**PHASE FORMATION IN ZR/FE MULTILAYERS
DURING KR ION IRRADIATION***

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ABSTRACT

A detailed study has been conducted of the effect of Kr ion irradiation on phase formation in Zr-Fe metallic multilayers, using the Intermediate Voltage Electron Microscopy (IVEM) at Argonne National Laboratory. Metallic multilayers were prepared with different overall compositions (near 50-50 and Fe-rich), and with different wavelengths (repetition thicknesses). These samples were irradiated with 300 keV Kr ions at various temperatures to investigate the final products, as well as the kinetics of phase formation. For the shorter wavelength samples, the final product was in all cases an amorphous Zr-Fe phase, in combination with Fe, while specially for the larger wavelength samples, in the Fe-rich samples the intermetallic compounds $ZrFe_2$ and Zr_3Fe were formed in addition to the amorphous phase. The dose to full reaction decreases with temperature, and with wavelength in a manner consistent with a diffusion-controlled reaction.

INTRODUCTION

The study of phase formation in metallic multilayers by both solid-state reaction and ion irradiation has received considerable attention in recent years [1-5]. Metallic multilayers represent a good model system to study the kinetics and thermodynamics of phase formation, because they can be manufactured at controlled thicknesses and compositions, and be subjected to thermal annealing or irradiation under precisely controlled conditions. The Zr-Fe system is of particular interest because it can serve as a model system for solid state reaction between the late and early transition metals, and because the presence of Fe allows the use of magnetic probes to complement traditional techniques in detecting the appearance of new phases. It is also a system that has technological importance [6-8].

At issue are the final products of the ion beam mixing or solid-state reaction process. The reaction path taken by a given multilayer system under irradiation depends on the ion type, energy, dose rate and total ion dose and irradiation temperature. In the case of thermal annealing, time and temperature govern the reaction path taken by a given multilayer system. There is a competition between crystalline phases and amorphous phases, depending on the reaction kinetics. Further, the kinetics and mechanisms of reaction are not well understood and there is no unique theoretical model that describes the reaction kinetics and predicts the final reaction products at equilibrium or steady state.

In previous studies Paesano and co-workers [5] used CEMS to show that the final products of solid state reaction depend on the overall multilayer composition. They found complete amorphization at the 50-50 composition after annealing at 773 K, and different combinations of intermetallic compounds, amorphous phases and pure Fe in the Fe-rich and Zr-rich cases. Other

researchers have used other techniques to study the problem and found evidence of phase separation in the amorphous phase, as well as demonstrated the importance of wavelength and composition in determining the final products [5], [9]. However no systematic study of these parameters, as well as a detailed study of the kinetics of the solid state reaction process have been attempted.

To help elucidate these questions we have conducted an investigation of the influence of modulation wavelength and composition on phase formation in Zr-Fe multilayers. In a previous work we presented preliminary results which are here expanded and interpreted [10]. We have used in-situ irradiation in a transmission electron microscope (TEM), which allows us to directly measure the reaction kinetics and obtain the final reaction products for precisely defined conditions. We discuss the results in terms of previous work, and of the existing models for solid-state reaction and irradiation mixing.

EXPERIMENTAL METHODS

Metallic multilayers of Zr and Fe were prepared by vapor deposition onto a NaCl substrate, in a Balzers UMS 500P dual gun system at pressures of 5×10^{-9} torr. The overall thickness was kept around 100 nm to make the multilayers electron-transparent at 300 keV. Both the modulation wavelength λ (the thickness of one Fe plus one Zr layer) and the overall composition were varied. These multilayers were characterized by Rutherford Backscattering spectroscopy (RBS), and Mossbauer Spectroscopy (CEMS) in addition to TEM.

These samples were floated in de-ionized water onto Cu grids and examined in the Intermediate Voltage Transmission Electron Microscope (IVEM) at Argonne National Laboratory. This is a Hitachi 9000, microscope operated at 300 keV with an ion beam attachment that permits the irradiation of the sample in-situ [11]. The irradiation temperature can be controlled from 15 K to 973 K. We conducted two types of experiments: controlled heating and heating plus irradiation. All samples were annealed and the irradiation experiments conducted are listed in table I. Irradiations were conducted with 300 keV Kr ions at temperatures from 25 K to 623 K, at a current of approximately $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ to doses up to $2 \times 10^{16} \text{ cm}^{-2}$ (corresponding to about 60 dpa). Diffraction patterns were taken at regular intervals to detect the formation of the new phases.

TABLE I: Irradiation Experiments Conducted on Zr-Fe Multilayers

# of layers	Thickness (nm)	Wavelength λ (nm)	Zr thickness (nm)	Composition (atom % Fe)	Irradiation Temperature (K)
10X	105	10.5	7	50	25, 293, 373, 473, 573, 623
7X	91	13	7.8	55	17, 293, 373, 473, 573
6X	90	15	10	50	None
5X	125	25	15.5	55	293
5X	95	19	10.8	58	None
4X	108	27	18	50	293, 373, 473, 573
13X	96	7.4	4	64	293, 373, 573
3X	100	33.3	18	64	17, 293, 373, 473, 573

RESULTS

Irradiation Experiments: The samples with near equiatomic composition underwent full amorphization under ion irradiation. In both equiatomic and Fe-rich multilayers the intensity of the Zr rings weakens faster than that of the Fe rings. This observation is consistent with the presumption that the mobile species is Fe and that the reaction occurs by diffusion of Fe into the Zr phase. If Fe is the mobile species, the amorphous phase forms within the previous Zr layer, at the lowest possible Fe concentration, and the Fe concentration in the amorphous phase slowly increases in time, until all the Fe is consumed.

Below room temperature the dose to full reaction is nearly independent of temperature. Above room temperature, for a given multilayer wavelength the dose to amorphization decreases with increasing temperature. For a given temperature, the dose to amorphization increases proportionally to the square of the wavelength. **Figure 1** shows a plot of the square of the half-thickness of the Zr layer divided by the dose to amorphization versus the reciprocal of the temperature. The curves for the experiments performed on samples of near equiatomic composition fall on top of each other, which indicates that for a fixed temperature, and overall

Figure 1: Square of the Zr half-layer thickness t , divided by the dose to amorphization (equiatomic samples) or dose to full reaction (see text) for Fe-rich samples, versus reciprocal temperature for various multilayer compositions and wavelengths. Open circles denote near equiatomic samples and full symbols denote Fe-rich samples.

composition the dose to amorphization increases as the square of the wavelength. This behavior is consistent with a diffusion-controlled process, if diffusion is understood to comprise all atomic transport, including ballistic processes and irradiation-enhanced diffusion. It is clear from figure 1 that there are two regimes of behavior in this material: a temperature-independent region below room temperature and a thermally activated process above room temperature. The thermally-activated process has an activation energy of 0.17 eV. Ding and co-workers found two regimes with activation energies 0.07 eV and 1.4 eV (above 500 K) [12].

The amorphization reaction takes place in a spatially homogeneous manner, i.e., all observed regions of the foil behave in a similar manner. This indicates that any departures from planar growth during formation of the amorphous phase, if they occurred, occurred in a scale smaller than the specimen wavelength, (and possibly smaller than the grain size, since at the end of the irradiation there was little evidence of unreacted pure Zr or Fe clusters). This process only breaks up at very high fluences, when small grains of Fe can be seen in a matrix of amorphous Zr-Fe. This shows that grain boundary diffusion is important only at the end of the process.

The behavior of the Fe-rich samples is more complex, as there are two competing reactions: amorphization and formation of the crystalline intermetallic compounds ZrFe_2 and Zr_3Fe , (identified by their diffraction lines). Samples do not undergo full amorphization but form the crystalline intermetallic compounds either after amorphization (small wavelength case -13X sample) or in parallel with the amorphization process (large wavelength case - 3X sample). For the 13 X sample, we plot the dose to amorphization in figure 1, while for the 3X sample we plot a dose to a steady state that includes intermetallic compounds and amorphous phase. Since there is not a definite endpoint, it is possible that the samples are still evolving at the end of the irradiation ($1-1.5 \times 10^{16} \text{ ion.cm}^{-2}$). Thus the results for the Fe-rich samples plotted in figure 1 are not directly comparable to the near equiatomic samples, but it is clear that their evolution was slower than that of near equiatomic samples.

The formation of crystalline intermetallic compounds occurs at all temperatures studied, including the lowest temperature (17 K) for the large wavelength Fe-rich sample. Preliminary results indicate that at low temperature the ZrFe_2 intermetallic compounds formed, while at room temperature and above, the Zr_3Fe compound formed.

Grain Growth under Irradiation: As the interfacial phase formation reaction proceeds, the grain size in the unreacted Fe layers increases from 10 nm to approximately 50 nm at $5 \times 10^{15} \text{ ion.cm}^{-2}$. This grain growth was visible in bright field/dark field, but was also indicated by the increased graininess of the Fe diffraction rings as the fluence increased. The increased graininess of the Fe ring demonstrates that the grain orientations of the grains sampled by the diffraction aperture are becoming less random, that is, the typical grain represents a larger fraction of the area covered by the aperture. This occurs at all temperatures studied with little difference in growth rate, but was especially prominent at low temperature. These results will be presented in more detail elsewhere [13].

DISCUSSION

The products from the Zr-Fe multilayer reaction under irradiation and thermal annealing are amorphous Zr-Fe and the intermetallic compounds ZrFe_2 and Zr_3Fe as would be expected from

the Zr-Fe phase diagram that includes the metastable amorphous phase [14]. Previous studies also observed either amorphous or crystalline intermetallic compounds [5, 15]. This is because the formation of the amorphous phase provides a sizable reduction in free energy compared to a mechanical mixture of Zr and Fe; the further reduction in free energy from amorphous Zr-Fe to the intermetallic compounds is comparatively smaller [14].

The kinetics of phase formation in multilayers is controlled by the intermixing of the two metals. In the case of irradiation of multilayers, the intermixing occurs by interdiffusion driven by thermal diffusion and by intracascade ballistic processes. Thermal diffusion is enhanced by the increased steady state point defect concentration present under irradiation. Ballistic processes within the cascade prevail within the first picoseconds after ion-atom impact. Within that time frame, processes are athermal since the typical cascade average energies are much higher than thermal energies. During the ballistic phase of cascade development chemical interactions are less important and the mixing is well described as a random process within the cascade. During longer times as the average energy of the cascade decreases, chemical interactions become more important.

One interesting observation in this study is that intermetallic compounds Zr_3Fe and $ZrFe_2$ were observed as reaction products in this study for the Fe-rich samples. Those compounds have previously been shown to be unstable under ion irradiation [16]. Zr_3Fe undergoes amorphization under Ar ion irradiation when irradiated at temperatures up to 500 K, to a dose of 5 dpa, whereas in the present study the intermetallic compounds were still present at doses of 30 and 45 dpa. Both $ZrFe_2$ and Zr_3Fe undergo amorphization at 17 K under electron irradiation, so it is puzzling to observe crystalline intermetallic compounds still present after Kr ion irradiation to very high dpa levels. We have at the moment no explanation for the discrepancy. In the case of the aforementioned experiments, the starting material is the pure intermetallic compound, whereas in this case the initial materials are multilayers. It is possible that the kinetics of the multilayer reaction process with large composition gradients (not present in the case of the irradiation of intermetallic compounds), can establish different dynamic equilibria between a bulk amorphous phase of constantly evolving composition and small crystallites of intermetallic compound.

The grain growth observed during irradiation indicates that phase formation occurred mainly by planar growth. The fact that the intensity of the Zr ring decreases faster than that of the Fe ring indicates that the amorphization is taking place in the Zr multilayers, by migration of the Fe into it. This indicates that the Fe is the mobile species. Eventually the planar growth process breaks up, leading to complete reaction between the phases in the near equiatomic samples.

Although a more detailed analysis of the results presented here will be published later [13], a simple quantitative analysis based on phase formation solely by ballistic processes, indicates that at low temperature the results are well-explained by a purely ballistic model with a cascade size of 2 nm. The decrease in the dose to amorphization at higher temperature clearly shows that the transformation occurs by a mixture of radiation and thermal processes. For the Fe-rich samples, more complex considerations of the kinetics of phase nucleation, formation and relative equilibrium will have to be taken into account to explain the results.

CONCLUSIONS

Solid state reaction of Fe-rich and near equiatomic Zr-Fe multilayers under irradiation was studied in-situ using the IVEM facility at Argonne National Laboratory. The wavelength and composition of the multilayers were varied independently to determine the final products and the kinetics of phase formation.

1. Near equiatomic samples (50-55%Fe) undergo amorphization under irradiation. Above room temperature the dose to amorphization decreases as the irradiation temperature increases, while below room temperature the dose to amorphization is independent of temperature. The dose to amorphization is proportional to the square of the wavelength.
2. In Fe-rich samples (64%Fe) amorphization competed with the formation of the crystalline intermetallic compounds $ZrFe_2$ and Zr_3Fe , which formed either after amorphization or in parallel with amorphization.
3. Grain growth occurs in Fe layers of the larger wavelength Fe-rich sample. This grain growth occurs at temperatures ranging from 17 to 473 K, and appears more pronounced at low temperature.

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