ION-BEAM MIXING AND SOLID-STATE REACTION IN ZR-FE MULTILAYERS

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ABSTRACT

Vapor-deposited Zr-Fe multilayered thin films with various wavelengths and of overall composition either 50% Fe or Fe-rich up to 57 % Fe were either irradiated with 300 keV Kr ions at temperatures from 25K to 623 K to fluences up to 2×10^{16} cm^{-2}, or simply annealed at 773K *in-situ* in the Intermediate Voltage Electron Microscope at Argonne National Laboratory. Under irradiation, the final reaction product is the amorphous phase in all cases studied, but the dose to amorphization depends on the temperature and on the wavelength. In the purely thermal case (annealing at 773 K), the 50-50 composition produces the amorphous phase but for the Fe-rich multilayers the reaction products depend on the multilayer wavelength. For small wavelength, the amorphous phase is still formed, but at large wavelength the Zr-Fe crystalline intermetallic compounds appear. These results are discussed in terms of existing models of irradiation kinetics and phase selection during solid state reaction.

INTRODUCTION

The study of solid state reactions in metallic multilayers both under purely thermal conditions and under the influence of irradiation has received considerable attention in recent years [1]. In particular, several researchers have focused on the Zr-Fe system using Mössbauer spectroscopy, X-ray diffraction and Rutherford Backscattering Spectroscopy [2] to study reaction rates and reaction products. At issue is the extent to which both multilayer wavelength and overall composition affect the final reaction products and the reaction kinetics.

In this work we demonstrate the use of in-situ observations in a TEM to study the kinetics of solid state reactions in Zr-Fe multilayers. Both the thermal and irradiation cases are considered, and the results are discussed in terms of existing models.

EXPERIMENTAL

Metallic multilayers of Zr and Fe were vapor-deposited onto a NaCl substrate, in a Balzers UMS 500P dual gun system at pressures of 1×10^{-8} mbar. The total thickness of the multilayers was kept between 90-125 nm to make them electron-transparent. Both the modulation wavelength λ (thickness of one Fe plus one Zr layer) and the overall composition were varied. In all cases the bottom layer was Fe and the top layer Zr. These multilayers were characterized by Rutherford Backscattering Spectroscopy (RBS), Mössbauer Spectroscopy (CEMS) and Transmission Electron Microscopy (TEM). It was found

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that the layers were polycrystalline bcc-Fe and hcp-Zr, respectively (figure 1a) for all compositions and wavelengths. The micrograins in the Fe layers were randomly oriented, but the Zr layers showed a preferentially basal texture, as evidenced by the absence of the (0002) reflection from the diffraction pattern. The following wavelengths and compositions were prepared:

Number of wavelengths	Total Thickness (nm)	Wavelength λ (nm)	Composition (atom % Fe)
10X	105	10.5	50
7X	91	13	57
6X	90	15	50
5X	125	25	53
4X	108	27	50

Table 1 : Composition and Wavelength for the Zr-Fe Multilayers examined.

In table 1, an even number of wavelengths is associated with a 50-50 composition and odd numbers with an Fe-rich composition. In the 50-50 composition, the thickness of the Zr multilayer was approximately half that of the Fe multilayer.

These samples were then floated 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 [3]. The irradiation temperature can be controlled from room temperature to 973 K.

We conducted two types of experiments: controlled heating and heating plus irradiation. Irradiations were conducted with 300 keV Kr ions at temperatures from 25 K to 623 K, at a current of approximately 1.7×10^{12} cm^{-2} s^{-1} until reaction was complete and a steady-state reached. In this case this meant fluences up to 2×10^{16} cm^{-2}. Thermal annealing experiments were all conducted at 773 K. Phase transformations in the multilayer thin film were followed by monitoring the diffraction pattern. Vacuum in the microscope was approximately 10^{-7} torr. Low temperature ion and electron irradiations were also conducted in the Kratos HVEM at the Center for Electron Microscopy at Argonne. This microscope also has the capability of having an ion beam irradiating the sample *in-situ*, and allows for irradiation down to 25 K.

RESULTS

Irradiation Experiments: Two irradiation series were conducted, one on 4X samples (λ=27 nm) and another on 10X samples (λ=10.5 nm). Irradiation of both types of samples produced the same result: as the fluence increases the Zr and Fe rings weaken and a broad halo associated with the Zr-Fe amorphous phase appears and becomes more intense. A unique steady state in the phase transformation is eventually reached for all temperatures studied, containing mostly amorphous Zr-Fe and some remnant hcp-Zr and bcc-Fe, as shown in figure 1b, 1c and 1d. The presence of zirconium oxide rings was detected after long high temperature exposures.

The dose to full reaction decreases with temperature and increases with wavelength of the layers, as shown in figure 2. The ratio of the dose to full reaction in the 4X sample to the dose to full reaction in the 10X sample is equal to the square of the ratio of the wavelengths (6.66). For the 10X

sample, the dose to amorphization remains nearly constant between room temperature and 25 K, indicating that the onset of the athermal regime is slightly below room temperature.
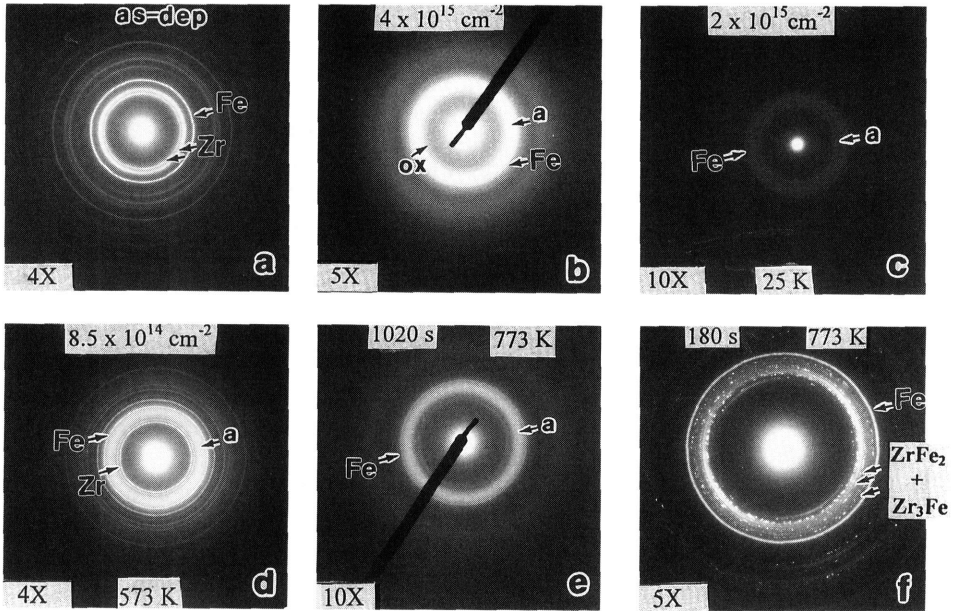

Figure 1: Diffraction patterns showing phase formation in Zr-Fe multilayers. (a) as-deposited multilayers (4X) showing typical pattern of bcc-Fe and hcp-Zr; (b) 5X after room temperature irradiation to 4×10^{15} cm^{-2}, (amorphous intermetallic + Fe) (c) 10X after irradiation to 2×10^{15} cm^{-2} at 25 K (amorphous intermetallic + Fe); (d) 4X after irradiation to 8.5×10^{14} cm^{-2} at 573 K (amorphous intermetallic + Fe); (e) 10X after thermal annealing at 773 K for 1020 s (amorphous intermetallic + Fe) and (f) 5X after thermal annealing at 773 K for 180 s (crystalline intermetallic compounds Zr$_3$Fe and ZrFe$_2$ + amorphous intermetallic + Fe).

Thermal Annealing: Contrary to the irradiation case, during purely thermal annealing at 773 K the final reaction products depend on the wavelength and on the composition of the multilayer. Three multilayers were examined with composition 50-50: 10X, 6X and 4X. Regardless of the wavelength, they all reach a steady state showing only an amorphous halo besides residual Zr and Fe (with no traces of zirconium-oxide), as shown in figure 1e. However, in Fe-rich films (7X and 5X, 57%at. Fe) different reaction products appear depending on the wavelength: the intermetallic compounds ZrFe$_2$ and Zr$_3$Fe form in the 5X films (as shown in figure 1f) while only an amorphous phase was observed in the 7X films (not shown). These intermetallic compounds are identified by their lines in the diffraction pattern, and they have the standard structures of the orthorhombic Zr$_3$Fe and cubic ZrFe$_2$ [4]. The intermetallic compounds were already present at the end of the temperature ramp (1.6 K.s^{-1}), and do not change

significantly afterwards. This thermal annealing experiment of 5X at 773 K was repeated with the same result. On the other hand amorphous phase formation in the small wavelength (7X) samples took more than an hour to complete. Finally, when these intermetallic compounds are irradiated after the reaction is complete, they quickly turn amorphous.
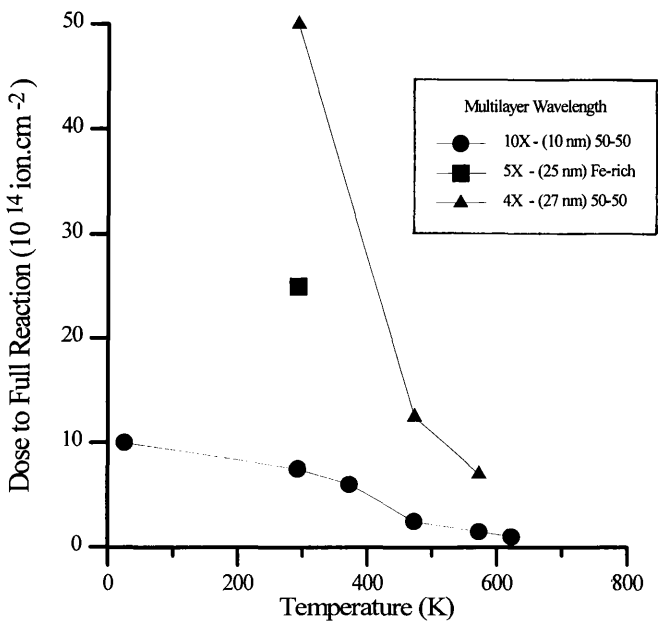

Figure 2: Dose to full reaction (amorphization) versus irradiation temperature for 300 keV Kr in-situ ion irradiation of Zr-Fe multilayers of the wavelengths specified. The 4X and 10 X samples have a 50-50 composition, while the 5X samples are Fe-rich.

DISCUSSION

The foregoing results indicate that the overall composition and the wavelength may determine the reaction paths or the reaction products of ion beam mixing and solid state reaction in multilayers. For the irradiation case the product is a combination of an amorphous phase, Zr oxide and some remnant α-Fe . The proportions of the individual phases, although not quantified in this work, appears not to vary between samples, i.e., all of them arrive at the same final combination of phases as reaction product. It is reasonable to expect that an amorphous phase with composition close to 50-50 forms under irradiation of Zr-Fe multilayers because of the large negative heat of mixing in this system [5]. There is thus a large energy gain in mixing the two components even if in a non-crystalline structure. In the irradiation case the crystalline intermetallic compounds were effectively precluded from forming since these irradiations were conducted below the critical temperature for amorphization under ion irradiation of Zr_3Fe and $ZrFe_2$ [6]. Accordingly, when we formed the intermetallic compounds by thermal reaction in this work, further irradiation causes them to amorphize.

The dose required to arrive at the common final state depends on the modulation wavelength. For the overall composition of 50-50, the dose to amorphization in the two samples examined varied as the inverse ratio of their wavelengths squared. This is in agreement with the models in the literature that describe amorphization by solid state reaction in terms of an interdiffusion coefficient either caused by irradiation [7] or enhanced by irradiation [8]. In such models, the time to reaction is proportional to the square of the diffusion distance. The dose to amorphization increases with decreasing temperature and remains constant between room temperature and 25 K. This indicates that below room temperature amorphization occurs by ion beam mixing while above room temperature amorphization occurs by a combination of ion mixing and solid-state reaction augmented by radiation enhanced diffusion [8].

One possible reason for the unreacted Fe observed in the irradiated samples is the formation of zirconium oxide (associated with long exposure in the TEM, and possibly aided by collisional incorporation of residual oxygen) leading to an unbalanced composition under irradiation. Another explanation is that since the multilayers are asymmetric, the outermost Zr and Fe take longer to amorphize as the reaction slows down after the formation of the amorphous phase throughout the rest of the sample. Previous Mössbauer studies showed that similar multilayers, (Fe-Zr films deposited onto SiO_2 substrates), amorphize completely after heating at 773 K [9] The apparent discrepancy could be due to a greater sensitivity of electron diffraction to the existence of small minority phases, or, conceivably, to an influence of the SiO_2 substrate present in the Mossbauer experiment.

For 773 K-thermally reacted samples, the results show that both wavelength and composition affect not only the time to full reaction but also the final product. For 50-50 composition at all wavelengths, the only reaction product is an amorphous phase, as already observed by Mössbauer Spectroscopy [9]. Simple model calculations of the free energy diagram for the system reveal the minimum of the amorphous curve close to the 50-50 concentration [10,11]. The system decreases its free energy by diffusion and amorphization at this composition. The amorphous phase is also observed for Fe-rich composition at small wavelength (7X), and (to a much smaller degree) at large wavelength (5X). However, besides the amorphous phase, intermetallic compounds formed in the 5X multilayer samples. From the thermodynamic point of view, if the stable intermetallic compounds are precluded from forming, the combination of phases with the next lowest overall free energy should form; the specific combination of phases is a function only of the overall composition and temperature.

Thus, the kinetic paths followed by the Fe-rich samples are different. This difference could be either a result of the small compositional difference between 7X and 5X or of the large difference in wavelengths. Concerning the latter hypothesis, the model of Gösele and Tu [12,13] which describes phase selection during solid-state reaction predicts that there is a critical thickness of a reaction product beyond which a second phase can start to form. In the present case it is possible that only in the longest multilayer wavelength the critical thickness, x_{crit}, of the first phase (amorphous layer) necessary to the growth of a second phase is reached. It should be noted however, that the predictions of the model are based on a situation where a precursor phase (in this case the amorphous compound) grows first and at a critical thickness gives way to another phase (in this case the crystalline intermetallic compounds). No such precursor phase was observed in the present study.

Finally, the kinetics of formation of the intermetallic compounds are initially faster than that of the amorphous phase. This can be interpreted as a case of competition between phases where the crystal phases grows faster than the amorphous phase, as previously observed in Zr-rich multilayers, during annealing at 773 K [14] . The growth of new phases depends on the elemental diffusivities in the different phases and on the interfacial reaction constants. Inasmuch as we have several phases present, the description of the evolution of the reacting layers may have a high degree of complexity but there is no restriction *a priori* to which should have the fastest growth.

CONCLUSIONS

The kinetics of solid state reaction and ion beam mixing of Zr-Fe metallic multilayers were studied using in-situ transmission electron microscopy. The main results are:

1. Irradiation of Zr-Fe multilayers with Kr ions at temperatures between 25 K and 623 K produces mostly a Zr-Fe phase amorphous with some remnant bcc-Fe, regardless of wavelength. The dose to reach full reaction decreases with increasing temperature and increases with wavelength. An athermal regime exists below room temperature.

2. Annealing of Zr-Fe multilayers at 773 K produces different results depending on multilayer composition and wavelength. For the 50-50 composition, a mixture of amorphous Zr-Fe, and small amounts of bcc-Fe and hcp-Zr was observed. For the Fe-rich samples, the same result was obtained at small wavelength while the crystalline intermetallic compounds $ZrFe_2$ and Zr_3Fe are the predominant phase at large wavelength.

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