Irradiation-induced Intermixing Effects at the Interfaces of Titanium and Titanium-dioxide Thin Films and Fe-12%Cr Substrate

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Abstract

Irradiation-induced compositional and structural changes at the interfaces between Fe-12%Cr binary alloy substrate and thin films of titanium and titanium-dioxide have been investigated. Irradiations were performed with 5 MeV Ni²⁺ ions at 300°C and 500°C, up to damage levels of 40 dpa (displacements per atom). For the 300°C irradiation case, irradiation enhanced the interdiffusion coefficient by a factor over twenty for the titanium film samples, but by a factor of only 1.2 for the titanium dioxide film samples. At 500°C, significant intermixing was observed in the titanium film samples and resulted in the formation of a wide Fe₂Ti reaction zone. For the titanium dioxide film samples, chromium was observed to diffuse into sub-stoichiometric regions of the film. Irradiation caused the formation of chromium-rich nanoprecipitates within the oxide film and promoted a phase transformation in the film from anatase TiO₂ to the Ti₂O₃ phase.

Keywords: Radiation damage; Thin Films; Intermixing; Stability; Ion Irradiation; Interface.

1. Introduction

The stability of interfaces is receiving considerable attention in the field of nuclear reactor materials, where nanostructured materials have been shown to exhibit higher radiation damage resistance compared to their conventional counterparts. This enhancement in radiation damage resistance has been attributed to a larger area of internal interfaces, which can act as sites for annihilation of defects formed during radiation [1]. For example, improved radiation damage resistance has been demonstrated in nanocrystalline materials which contain large fraction of grain boundaries, such as nickel and copper [2], gold [3], ZrO₂ [4] and steels [5], and this has been corroborated in some cases by computational modeling [6]. Multilayered structures built with individual layers of nanometer-scale thicknesses, including metals [7–11] and metal-oxides [12,13] have also shown similar improvements. Nanostructured alloys, such as oxide dispersion strengthened (ODS) steels have been identified as potential candidate materials for core internals and claddings in Generation IV nuclear reactors. In ODS steels for example, a large number density of small oxide phase particles (typically in the size range of 2-50 nm [14] and with different chemistries, including Y₂Ti₂O₇, Y₂TiO₅, Y₂O₃, TiO₂ and Y-Ti-O non-stoichiometric oxides) effectively pin dislocation movement to impart improvements in creep strength [15,16]. Additionally, these nanoparticles may also enhance radiation damage tolerance due to the metal/oxide interfaces acting as sinks for recombination of vacancies and self-interstitials [12,13] and as trapping sites for helium bubbles as they form under radiation [17,18]. Therefore, the

morphological and compositional stability of the oxide-matrix interface under irradiation will play an important role in the in-service performance of these materials. A crucial issue within the nuclear materials community is the solute redistribution at internal interfaces [19,20]. In ODS steels for example, Cr segregation at the metal/oxide interfaces [21] can potentially affect the corrosion resistance of the alloy [22].

However, irradiation and compositional stability studies at these oxide/matrix interfaces are challenging due to the small size of the oxide phase particles [14], their complex chemistry, and the differing affinities of oxygen to the various metallic constituents of the alloy, which might play an important factor in the changes in the microstructure and microchemistry at the metal/oxide interface [23]. Therefore, in order to reduce the complexity of the analysis, ideal 2-D emulations, with a simplified chemistry, can be performed by synthesizing thin film bilayer or multilayer composite and used as model systems for studies concerning radiation response of solid interfaces [24,25].

With the above background, the present study is aimed at examining the morphological and compositional evolution, after irradiation with 5MeV Ni^{2+} ions at 300°C and 500°C, between a metallic substrate and thin films of a metal (titanium) and its oxide (titanium-dioxide), and to study elemental diffusion at interfaces and chromium segregation in the metal/oxide system. The substrate used for this work was Fe-12%Cr binary alloy, with a simplified composition representative of widely used class of ferritic steels.

2. Experimental Details

2.1 Sample preparation and thin film deposition

A Fe-12 wt. % Cr model alloy was used as a substrate for the thin film depositions. This model alloy with its simplified chemistry precludes the formation of multiple phases as may be the case in multi-component alloy substrates. The composition of the substrate model alloy is shown in Table I.

Table 1. Chemical composition of Fe12%Cr binary alloy substrate in wt.% (Fe balance).

	C	Si	Mn	P	S	Ni	Cr	Co	Ti	O	N	Al
wt.%	0.009	0.02	<0.01	0.015	0.002	<0.01	12.02	<0.01	<0.01	0.27	<0.001	0.014

Substrate samples sectioned to dimensions of 20 mm x3 mm in width were progressively ground and finally mirror polished with 0.5 μm diamond paste, rinsed in water, acetone, ethanol, and plasma cleaned prior to thin film deposition.

Titanium thin films were deposited with a DC sputterer using pure titanium (99.99% purity) sputter cathodes. The depositions were performed at a base pressure of less than 2×10^{-6} Torr. Argon was used as a sputtering gas and the chamber pressure was 1.8 mTorr. Titanium-dioxide film depositions were performed using an RF sputter deposition system and titanium dioxide (99.9% purity) sputter cathodes. The base pressure for deposition was less than 2×10^{-6} Torr. Argon inlet pressure of 1 mTorr was employed for the depositions.

2.2 Heavy Ion Irradiation

The samples were irradiated at the Environmental and Molecular Science Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL) using 5 MeV Ni^{2+} ions. The temperatures for

irradiation were 300°C and 500°C and the base pressure during radiation was in the 10^{-7} Torr range. The ion beam was rastered over an irradiated area of $3 \times 3 \text{ mm}^2$, and this allowed for irradiation of selected regions of the sample, while also providing for neighboring regions (referred to as thermally exposed) that are not irradiated but experienced identical thermal effects as the irradiated regions. Figure 1 shows the experimental arrangement of the samples on the stage.

Figure 1. Experimental arrangement of the samples on the stage for the 5 MeV Ni^{2+} ion irradiation, showing the irradiated regions. The neighboring regions were not irradiated but exposed to the same thermal conditions.

The damage exposures, expressed in dpa (displacements per atom) are calculated from ion fluences with the Stopping Range of Ions in Matter (SRIM) software [26] according to the procedure described by Stoller *et al.* [27] with displacement energies of 40 eV for Fe and Cr, 30 for Ti, and 28 for O. The materials were irradiated to a dose of 8.74×10^{16} ions/cm² and this corresponds to a damage of approximately 35 dpa at the substrate/thin film interface and leads to a nickel peak concentration of ~1.8 atomic % at a depth of more than 1.5 μm underneath the interface. The temperature of the samples was monitored using a K-type thermocouple that was kept in contact with the surface of the sample, but away from the region impinged by the beam.

2.3 TEM sample preparation and microscopy

TEM samples were prepared with conventional focused ion beam (FIB) technique and were analyzed with a FEI Titan S-Twin D2080 transmission electron microscope (TEM) with an accelerating voltage of 200 KV. This microscope is equipped with EDAX energy dispersive x-ray spectroscopy (EDS) detector and spectrum image acquisition capabilities. Quantification of the acquired spectra was performed using the FEI's TEM Imaging and Analysis software (TIA). Beam drift was minimized to reduce position error over the duration of the scan. STEM investigations were performed using annular dark field (ADF) STEM imaging, which provides for a strong diffraction contrast as compared to High Angle (HA)-ADF imaging. Ex-situ x ray diffraction (XRD) experiments were carried out with a Bruker D8 x-ray diffractometer using Cu-K α radiation in order to identify the phases formed after both thermal exposure and irradiation. A low angle incident beam (kept at 2°) was used to maximize the signal from the thin films. Spectra were collected from the as-deposited thin film samples, as well as the thermally exposed and the irradiated regions of the specimen.

3. Results and Discussion

3.1 Titanium Thin Film on Fe-12%Cr Substrate

Bright Field (BF), Dark Field (DF) TEM images and a diffraction pattern of the as-deposited titanium thin film are shown in Figure 2. The film exhibits a columnar grain structure (typically observed for metallic thin films deposited by sputtering at low temperature) that grow through the entire thickness of the film [28]. STEM-EDS line scans across the interface of these samples showed a clearly defined interface with no intermixing between the substrate and the film (not shown).

Figure 2. TEM BF/DF analysis of the as-deposited titanium film on Fe-12%Cr substrate, (a) BF image and diffraction pattern and (b) DF image.

In order to characterize the structure of the films and evaluate intermixing effects between the substrate and the thin film on a nanometer scale, STEM-EDS analysis was performed. Figure 3 shows typical composition profiles for Fe, Cr and Ti for the 300°C experiment for the irradiated and the thermally exposed conditions.

Figure 3. STEM-EDS elemental concentrations profiles across the Fe-12%Cr substrate - Ti thin film interface in the thermally exposed and irradiated regions at 300°C. (a and b) thermally exposed region (c and d) irradiated region. Compositional line scans were acquired along the orange line indicated in the ADF images.

Comparing the elemental compositional profiles for the two conditions, it is evident that irradiation significantly enhanced the interdiffusion between the Ti film and the Fe-Cr substrate, across the interface. In order to quantify the intermixing between the substrate and the film for the irradiated and thermally exposed regions, the interdiffusion coefficient was calculated analogous to a diffusion process between two semi-infinite solids. In the quantification process, in order to obtain

elemental composition ranging between 0 and 100%, iron and chromium concentration were summed up. Starting with Fick's second law, the solution for the concentration in the case of a bilayered system can be fitted by an error function (and its complement), which is also the solution of the equation in the case of a semi-infinite source:

$$C(x, t) = \frac{C_0}{2} \operatorname{erf} \left(\frac{(x - x_0)}{\sqrt{4\tilde{D}t}} \right) \quad 1$$

where $C(x, t)$ is the concentration profile of the diffusing atoms, erf is the error function, C_0 is the initial concentration, x_0 is the center of the mixing profile, $\tilde{D}$ is the interdiffusion coefficient, and t is the exposure time. The experimental profiles were interpolated by integral fitting of the functions representing the elemental compositions, following the approach outlined in literature [29]. The relevant parameters to perform the fit are x_0 and $\sqrt{4\tilde{D}t}$. Other parameters are used in the fitting process but they serve only to shift and scale the functions along the y-axis and therefore do not represent any physical phenomena. Figure 4 shows typical composition profiles for Ti and Fe+Cr in the 300°C experiment for the titanium coated samples. The interdiffusion coefficients calculated and averaged for five separate line scans were determined to be $(4.09 \pm 0.31) \times 10^{-18} \text{ cm}^2/\text{s}$ and $(9.02 \pm 1.37) \times 10^{-16} \text{ cm}^2/\text{s}$ in the thermally exposed and irradiated samples, respectively. As can be seen, irradiation caused an increase in the interdiffusion coefficient by a factor greater than 20. Also, because ion beam mixing is a symmetrical process [22], the interdiffusion coefficients calculated from the compositional profiles of Ti and Fe+Cr are equal, within the experimental error.

Figure 4. STEM-EDS elemental concentration profiles across the Fe-12%Cr substrate - Ti thin film interface in the thermally exposed and irradiated regions at 300°C, (a) Fe+Cr profile (b) Ti profile. Insets represent the ADF STEM images of the thermally exposed (left image) and irradiated exposed (right image) regions. Compositional line scans were acquired along the orange line indicated in the ADF images. Arrows indicate the reaction layer thickness.

STEM-EDS analysis was performed on the thermally exposed and irradiated regions of the samples irradiated at 500°C, and typical line scans are shown in Figure 5. At this temperature thermal effects are expected to play a more dominant role in the evolution of the system, because of the high chemical affinity between iron and titanium due to the large negative enthalpy of mixing ($\Delta H_{\text{Fe-Ti}} = -25 \text{ KJ/mol}$ as calculated by the Miedema's model [30]). As can be seen from Figure 5 (a) and (b) thermal exposure alone results in the formation of a wide *interdiffusion region* (~340 nm) between the substrate and the thin film, with a reaction layer consistent in composition with Fe_2Ti intermetallic phase. In this region, spikes in the iron and titanium concentrations suggest the formation of nanoscale precipitates enriched in titanium and depleted in iron, as compared to the reaction layer matrix composition. These precipitates are speculated to be FeTi intermetallics. The deviation of the observed composition from the one expected for FeTi may be due to the juxtaposition of the nanoprecipitate dispersion and the matrix material, both of which contribute to the measured EDS signal. **These two intermetallic compounds are the only equilibrium ones**

between Fe and Ti, as dictated by the Fe-Ti equilibrium phase diagram [31]. As shown in Fig 5 (c) and (d), irradiation enhances the spatial extent of the intermixed layer (~490nm), and additionally promotes diffusion of Cr from the substrate into this region. In both the irradiated and thermally exposed regions, chromium concentration was found to be higher at the substrate-thin film interface, as compared to the substrate matrix composition.

Figure 5. STEM-EDS analysis of the interface between the Ti film and the substrate after 500°C irradiations. (a and b) STEM image and EDS line profile for the thermally exposed region (c and d) STEM image and EDS line profile for the irradiated regions. Compositional line scans were acquired along the orange line indicated in the ADF images.

To identify the phases formed in the near-surface regions of the film-substrate system, XRD analysis was performed on the samples and the results are shown in Figure 6. As can be seen, after both thermal exposure and irradiation the peaks corresponding to Fe_2Ti are clearly observed. Moreover, irradiation causes a slight shift of the Fe_2Ti peaks toward higher 2θ angles, which indicates a reduction (relaxation) of the lattice parameter for this phase after irradiation.

Figure 6. XRD spectra of the titanium thin film deposited sample on Fe-12%Cr substrate in the as-deposited condition, thermally exposed and irradiated regions at 500°C. After thermal exposure and irradiation, the peaks corresponding to Fe₂Ti are observed. The peak close to $2\theta=45^\circ$ is due to the substrate.

Previous studies on irradiation stability of Fe/Ti multilayers, performed at room temperature, have observed the formation of a solid solution and amorphous compounds [32–34]. Intermixing studies performed at temperature ranges comparable to our study have observed the formation first of a Fe-Ti solid solution, followed by the precipitation of FeTi intermetallics [35–37]. The difference with our observations (formation of Fe₂Ti layer along with, possibly, nanometer sized FeTi precipitates) is speculated to be due the difference in the relative Fe/Ti compositions between the cited studies (Fe/Ti ~1) and our experiment (Fe>>Ti).

3.2 Titanium-dioxide Thin Film on Fe-12%Cr Substrate

The as-deposited titanium-dioxide films were amorphous. A BF-TEM micrograph of the as-deposited film is shown in Figure 7, along with its diffuse ring diffraction pattern indicating its amorphous nature. STEM-EDS line scans acquired across the interface of this sample showed a clear, well-defined interface and no appreciable intermixing between the substrate and the film (not shown).

Figure 7. TEM-BF image of TiO₂ thin film deposited on Fe-12%Cr substrate. The diffraction pattern for the film (inset) shows diffuse rings typical of amorphous phase.

Figure 8 shows the STEM-EDS analysis of the samples irradiated at 300°C for the irradiated and thermally exposed regions along with the ensuing composition profiles determined using the procedure described earlier for the Ti-films. The length-scales for intermixing for the TiO₂-film are shown in Figure 8 and are significantly smaller than the ones observed earlier for Ti films (Figure 4): irradiation had a less significant effect on the interdiffusion between the substrate and the film. In fact, quantitative analysis of the substrate-thin film interdiffusion coefficient indicates an increase by a factor of 1.2, from $(5.97 \pm 0.28) \times 10^{-18} \text{ cm}^2/\text{s}$ in the thermally exposed region to $(7.11 \pm 0.34) \times 10^{-18} \text{ cm}^2/\text{s}$ for the irradiated region, indicating that the metal-oxide bilayered system is more resistant to intermixing than the metal-metal system.

Figure 8. Experimental elemental profiles across the substrate-thin film interface in the thermally exposed and irradiated regions of the TiO₂ film samples at 300°C. (a and b) Fe+Cr profile (c and d) Ti+O profile. Insets represent the ADF STEM images of the thermally exposed (left image) and irradiated exposed (right image) regions. Compositional line scans were acquired along the orange line indicated in the ADF images.

Analysis of the samples irradiated at 500°C was complicated due to the evolution of various phases in the TiO₂ film in both the irradiated and thermally exposed regions. Figure 9 shows the results of XRD analysis indicating phase evolution in the TiO₂ film. The XRD pattern for the as-deposited film does not indicate any crystalline peak confirming its amorphous nature. This is consistent with the observations made in Figure 7. After thermal exposure at 300°C, XRD results reveal that the amorphous TiO₂ film transforms to crystalline anatase TiO₂. On the other hand, irradiation at 300°C results in the formation of an oxygen deficient Ti₂O₃ phase. After thermal exposure at 500°C, the TiO₂ anatase phase was detected along with other sub-stoichiometric phases of titanium dioxide. For films irradiated at 500°C, Ti₂O₃ was the predominant phase. Based on these observations, irradiation appears to promote the formation of the sub-stoichiometric Ti₂O₃ phase. We note here, that for films irradiated at 300°C, and those thermally exposed as well irradiated at 500°C, a peak positioned at a 2θ angle of 26.3° could not be uniquely assigned to any specific oxide phases of titanium dioxide.

Figure 9. XRD patterns of samples of TiO_2 thin film deposited on Fe-12%Cr substrate samples. Upon exposure at 300°C the initially amorphous coating crystallizes in the anatase form of TiO_2 , however irradiation appears to promote the formation of Ti_2O_3 phase.

In the 500°C thermally exposed regions, STEM-EDS examination indicated that Cr diffusion had occurred in some grains of the TiO_2 film while other grains were devoid of Cr diffusion. Therefore grains with and without Cr diffusion were selectively analyzed by TEM to identify the phases constituting these grains. Phase identification in TEM relies on the acquisition of multiple diffraction patterns using multiple zone axis and these diffraction patterns and their respective angles can then be compared to the theoretical values obtained by simulating the expected zone axis of potential phases [38] (in this case Ti_4O_7 , Ti_2O_3 , Ti_3O_5 , TiO , anatase and rutile were chosen as possible candidates). Figure 10 shows the analysis of a grain in which chromium diffusion was not observed while Figure 11 shows the analysis of an adjacent grain in which chromium diffusion was observed, along with EDS line scans and the diffraction patterns acquired for these grains.

Figure 10. Phase identification in the TiO_2 film in the thermally exposed region after 500°C experiment, (a) STEM image b) TEM image with the grain which was analyzed circled in red (c) EDS line profile (oxygen was excluded from the analysis), showing that diffusion of chromium is not present in the grain analyzed.

In Figure 10, a low index zone axis DP, belonging to the $[100]$ pole was acquired first, and then the analyzed grain was tilted following one Kikuchi line (the tilting direction

is represented by a dashed white line in Figure 10) until the next zone axis was found. DPs were acquired sequentially and compared with simulated DPs (shown as superimposed red dots in Figure 10 (e) – (g)). The following zone axis identified match well the $[50\bar{1}]$, the $[20\bar{1}]$ and the $[10\bar{1}]$ zone axis of anatase. The experimentally determined angles between the $[100]$ zone axis and the following ones are 26.39° , 51° and 66.9° degrees respectively, very consistent with the ones expected theoretically for anatase, which are 26.7° , 51.5° and 68.31° . According to this analysis the phase of this grain is identified as TiO_2 -anatase.

Figure 11 shows the phase identification performed on a neighboring grain in which chromium diffusion was observed.

Figure 11. Phase identification in the titanium-oxide film (a) STEM image (b) TEM image of the analyzed gain (shown with dark contrast) (c) EDS line profile (oxygen was excluded from the analysis), showing that diffusion of chromium in the grain analyzed. The analyzed grain is the dark grain, while the circled one is the grain analyzed in Figure 10.

Successful phase identification in this Cr-diffused grain was not achieved as the zone axis acquired could not be uniquely matched to any of the possible phases hypothesized. It was however confirmed that this grain was not anatase or rutile. The zone axes shown in Figure 10 are compatible with the k) $[210]$, l) $[42\bar{1}]$, m) $[541]$ and n) $[120]$ zone axis of Ti_2O_3 . Simulated DPs (red dots) for the Ti_2O_3 structure are superimposed the experimentally obtained data. Dashed white line indicates the direction, in the reciprocal space, followed while tilting the specimen to acquire the different DPs. Angles between the $[120]$, the $[42\bar{1}]$ and the $[210]$ zone axis were measured to be respectively 37.64° and 58.93° and are consistent with theoretical values of 37.34° and 60° , respectively for Ti_2O_3 . Angles between the $[42\bar{1}]$, the $[66\bar{1}]$ and the $[120]$ zone axis are 16.88° and 67.67° which also compare well to the theoretical values of 17.48° and 66.58° , respectively, for Ti_2O_3 . It must be noted however that following the Kikuchi lines connecting the $[210]$ zone axis to the $[120]$ zone axis, a zone axis that did not match the expected $[110]$ for Ti_2O_3 was observed. Thus the Ti_2O_3 phase was identified in the Cr-diffused grain with a high degree of certainty. It was however confirmed that the phase of this grain was not TiO_2 anatase or rutile.

It is worth noting that in Figure 10, enrichment of Cr at the substrate-thin film interface was observed. This was not observed in the entire coating, but only in small regions of it. It is likely that this selective enrichment of Cr in certain regions of the interface will be influenced by the relative orientation (or misalignment angle) between grains of the substrate and the grains of the film, similarly to what is observed for grain boundaries in steels [39].

It is interesting to note that diffusion of Cr from a FeCr thin film into a TiO₂ thin film, after thermal exposure and irradiation with nickel ions at the same temperature (500°C), has been already observed by Xu et al. [25], where diffusion of Cr inside titania was correlated with the presence of an oxygen deficient phase of TiO_{2-x}. Our observations are consistent with these results. Regarding the mechanism for Cr diffusion into this oxygen deficient phase, there are three possibilities: (i) interstitial diffusion after Cr has dissolved substitutionally, (ii) diffusion of Cr along grain boundaries, which provide a fast diffusion pathways in the oxide, and (iii) diffusion through vacancy exchange mechanism into the oxide. Following the reasoning in ref. [25], the third mechanism is deemed to be the most likely. Cr diffusion is observed after thermal exposure, where interstitials are unlikely to be present, and the Cr distribution appears to be homogenous in the TiO_{2-x} phase and no enrichment is found on film's grain boundaries.

Figure 12 shows results of STEM-EDS analysis of samples irradiated at 500°C. As can be seen, the substrate thin film interface is still intact. However, Cr-rich precipitates (as shown in Figure 12 (c and d)) were observed within the oxide. Although Cr diffusion was observed even in thermally exposed samples, radiation clearly facilitates the formation of Cr-precipitates.

Figure 12. Experimental elemental profiles across the substrate-thin film interface in the TiO₂ thin film samples irradiated at 500°C. (a and b) profile across the interface and (c and d) Cr-rich precipitates formed within the Ti-oxide coating. Oxygen was excluded from the quantification process.

4. Conclusions

Film-substrate interface mixing effects in titanium and titanium dioxide thin films deposited on Fe-12%Cr alloy substrate due to 5 MeV Ni²⁺ ion irradiations at 300°C and 500°C have been investigated at nanometer length scales by using STEM-EDS, TEM and XRD techniques. Radiation-induced effects were isolated from purely thermal effects by also examining regions of samples that were not irradiated but experienced the same thermal history. At 300°C, irradiation enhanced the extent of mixing between titanium and the alloy substrate, but the effect was not as pronounced for the titanium dioxide thin films. Therefore, the metal-oxide bilayered system is more resistant to intermixing than the metal-metal system. At 500°C, an intermixed reaction layer consisting of Fe₂Ti intermetallic phase was observed for both thermally exposed and irradiated Ti-film samples, with irradiation enhancing Cr diffusion into the Ti film. For the titanium dioxide film, irradiation had a marginal effect in enhancing mixing at 300°C, but at 500°C enhanced diffusion of Cr inside sub-stoichiometric regions of the oxide thin films was observed. Irradiation promoted the formation of Cr-rich nanoprecipitates in the oxide and a phase transformation in the film from anatase TiO₂ to the Ti₂O₃ phase.

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