as fluence, temperature and ion species, therefore an *in situ* TEM ion irradiation study could probe whether such TiN thin films can be regarded as a good candidates for hard coatings in the nuclear industry, while also revealing possible mechanisms of degradation. We report in the present work a heavy ion irradiation study *in situ* within a TEM that assesses the microstructural evolution of the TiN thin films as a function of the irradiation dose. The thin films were irradiated at 473 K and the post-irradiation characterisation has been performed using the analytical techniques of Energy-Filtered TEM (EFTEM) and Energy-Dispersive X-ray Spectroscopy (EDX) within a Scanning Transmission Electron Microscope (STEM). The observation of radiation damage in real time at the nanoscale of the TiN thin films reported in this work, has led to an improved understanding of the radiation damage mechanisms at the fundamental level.

2. Materials and methods

2.1. Synthesis of the TiN thin films

TiN thin films were deposited on Al–Si alloy substrates by the DC grid-assisted magnetron sputtering (GAMS) technique in an Ar + N_2 discharge. This technique is described further elsewhere [21–23]. The substrate was polished and ultrasonically cleaned in tetrachloroethylene for 10 min prior to deposition. The system's chamber was then pumped down to a base pressure of 10^{-2} Pa and the substrate temperature was held at 573 K throughout the deposition. The 99.5% pure Ti target was sputtered prior to deposition to remove any oxide or surface contamination. The grid was grounded and placed 20 mm from the target. The substrate distance from the sputtering target was 60 mm. The deposition was performed at a working pressure of 0.40 Pa with a discharge current of 2.00 A. A DC bias of −30 V was applied to the substrate. The total deposition time was 30 min and the N_2 flow was fixed at 7.7 sccm. The deposition rate was around of 65 nm·min^{-1}. A Ti interlayer was deposited during 2 min, in order to improve TiN film adhesion. After deposition, the thickness of the deposited thin films were measured cross-sectionally in the FIB to be around of 1.5–2 μm.

2.2. Focused ion beam

In order to produce electron-transparent lamellae from the deposited TiN thin film, the conventional focused-ion beam (FIB) technique for TEM sample preparation was used, and a top protection layer of Pt with a thickness of 2.0 μm was deposited onto the thin film surface to reduce FIB damage/gallium contamination (as recommended by Refs. [24,25]).

2.3. In situ TEM with heavy ion irradiation

The *in situ* TEM with heavy ion irradiation was carried out at the MIAMI facility using the MIAMI-2 system with 134 keV Xe^{+} ions at 473 K with a flux of 1.6×10^{13} ions·cm^{-2}·s^{-1}. Considering that TiN has a melting point higher than 3200 K [26], the irradiation was performed at a homologous temperature of around $0.15T_m$ which is close to the primary inlet (coolant) temperature of most LWRs. Additionally, this temperature was chosen in order to minimise bulk diffusion. The microstructural evolution of the TiN thin film was monitored during irradiation with a Hitachi H9500 Transmission Electron Microscope operating at 300 keV and images were recorded using a Gatan OneView digital camera with 16 Mpx.

2.4. Monte Carlo calculations and fluence-to-dpa conversion

Fluence-to-dpa conversions were performed using the Monte Carlo code Stopping and Range of Ions in Matter (SRIM) outputs [27] and a mathematical procedure suggested by Stoller et al. [28]. The thickness of the thin film lamellae was assumed to be 100 nm. Additional parameters used in the conversion were the TiN density of 5.4 g·cm^{-3} and its atomic density of 1.058×10^{23} atoms·cm^{-3} [29]. In this work the thin films were irradiated up to a fluence of 6.7×10^{15} ions·cm^{-2} corresponding to 6.2 dpa. Due to the observed microstructural alterations in the damaged microstructure of the thin films, the irradiations were stopped at 6.2 dpa aiming at further post-irradiation characterisation.

2.5. Post-irradiation characterisation

Post-irradiation analysis was performed using a Gatan GIF Quantum SE camera model 693 for Energy Filtered Transmission Electron Microscopy (EFTEM) in the Hitachi H9500 TEM at the MIAMI-2 Facility and with a FEI Talos F200X Scanning Transmission Electron Microscope operating at 200 keV for Energy Dispersive X-ray (EDX) mapping located at the Low-Activation Materials Development and Analysis (LAMDA) Laboratory at the Oak Ridge National Laboratory. This instrument combines high-resolution