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Metastable phase equilibrium during solid-state amorphization reaction of Zr-Co layers

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The crystal-glass transition of Co-Zr layers via interdiffusion has been followed by Rutherford-backscattering spectrometry and x-ray-diffraction analysis. Thin-film multilayer samples of Co and Zr were annealed at 250 °C for different times up to 21 h. Planar growth of the amorphous layer is observed. The changes in the concentration profiles, as observed with Rutherford-backscattering spectrometry, in combination with corresponding x-ray analysis, indicate an interstitial solid solution of ≈ 3 at. % Co in crystalline Zr probably preceding the glass transition. This effect is discussed in the context of a metastable phase diagram.

I. INTRODUCTION

Amorphous metallic alloys are traditionally produced by rapid quenching from the vapor phase or liquid state.[1] However, several transition-metal combinations can also be obtained in the glassy state by solid-state interdiffusion of crystalline multilayers at temperatures well below the glass transition.[2] This process, as well as amorphization by hydrogen charging,[3] electron irradiation,[4] and mechanical alloying,[5] does not include any rapid quenching of the material. The alloying requires a strong thermodynamic driving force from a large negative heat of mixing of the two elements involved. In addition, the mobility of one of the components has to be high enough to yield substantial mixing at the given temperature. Furthermore, the kinetic conditions have to be chosen such that nucleation and/or growth of competing stable crystalline intermediate phases is prevented. As the buildup of crystalline compounds requires the mobility of all components, the solid-state amorphization reaction is likely to depend on a large difference in diffusivities of the two elements. Such a difference exists for combinations of early and late transition metals in the crystalline[6] as well as in the amorphous state.[7] Recent crystallization experiments indicate indeed that the occurrence of crystalline phases is connected with the mobility of the second component.[8] A crucial role of grain boundaries for nucleation of the amorphous phase has been suggested.[9,10]

In the Co-Zr system, the transition from a crystalline to an amorphous state by interdiffusion of multilayers has been subject to a number of studies. A large amount of information from x-ray data,[11] cross-section transmission-electron-microscopy (TEM) pictures,[12] and resistivity measurements[9,13] is available. These techniques indicate an interface-controlled start followed by a two-stage diffusion-limited reaction, as also observed for the systems Ni-Hf,[14,16] Ni-Zr,[15] and Co-Hf.[16] With respect to the concentrations of the evolving amorphous layers, the reported indirect results are somewhat contradictory. Therefore, we have studied the process by use of Rutherford-backscattering spectrometry[17] (RBS), which gives direct concentration information, to study the time dependence of the reaction. In addition, the samples were analyzed by x-ray diffraction to check the absence of crystalline intermediate phases after diffusion, and to follow changes in the lattice parameters of the original multilayers.

II. EXPERIMENTAL DETAILS

The multilayer samples were prepared by sequential evaporation of the elements by two independently rate-controlled electron guns onto sapphire or silicon substrates in a vacuum better than 10^{-7} Pa. The substrate temperature was kept at about $-5\,^{\circ}\mathrm{C}$, the evaporation rate was approximately 10 Å/s, and the time for switching from one element to the other was less than 2 s, during which the main shutter was closed. Three different configurations were investigated: Zr-Co-Zr and Co-Zr-Co trilayers with a thickness of 300 Å per individual layer, and a bilayer type of 800 Å Zr on top of 2000 Å Co. Depth profiles of the films were analyzed by RBS,[17] with 2-MeV He^{+} from a Van de Graaff accelerator. The analysis by x-ray diffraction was carried out in a conventional theta-2 theta arrangement with Cu $K\alpha$ radiation selected by an analyzing carbon crystal in front of the detector. The heating for diffusion took place at 250 °C up to 21 h in a vacuum of 2×10^{-5} Pa.

III. RESULTS

A. Backscattering measurements

RBS spectra of a Zr-Co-Zr thin-film trilayer are shown in Fig. 1, taken from the as-deposited sample and after annealing at 250 °C for 21 h. Extensive interdiffusion is clearly seen at both Co-Zr interfaces. The detailed studies were mainly carried out analyzing the Co peak, because it is well separated from the other signals. The results from the Co signal were checked by comparing them with the corresponding Zr signal. The spectra from samples that

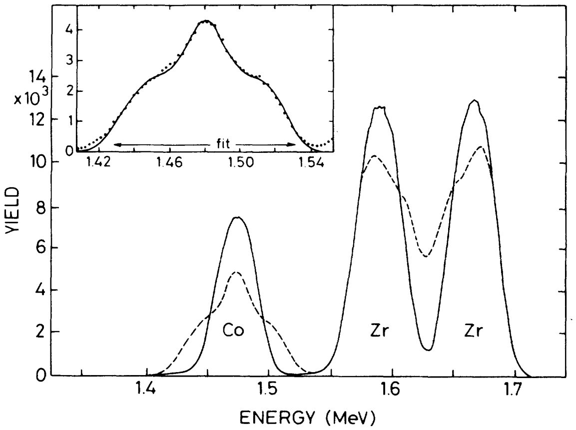

FIG. 1. Backscattering spectra of Zr-Co-Zr trilayer as-evaporated (solid line) and after annealing at 250 °C for 21 h (dashed line). The signal from the substrate is not shown. The inset shows the Co signal of the annealed sample with a model concentration profile fitted to the data.

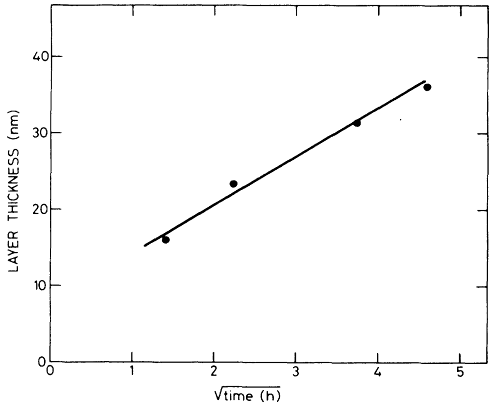

FIG. 2. Thickness of the amorphous layers as determined by the fitting procedure described in the text, vs square root of time. The solid line corresponds to a diffusion constant of 5.3×10^{-21} m^2/s.

have been heated for longer times (14 and 21 h) show a clear plateau which already begins to form after 5 h. The reaction occurs almost symmetrically at the two interfaces. However, the plateau is more pronounced and better defined at the upper interface. This slight asymmetry can be reduced by irradiating the film with heavy ions (see inset of Fig. 1). We have irradiated selected films with 500-keV Kr$^+$ with doses between 1×10^{14} and 1×10^{15} ions/cm^2. The solid-state reaction in Co-Zr seems, however, to be much less sensitive to pre-ion-irradiation than the corresponding Co-Hf and Ni-Hf (Ref. 16) reactions. This might be due to less stress release in the present case, as shown by the x-ray data.

We have fitted the measured spectra with functions based on a simple model of the concentration profiles which neglects the solubility of Co in Zr and vice versa, as well as possible contributions from grain-boundary diffusion. Furthermore, planar growth of the amorphous layers with linear concentration gradient is assumed.[12] The model concentration profiles were folded with a depth-resolution function, taking both straggling and detector resolution into account. The fitted test profiles reproduce the experimental data quite well. The inset of Fig. 1 shows the experimental data together with a fitted test profile.

Several important conclusions can be drawn from these fits. (i) The interfaces of the amorphous layers are, at least at the upper reaction front, as sharp as can be expected from the resolution of our system. This means that there is a planar growth throughout the area of the beam spot (1×2 mm^2). (ii) The data indicate only a small gradient with a concentration variation in the amorphous layer equal to about 5 at. %. (iii) The average composition of the amorphous phase, as determined from the relative yields of Co and Zr, is $Co_{42}Zr_{58}$, with an uncertainty of about 3 at. %. This composition is the same after 5, 14, and 21 h of interdiffusion and is in good agreement with the composition stated in Ref. 11 ($Co_{47}Zr_{53}$). There, the average concentration is also observed to stay constant during the whole reaction. For shorter annealing times, the width of the layer is too small to allow a determination of the concentration. (iv) The time dependence of the thickness of the amorphous phase is found by the fitting procedure described above is shown in Fig. 2. For the 2-h annealing, the composition was fixed to that found for longer times. The data closely follow a $\sqrt{t}$ growth law, as expected for diffusion-controlled development of the amorphous layer. However, as also observed in other experiments, the curve is shifted due to the fact that the reaction rate has already slowed down.[9,11,14] The diffusion constant derived from annealing times longer than the 2 h is $D=5.3\times10^{-21}$ m^2/s. For shorter times we are only able to give a lower limit of $D=1.6\times10^{-20}$ m^2/s. This means that the diffusion in the beginning is about a factor of 3 higher. The values of D as well as the time dependence are in excellent agreement with those derived from resistivity measurements[13] and cross-section TEM of $D=1.5\times10^{-20}$ and 1.0×10^{-20} m^2/s, respectively, and slightly higher than those from x-ray-diffraction data.

The RBS spectrum taken after 2 h annealing at 250 °C, Fig. 3, shows two main features. A slight broadening of the Co signal is visible and pronounded long tails can be seen. Comparison with the spectra taken before annealing shows that the dominant contribution in these tails are not artifacts of the analysis. It should be noted that already after 2 h annealing Co extends throughout the sample. Subtracting the background (multiple scattering and slit scattering) and a contribution from the amorphous layer due to the finite depth resolution, the averaged concentration in the tails is 3 at. % Co. For longer annealing times, the intensity in these tails stays approximately constant, while the amorphous phase growths with its well-defined composition (see spectrum after 5 h in Fig. 3).

In order to investigate this behavior in more detail, the bilayer configuration with 800 Å Zr on top of 2000 Å Co was chosen. These samples were tilted 60° for backscattering analysis, so that the depth resolution was enhanced by a factor of 2. In addition, due to the thicker

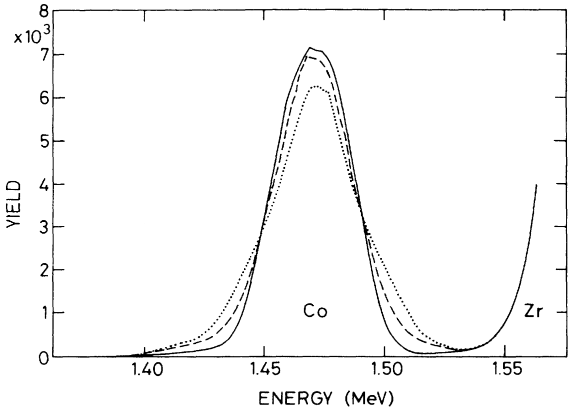

FIG. 3. Cobalt backscattering signal from a Zr-Co-Zr sample before annealing (solid line) after 2 h (dashed line) and after 5 h (dotted line) at 250 °C.

Zr layer, a solution of Co in Zr is more easily separated from the amorphization front itself. Backscattering spectra from such a bilayer in the beginning of the reaction are shown in Fig. 4. After $\frac{1}{2}$ h at 250 °C, between 1 and 2 at. % Co is seen in the crystalline hcp Zr layer. Further annealing for 1 h results in an almost constant concentration of ≈4 at. % Co in the tail, which is also nicely reflected in a uniform decrease in the intensity of the Zr plateau. At this stage of the reaction, shoulders at the peaks also indicate the beginning growth of the amorphous phase. So, the spectra from the bilayer-type sample confirm all the main features in the solid-state reaction found with the thinner trilayers.

In contrast, the Co-Zr-Co layers did not form an amorphous phase via interdiffusion. The solution of Co in crystalline Zr takes place in the first 1.5 h at 250 °C, but the amorphization itself is prevented. There is no change in the depth profiles when additionally heating the samples for up to 20 h.

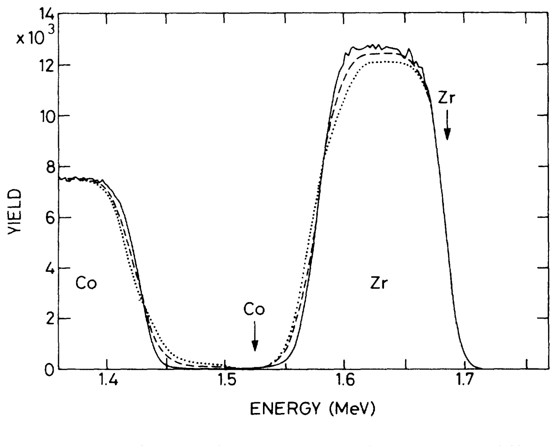

FIG. 4. Backscattering spectra of a Co-Zr bilayer as-evaporated (solid line) and annealed at 250 °C for 0.5 h (dashed line) and for 1.5 h (dotted line). The arrows indicate the surface positions for the Co and Zr signals, respectively.

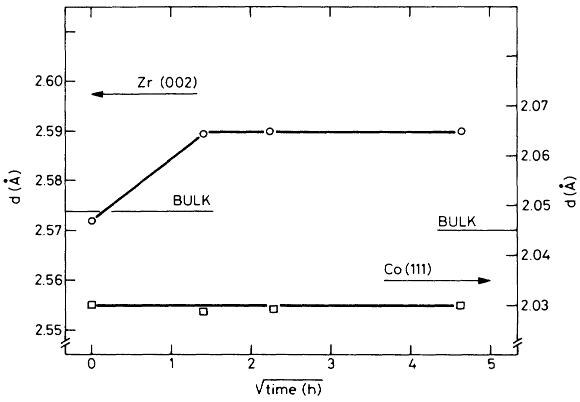

FIG. 5. Change of the Zr(002) and Co(111) lattice parameters during annealing at 250 °C.

B. X-ray-diffraction analysis

For the Zr-Co-Zr trilayer samples, x-ray diffraction was applied after each annealing step to follow the microstructural changes in the samples. The above-mentioned heavy-ion irradiation of 1×10^{14} ions/cm^2 does not change the angle of Zr(002) reflection, in contrast to the same type of Hf-Co-Hf trilayer configuration,[16] indicating no change of internal stresses in the present case. This is not surprising, as the Hf layers in Ref. 16 exhibited high internal stresses after evaporation that could be released by ion irradiation, whereas the Zr layers in these experiments show very little stress. Heating for 2 h at 250 °C leads to an increase in the lattice spacing of the observed Zr(002) reflection of about 0.8%. Longer annealings only cause a reduction in the intensity, but no prounced peak shift; see Fig. 5. The position of the Co(111) reflection is almost not affected by the solid-state reaction.

The x-ray spectra do not reveal any sign of intermediate crystalline phases, implying that only amorphous material forms during interdiffusion. As all crystalline material which undergoes phase change seems to directly transform into the amorphous state,[11] we have tried to estimate the concentration in the amorphous layer from the relative decrease of the Zr(002) and Co(111) reflections. For longer annealing times, the estimate yields a composition of $Zr_{57}Co_{43}$, in extremely good agreement with the RBS result, $Zr_{58}Co_{42}$.

The Co-Zr bilayers exhibited the same behavior as the Zr-Co-Zr samples, whereas the trilayer type with the opposite sequence shows a peak shift of the Zr(002) reflection for short annealing times (<2 h) corresponding to the lattice expansion of Zr. However, as in the backscattering spectra, there is no change after further heating.

IV. DISCUSSION

At present, a clear understanding of the initial nucleation and growth process in the solid-state amorphization reaction is not available. In the present studies of Co-Zr, this period is about the first hour at 250 °C. The RBS analysis shows that a concentration of about 3–4 at. % Co builds up within an hour almost throughout the crystalline Zr layers, indicating a very fast, concentration-limited diffusion. The fast diffusion could be due to either grain-boundary diffusion[18] or an interstitial diffusion mechanism in the bulk. Grain-boundary diffusion is in this case unlikely: an average concentration of 3 at. % Co would lead to an extremely high amount of Co in Zr grain boundaries with the present grain sizes (100–200 Å). In addition, the observed increase of the Zr lattice parameter, starting with about the bulk value, can be easily understood if Co occupies interstitial sites (most likely octahedral sites). A concentration of 3 at. % Co results in a lattice expansion of 0.5% in a simple hard-sphere model.

The possibility of enhanced mutual solid solubility has to be considered in the context of a metastable phase diagram. Free-energy curves for different phases were calculated according to Ref. 19. In Fig. 6 the free energies for the crystalline hcp Zr phase and the extrapolated liquid phase (totally disordered) are shown. The equilibrium phase diagram exhibits a very low (<0.2 at. %) (Ref. 20) solubility for Co in α-Zr due to the favorable compound phases. However, as seen in Fig. 6, if the intermetallic phases are suppressed, the common-tangent rule leads to around 4 at % *Zr*Co solution in metastable equilibrium with an totally disordered liquidlike phase containing about 36 at. % Co at 250 °C. Since we found an interstitial solution of Co in hcp Zr, an additional amount of stress energy has to be considered, which will change the free-energy curve with increasing Co concentration. For the quasiequilibrium found, the elastic energy only contributes with less than 1 kJ/mol. The free energy of the relaxed amorphous phase at ambient temperature can be estimated to be about 10 kJ/mol lower than the extrapolated liquid,[19] due to an excess energy contribution. The energy difference can be expected to be smaller at the reaction temperature (250 °C). Both effects (interstitial solution and relaxed amorphous phase) might change the metastable "equilibrium" concentrations according to the common-tangent rule slightly.

Extrapolation of the measured tracer diffusion coefficients[21] in α-Zr down to 250 °C yield $D_{\mathrm{Co}}(250\,^{\circ}\mathrm{C}) \approx 10^{-16}$–$10^{-17}$ m^2/s. This value is indeed about several orders of magnitude higher than a rough estimate of the lower limit needed for the diffusion of Co in crystalline Zr (the tails) in our experiments ($D \approx 10^{-18}$–10^{-19} m^2/s). The extremely fast diffusion led to the assumption that Co diffuses interstitially in hcp Zr,[21] as mentioned above. This is, in the present experiments, corroborated by the observed expansion of the Zr lattice.

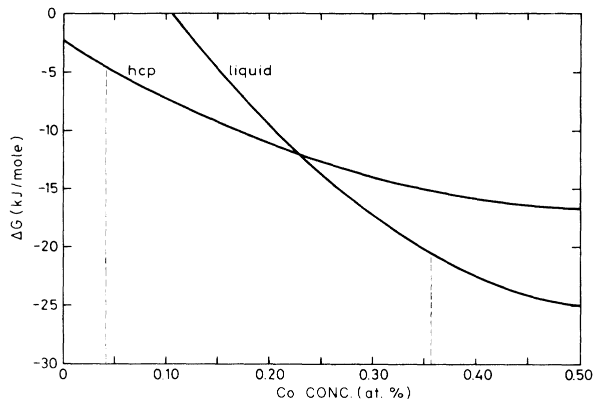

FIG. 6. Free-energy curves of the undercooled liquid and the hcp phase in the Co-Zr system at 250 °C as calculated according to Ref. 19. A solid solution of ≈ 4 at. % Co is seen to be in metastable equilibrium with an unordered phase with ≈ 36 at. % Co.

Summarizing the discussion given above, we suggest that initially Co starts to diffuse interstitially into crystalline Zr. The Zr lattice is expanded and would become unstable if more and more Co would diffuse in. This threshold concentration can be avoided by the formation of a metastable equilibrium between an amorphous phase built up at the interface and the crystalline *Zr*Co layer. The amorphous phase probably forms first at the Zr-grain boundaries, where a high defect density and no Zr mobility is present.[22] A massive (polymorphic) transformation from crystalline to amorphous might be possible from lattice-stability theory,[19] but it neglects the concentration gradient and the parabolic time law found in any of these diffusion couples.

The empirical statement that amorphization by solid-state reaction is connected with fast diffusion of one element in the crystalline matrix of another one[23] has to be viewed in a new way. In this context the notation "fast diffuser" has meaning only because it implies interstitial diffusion that destabilizes the lattice and is fast enough so that the diffusion within the amorphous layer is soon the process dominating the reaction.

ACKNOWLEDGMENTS

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