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Phase separation in amorphous Fe-Zr: Comparison of sputtered and solid-state-reacted films

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Amorphous Fe-Zr films of the same average Fe and Zr concentration of 50 at.%—made by cosputtering as well as by solid-state reaction of multilayers— have been compared by x-ray anomalous scattering experiments, magnetization measurements at low temperature, and transmission electron microscopy. After preparation the samples are notably different. However, annealing at temperatures between 350 and 450 °C results in the same phase separation of the amorphous state.

A few years ago it was discovered by Johnson and coworkers[1-3] that it is possible to form amorphous materials by fast interdiffusion of crystalline element multilayer structures at a temperature of typically 250–350 °C. The driving force for this solid-state reaction (SSR) is supplied by the free-energy difference between the amorphous phase and the crystalline multilayer structure and is usually calculated from Miedema's semiempirical model.[4] Whereas most investigations describe the diffusion process itself,[5-7] it is interesting to know to what extent the properties of the amorphous alloys made by the well-known methods—melt spinning, sputtering, or evaporation—are comparable to those made by SSR, a method which allows one to get amorphous bulk material for applications.

In this paper we will compare amorphous Fe-Zr films which are made by cosputtering and by SSR of multilayer structures. This system was chosen because it is possible to get completely amorphous samples with both methods. Further, there is enough contrast between Fe and Zr to allow investigations of the structure by synchrotron radiation and of the microstructure by transmission electron microscopy (TEM) as well. We also use magnetic properties as a probe, since Fe-rich amorphous Fe-Zr films are ferromagnetic at low temperatures with a Curie temperature (T_C) and Fe moment that are strongly composition dependent.[8] Using these complementary techniques we will show that samples produced by those two methods are significantly different. However, after annealing they reach *the same final phase-separated amorphous state.*

All films were prepared by magnetron sputtering in a vacuum system with a base pressure of 1×10^{-7} Torr at a deposition temperature of about -50 °C. About 150-Å Cr was predeposited on the substrate (single-crystal Si or Al_2O_3) and on top of the film to protect against oxidation during subsequent annealing.

Electron microprobe analysis was performed to confirm the average composition. X-ray anomalous scattering experiments were done using synchrotron radiation to determine total (RDF) and differential (DDF) radial distribution functions as described in Ref. 9. The samples had to be tilted slightly to move the single-crystal substrate planes out of the Bragg condition while not measurably changing the amorphous peaks. Transmission electron micrographs were made of cross sections of the multilayer structures. Magnetization measurements have been done with a vibrating-sample magnetometer. All annealings were performed in a vacuum of 1×10^{-7} Torr.

While it is possible to form amorphous Fe-Zr films over nearly the whole concentration region by cosputtering, one can form completely amorphous films by SSR of the multilayers only over a limited range of compositions near 50 at.%. Here we will discuss only our measurements on two types of $Fe_{50}Zr_{50}$ films: (1) homogeneous cosputtered samples and (2) multilayered films consisting of 100 layers of 50-Å Fe and 100-Å Zr yielding the same average composition.

The multilayered film is completely amorphous after annealing at 350 °C for 1 h. Only broad maxima are evident in x-ray and electron diffraction measurements as well. Also, the room-temperature magnetization shows that less than 0.1% of the original Fe layer is left. However, the sample still has a structure which can be seen as layers of different contrast in the TEM picture (Fig. 1) as well as in low-angle x-ray peaks (not shown here). Both measurements indicate layers of alternately Fe-poor and Fe-rich amorphous phases in our reacted sample. The Fe-poor layers [dark in Fig. 1(b)] are only about half as thick as the Fe-rich layers. No indications of Kirkendall voids, which are typical for a fast diffusion of only one element,[6] were seen.

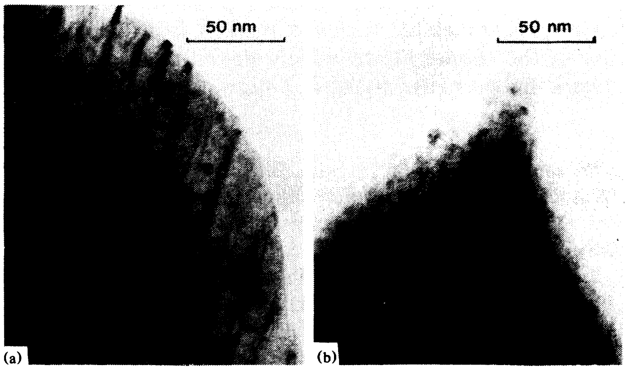

FIG. 1. Cross-sectional TEM picture of the $Fe_{50}Zr_{50}$ multilayer (a) unreacted and (b) annealed at 350 °C for 1 h.

In order to study and compare the structure of both samples in detail, anomalous scattering experiments were performed at energies of 10 and 160 eV below the Fe absorption edge, where the anomalous term $f'(\mathrm{Fe})$ increases from -3.38 to -6.9 electrons. Therefore the *difference* of the two measurements and its Fourier transformation, the DDF, gives information only about the Fe environment. *Already* the corrected and normalized intensity curves taken at 6952 eV [Fig. 2(a)] indicate that the structure of the reacted sample is quite different from the homogeneous film. The first maximum for the reacted sample at 2.63 $\mathrm{\AA}^{-1}$ is lower by 0.06 $\mathrm{\AA}^{-1}$ and broader than that of the homogeneous film. This can be explained by the existence of layers of different concentrations in this sample according to the TEM measurement, which leads to a superposition of the x-ray intensity measurements for each layer where the peak position is dominated by the Zr-rich layers. If we use the concentration dependence of the first peak position for homogeneous Fe-Zr samples[10,11] the Zr-rich layers in our sample seem to have less than 37 at.% Fe.

The difference functions of the measurements at 7102 and 6952 eV [Fig. 2(b)] are very similar at the first maximum for both samples, but the second peak is more pronounced in the SSR sample. The DDF's (Fig. 3) do not show any difference at the first maximum (at 2.82 Å). This peak position which was earlier found as the Fe-Zr nearest-neighbor distance,[11] and the average number of first-neighbor atoms around an Fe atom are the same in each case. Also, the first peak in the RDF of the SSR sample is at the same position (3.03 Å), but much higher and sharper than that of the cosputtered film. This must be due to a more well-defined Zr-Zr distance in the SSR film, because the average nearest-neighbor environment of the Fe atoms looks the same in both samples. Altogether the short-range order of the SSR sample looks structurally relaxed, which is not surprising since the SSR sample was made by annealing at 350 °C. This relaxation can especially be seen in the second neighborhood: The peaks in the RDF as well as in the DDF are more pronounced and the positions are less random than in the other film.

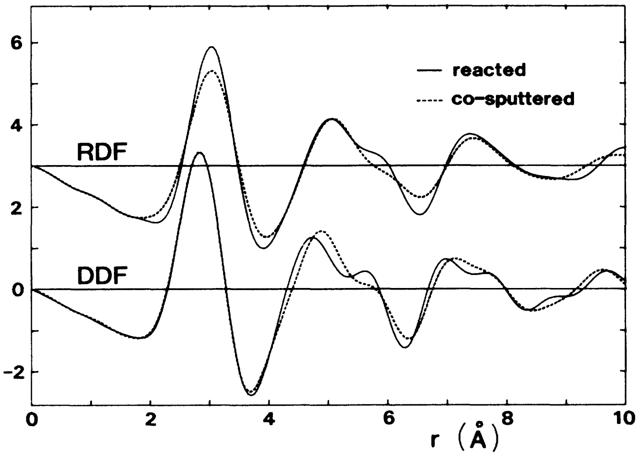

FIG. 3. Reduced RDF and DDF of the $\mathrm{Fe}_{50}\mathrm{Zr}_{50}$ films.

The magnetization measurements (in 500 Oe) as a function of temperature [Fig. 4(a)] show that the as-deposited homogeneous film has a sharp transition with a Curie temperature (T_C) of 25 K. This T_C is in good agreement with Mössbauer experiments[8] on similar samples, which show that T_C is a strongly increasing function of the Fe composition between about 47 and 80 at.% Fe. The SSR film, after the initial annealing, apparently has a high T_C and a broad transition. However, measurements in applied fields of less than 10 Oe show that the transition is sharp and the T_C is equal to 75 K.

The high T_C is a further indication for concentration fluctuations in the sample. One expects that only the Fe-rich part is ferromagnetic and contributes to these measurements. With this assumption the T_C of 75 K corresponds to a concentration of about 60 at.% Fe in the Fe-rich layers. Due to the thickness proportion of about 2:1 for the Fe-rich and Fe-poor layers in the TEM picture, respectively, we therefore estimate that the Fe-poor layers have a concentration of about 30–35 at.% Fe in agreement with the anomalous scattering experiments.

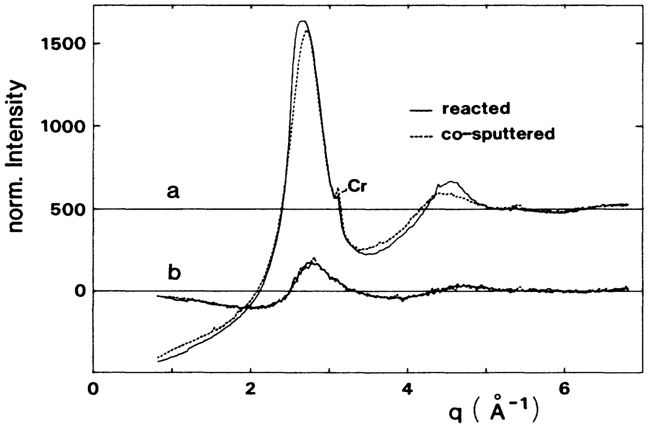

FIG. 2. (a) Reduced x-ray intensities of the $\mathrm{Fe}_{50}\mathrm{Zr}_{50}$ films at 6952 eV and (b) difference functions of the measurements at 6952 and 7102 eV (note the small Cr top-layer peak).

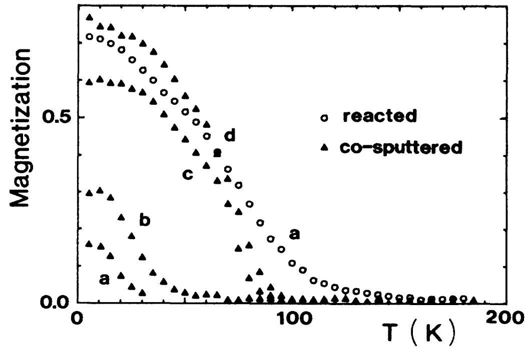

FIG. 4. Low-temperature saturation magnetization of the $\mathrm{Fe}_{50}\mathrm{Zr}_{50}$ films: (a) as made and (b)–(d) annealed for 1 h at 350, 400, and 450 °C, respectively.

One could assume that the sample is only inhomogeneous because the diffusion process is not completed after the first anneal and that it simply needs further annealing in order to homogenize the already amorphous film. This is not the case. Prolonged annealing at 350 °C or even as high as 450 °C does not change the magnetization curve much. The high T_C in the SSR film is a result of the coformation of two amorphous phases, and the lack of a decrease in T_C upon further annealing shows that the phase separated state is more stable than a homogeneous phase.

Also, crystallization experiments suggest a phase separation in the SSR film. After heating both samples rapidly to 520 °C and keeping that temperature for 1 h the cosputtered film is completely crystallized into Zr_2Fe and Fe_2Zr, while for the SSR sample only Zr_2Fe is present in an x-ray diffraction scan and the Fe-rich regions crystallize at higher temperature. The SSR film clearly shows a well-defined two-step crystallization similar to preannealed phase-separated $Cu_{50}Zr_{50}$.[12]

Annealings of the homogeneous sample for 1 h at 350, 400, and 450 °C result in a steady rise of the magnetization and T_C (Fig. 4) indicating a continuous increase of Fe-concentration fluctuations in this sample. Such a development of the phase separation is typical for a spinodal decomposition. The highest T_C reached (85 K) corresponds to a concentration of about 62 at.% Fe in the Fe-rich regions.

So in both amorphous annealed samples the same phase separated final state is obtained. The different ways to reach this "final" phase separated state can be explained as the result of a *local maximum* in the free-energy curve of the amorphous phase (schematically shown in Fig. 5). Applying the common tangent rule to these free-energy curves determines the compositional ranges for stability of the one-phase structures.

The multilayer film starts with a free energy given by the connecting line between the free energy of the elements. During the diffusion process it can lower the energy by forming layers of the two amorphous phases. The higher-energy state of the as-deposited cosputtered sample cannot be reached during subsequent annealing. Each amorphous layer can only homogenize until the metastable "equilibrium" concentrations given by the common tangent are reached. The film thereby keeps its layered microstructure.

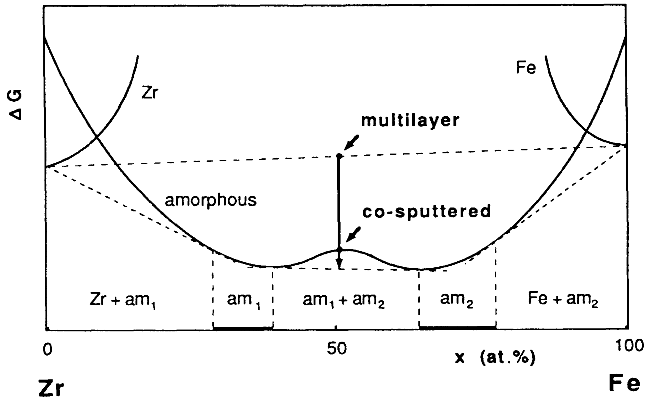

FIG. 5. Schematic free-energy curve of amorphous Fe-Zr and the crystalline elements Fe and Zr. The concentration ranges of the two amorphous phases am_1 and am_2 are given by the common tangent rule. The starting points of the multilayer and the homogeneous cosputtered film are marked.

The cosputtered sample is homogeneous after deposition because of the fast cooling process during deposition and starts in a state near the top of the free-energy maximum. During annealing it can lower the free energy by forming regions of different concentration by spinodal decomposition (due to the negative curvature of the free-energy curve in the middle of the concentration region) until the two amorphous phases reach the final concentrations.

In conclusion, we have shown that amorphous samples made by solid-state diffusion are very similar to those produced by other methods *only* after they have each been annealed to produce their "relaxed" states. We have found that in amorphous Fe-Zr in the middle of the concentration range this state is phase separated and can be reached from different starting points. We have studied the development of the phase separation as it progresses by a spinodal decomposition of the homogeneous film and have explained why it exists with a layered structure in the reacted sample. From our measurements we estimate that the final equilibrium concentrations of these two amorphous phases are close to the 1:2 and 2:1 concentrations in which the samples crystallize at higher temperature. More experiments to study these reactions in detail are in progress.

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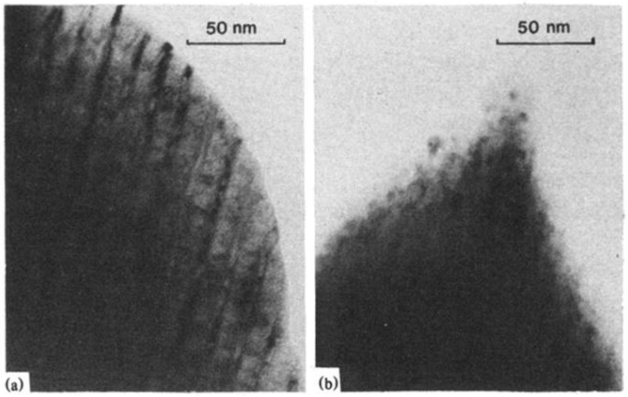

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