

Irradiation-Enhanced Second-Phase Precipitation in Zr-Fe Nanocrystalline Thin Films

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ABSTRACT

In situ observations in a transmission electron microscope (TEM) were used to study ion-beam enhancement of second-phase precipitation in Zr-Fe nanocrystalline thin films. The free-standing films were prepared by co-sputter deposition with an Fe content of 1.2 at%. TEM diffraction analysis showed that only the hcp Zr crystal structure was present in the as-deposited films. No second phases were detected, although Rutherford Backscattering Spectroscopy (RBS) confirmed a Fe content beyond the solubility limit of Fe in Zr (of the order of ppm). This means the thin films were Zr solid solutions supersaturated with Fe. Heat treatment in the absence of irradiation was observed to cause precipitation of the Zr₂Fe intermetallic phase, but only above 673 K. The same second-phase precipitation can occur at lower temperatures in the presence of ion irradiation. Samples were irradiated in-situ at the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory with Kr ions to fluences in excess of 10¹⁶ ion/cm², at temperatures ranging from 50 to 573 K. Second phase precipitation was detected by electron diffraction patterns and by dark field imaging comparing regions exposed to the beam with regions protected from the beam by the TEM support grid. Precipitation of Zr₂Fe intermetallic phase was observed at all irradiating temperatures above room temperature. In the bulk, this phase is thermodynamically metastable in the range of temperatures investigated (relative to the orthorhombic Zr₃Fe intermetallic phase). The kinetics of the irradiation-enhanced second-phase precipitation was followed by recording the diffraction patterns at regular intervals. The dose to precipitation was found to decrease with increasing irradiation temperature.

INTRODUCTION

The binary Zr-Fe alloy system has been the focus of a number of studies because of its technological importance especially in the nuclear industry where Fe-containing Zr alloys are used as fuel cladding material. The system has also received attention because the Zr-Fe binary alloys are excellent glass formers over a wide range of compositions. Studies of the crystallization of Zr-Fe glasses showed that the immediate products of crystallization are often metastable phases which would not have been predicted from the Zr-Fe phase diagram [1]. In general, the problem of irradiation induced or irradiation enhanced precipitation, and more generally phase formation, has received both experimental and theoretical attention [2-5]. One of the problems with studying irradiation induced phase transformations is that the kinetics are not usually accessible to the experimentalist and thus the mechanisms of phase transformation are difficult to determine. In this study, we use in-situ ion irradiation in an electron microscope to study phase formation in supersaturated metallic solid solutions. The Zr-Fe system is chosen as a model system to study and ultimately understand the kinetics and mechanisms of precipitation reactions in metallic alloys under irradiation.

EXPERIMENTAL METHODS:

Sample preparation: The polycrystalline Zr-(1.2 at.%)Fe films were co-sputter deposited onto NaCl substrates and onto Si wafers (for Rutherford Backscattering Spectroscopy (RBS) characterization) using a dual gun system at a base pressure of the order of 10^{-7} Torr at room temperature at the Materials Research Laboratory (MRL, Penn State University). The coated NaCl substrates were cleaved into small pieces and the specimens were floated on a de-ionized water-ethanol solution onto TEM copper grids, cleaned in de-ionized water, and dried before they were irradiated.

Characterization of the as-deposited thin-films: Figure 1 shows a bright field TEM micrograph and the associated diffraction pattern of a typical film in the as-deposited state. These films are $\sim 800\text{\AA}$ thick, laterally homogeneous, and nanocrystalline, with an initial mean grain size between 15 and 20 nm. The diffraction patterns show rings which can be indexed as the hexagonal α -Zr phase with no second phase present, although the Rutherford Backscattering (RBS) analysis confirmed an iron content in the Zr-Fe films beyond the solubility limit of Fe in Zr which is on the order of a few ppm at room temperature [6]. For the iron content and temperature range of interest in this study, according to the phase-diagram the equilibrium state is a two-phase system composed of α -Zr and orthorhombic Zr_3Fe phases. However, because of the rapidity of the effective quench during thin film deposition, second phases do not form and these films are formed as supersaturated solid solutions of Fe in α -Zr. As such, they are thermodynamically in a metastable state. The Zr grains were preferentially oriented with the basal planes perpendicular to the foil surface, as verified by the high 002 intensity in the diffraction pattern.

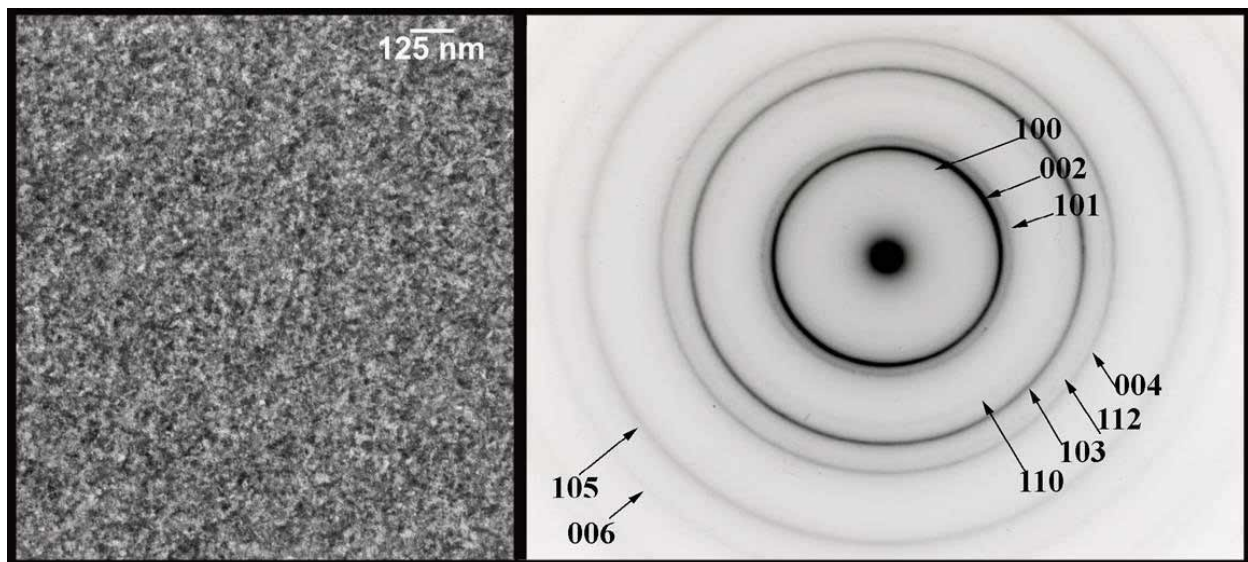


Figure 1: On the left, TEM bright-field image of the as-deposited Zr-1.2%Fe thin films. On the right, the corresponding diffraction pattern (DP): all rings were indexed as α -Zr.

Experiment: The thin films were irradiated at the Intermediate Voltage Electron Microscope (IVEM)-TANDEM facility at Argonne National Laboratory, where an ion accelerator is attached

to an electron microscope operated at 300 keV [7]. Samples were irradiated with 600 keV Kr^+ ions at fluxes typically around 2.50×10^{12} ions/cm².s, at different temperatures ranging from 50 K to 573 K. The ion-beam energy was chosen on the basis of computer simulations using the Monte Carlo program SRIM2003 [8] so that ion-implantation is minimized in the films. The evolution of the microstructure was followed by sequentially taking images and diffraction patterns (DP) of the films while they were being irradiated, which made it possible to follow the kinetics of the induced phenomena. Ion beam heating was quantified in order to determine its contribution to the irradiation enhanced second-phase precipitation. Calculations showed that in the given configuration, with the sample holder in contact with the grid, itself in total contact with the sample, the temperature rise in the sample was no more than 10 K. This increase is negligible in terms of thermal activation processes involved in thermal induced precipitation as shown by thermal ramp runs done in this study. In these experiments, the temperature was increased gradually and held for short times (less than 20 min) at each stage in order to determine at which temperature the phase precipitation occurred readily without irradiation. The new rings associated to Zr_2Fe appeared on the diffraction patterns only upon reaching 673 K. As the temperature was further increased, inner rings identified as oxide rings appeared on the diffraction pattern.

RESULTS AND DISCUSSION:

For all irradiation temperatures ion irradiation of the Zr-Fe thin films showed the formation of a new phase, as indicated by the presence of new rings in the diffraction pattern. For irradiation temperatures above room temperature these new rings were identified as the body-centered tetragonal Zr_2Fe phase. Figure 2 shows both bright-field and dark-field micrographs obtained during in-situ 600 keV Kr ion irradiation at 573 K and the corresponding diffraction patterns. The diffraction pattern associated with the unirradiated area shows only the rings associated with the α -Zr hcp phase, while the diffraction pattern from the irradiated region shows the new rings from the irradiation induced precipitates. The dark field micrographs were obtained as much as possible from the Zr_2Fe rings, although they are close to the Zr rings, and thus it is not completely possible to eliminate the Zr intensity from the dark field. The right-hand-side region in Figure 2 was shadowed from the beam by a specimen grid and is therefore unirradiated while the left-hand-side region was irradiated to a fluence of 10^{16} ion/cm² Kr ions. The dark-field image (figure 2 (right)) shows the presence of irradiation-induced precipitates in the region exposed to the beam. As mentioned above, at temperatures below the eutectoid temperature (795°C) and concentrations less than 24 at%, the equilibrium phase diagram indicates that the stable phases are α -Zr and Zr_3Fe [9]. In this range, the Zr_2Fe phase is therefore a metastable phase. The formation of Zr_2Fe is often observed in melts of compositions where the formation of the thermodynamically stable orthorhombic Zr_3Fe phase is very sluggish [10]. The apparent inability of Zr_3Fe to nucleate may possibly be attributed to a high interfacial energy between the Zr_3Fe phase and the Zr matrix and to the large difference (~15%) in molar volume between Zr_3Fe and α -Zr. At the irradiation temperature of 50 K it is clear that a new phase is formed, (new lines appear in the diffraction pattern) but the new phase is not yet indexed. Interestingly, some amorphous intensity is visible in parallel with the appearance of the crystalline rings corresponding to the new phase.

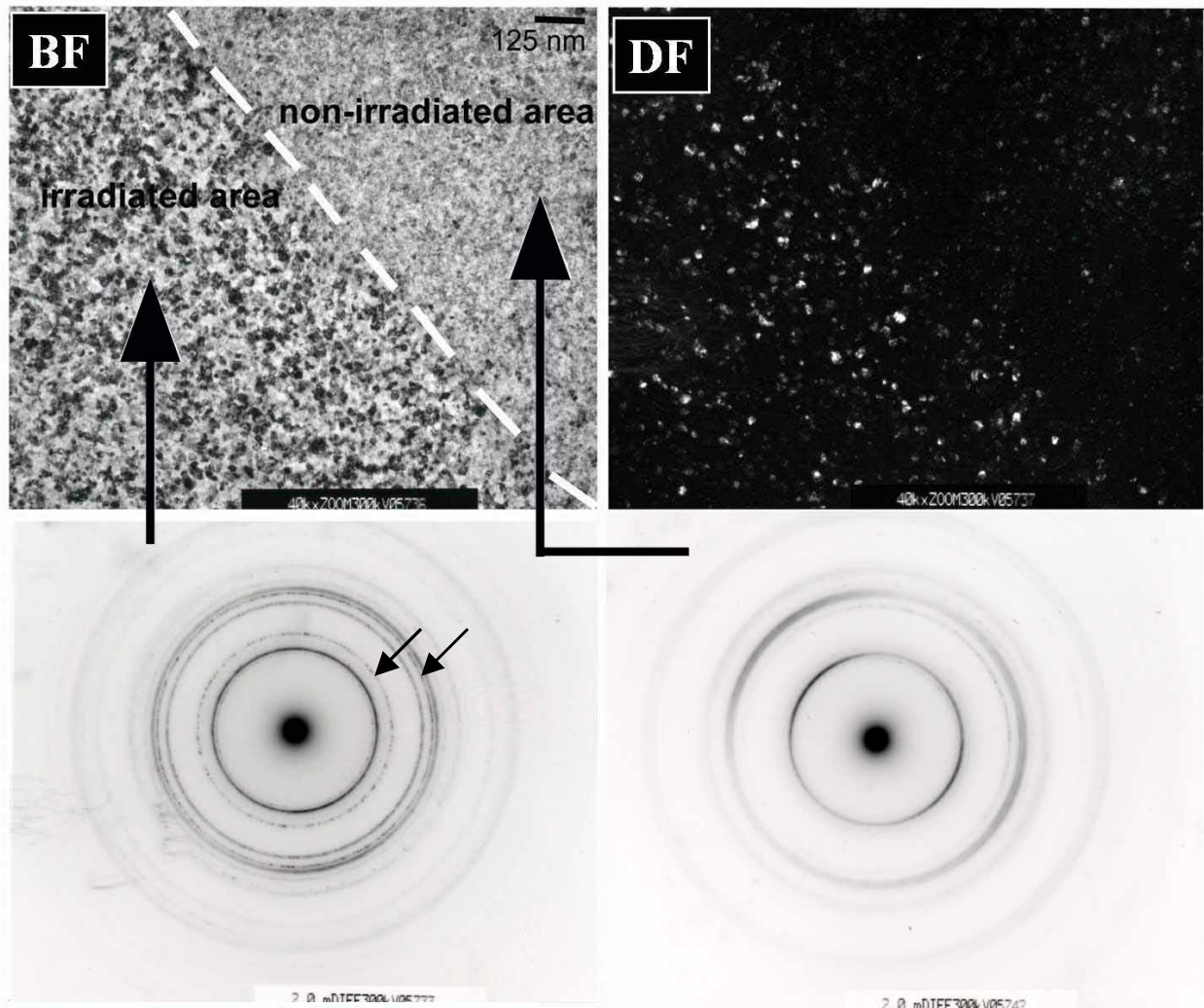


Figure 2: Zr-1.2%Fe sample irradiated at 300°C with 600 keV Kr-ions (fluence of 5×10^{15} ions/cm²).

“Dose-to-reaction” vs. irradiation temperature curve: the dose-to-reaction is defined as the dose at the onset of the reaction which is the time when the new rings appear around the ring indexed as α -Zr (101) on the initial diffraction pattern with reasonable intensity. The dose to the onset of precipitation was determined by eye, from examination of the negatives. Previous studies have shown this is a reliable way to obtain a reasonable estimate of the amount of reaction [11]. Figure 3 shows the dose to onset of precipitation as a function of temperature for Zr-1.2%Fe film irradiated with 600 keV Kr ions at different temperatures. It is clear that the dose to precipitation decreases with increasing irradiation temperature, reflecting the fact that this is an irradiation enhanced rather than induced process. Above 673 K the precipitation can occur in the absence of irradiation as thermal processes suffice for the second phase to form.

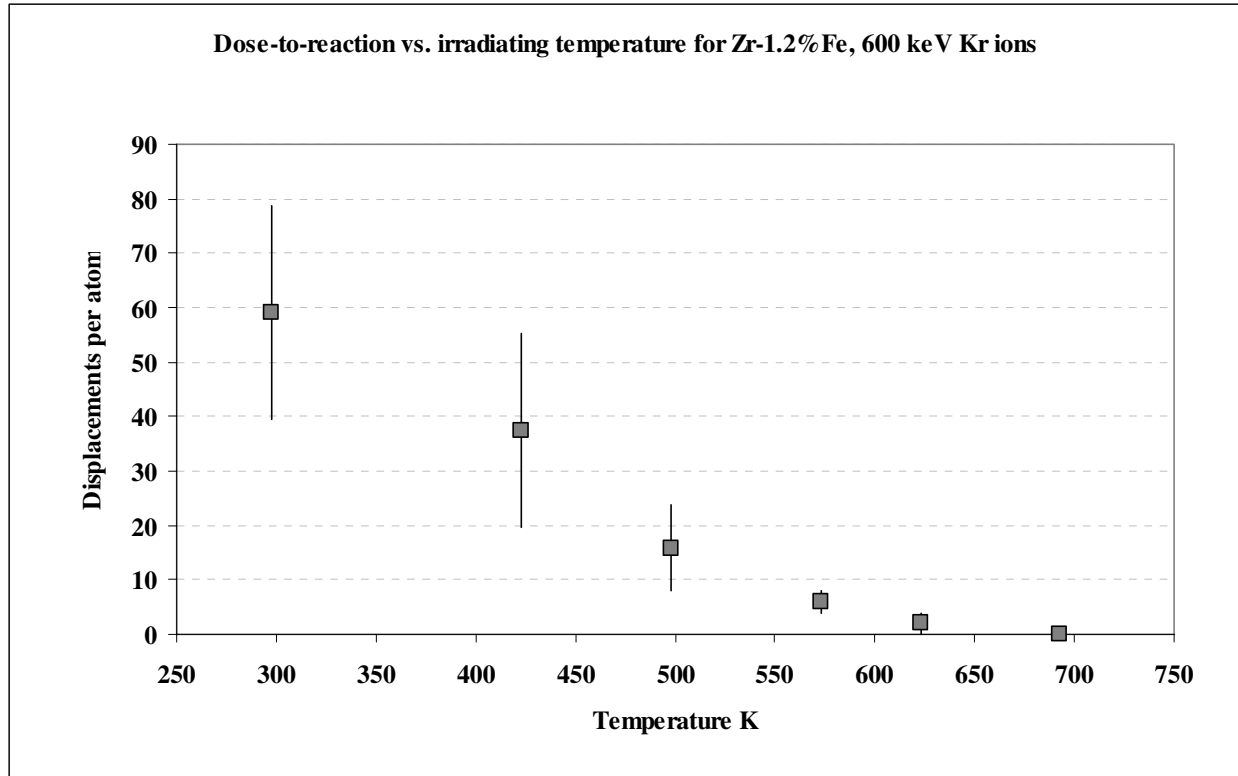


Figure 3: Dose-to-reaction vs. irradiating temperature for Zr-1.2%Fe thin-films irradiated with 600 keV Kr ions.

Examining the results it is clear that at irradiation temperatures above room temperature the precipitation process is similar to that observed under purely thermal conditions, i.e., showing precipitation of the metastable Zr_2Fe phase evenly distributed in the Zr matrix. The dose necessary for precipitation decreases with increasing irradiation temperature indicating that the precipitation process is not a purely collisional process, with precipitate nucleation and growth occurring solely within the region where displacement cascades occur. The fact that irradiation enhances a naturally occurring process suggests that the irradiation induced point defect fluxes allow the Fe atoms in metastable solid solution to arrive at the precipitates nuclei and cause them to grow. At 50 K, although there is second phase formation, the new phase is not yet identified. The appearance of amorphous rings suggests that at low temperature the mobility of the Fe atoms is not enough to make some of the amorphous nuclei formed in cascades grow into crystalline precipitates.

CONCLUSIONS:

A study was performed of irradiation enhanced precipitation in solid solutions of Zr supersaturated with Fe by exposing free-standing thin-film samples to an ion beam while observing *in situ* the evolution of the microstructure in a transmission electron microscope. The results presented here indicate that at irradiation temperatures between 273 and 573 K the metastable Zr_2Fe phase is formed instead of the thermodynamically more stable Zr_3Fe . At 50 K second phase formation occurs but the phase formed has not yet been identified. The ion-

irradiation dose necessary to cause significant precipitation decreases with increasing irradiation temperature. At temperatures above 673K the reaction occurs readily without irradiation assistance.

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