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PART I

**Interface Reactions,
Amorphous Phase Formation,
and Phase Separation**

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DIFFUSIONAL ASYMMETRY IN AMORPHOUS ALLOYS: IMPLICATIONS FOR INTERFACIAL REACTIONS

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ABSTRACT

Early/late transition metal systems such as Ni-Zr and Co-Zr exhibit solid state amorphization (SSA) in which the amorphous phase is formed by reaction between the crystalline elements. The rate of the amorphization is governed by the diffusion of the faster species, Ni or Co. Here results are presented on the homogenization of compositionally modulated thin films which show that the Zr diffusion is up to 10^6 times slower. The difference in diffusivities is correlated with atomic size. The consequences of the marked diffusional asymmetry are considered, particularly for the interpretation of results on the interdiffusion of Co into amorphous Co-Zr. It is proposed that for amorphous alloys such as Ni-Zr and Co-Zr, changes in composition by rapid diffusion of Ni or Co can yield structures which are not in internal equilibrium. This would affect, for example, the validity of the common tangent construction as applied to predict the limiting compositions of the amorphous phase in contact with the elemental layers during SSA.

1. INTRODUCTION

Interfacial reactions in thin films, particularly of metals on silicon, have been widely studied because of their great technological and scientific interest. The sequence of phases appearing in the reaction may be quite different from that observed in bulk samples. For example, in thin film Ni-Si only one phase, Ni₂Si, is observed instead of the sequence of up to six equilibrium phases found in bulk diffusion couples [1]. The phase selection has been analysed by Gösele and Tu [2]: the rate of thickening of a reaction layer can be governed not only by diffusional transport through the layer, but also by interfacial reactions at the boundaries of the layer. The limit on interfacial reaction rate when diffusion distances are short can prohibit the appearance of some phases. Silicide formation in thin film reactions exhibits another feature, namely the appearance of a metastable, amorphous phase. This was first found in Rh-Si [3], and is not easy to explain on a competitive growth model such as that of Gösele and Tu. It may be evidence for preferred nucleation of the amorphous phase (either during deposition or subsequent annealing). Some nucleation aspects of phase selection are discussed in [4].

Interest in thin film reactions and in amorphous phase formation has been heightened by the discovery of solid state amorphization (SSA) during homogenization of multilayered alloys. This was first reported by Schwarz and Johnson [5] for the system Au-La. The elements, in the form of alternating polycrystalline thin films, react on annealing to yield the amorphous alloy which grows at the interfaces between the elements as planar layers, thickening at a diffusion-controlled rate. The phenomenon has since been found in several binary alloys, notably of those of an early transition metal with a late transition metal. In general, one of the elements in a system showing SSA is a fast diffuser in the other crystalline element. This asymmetry in the diffusion coefficients in the crystalline elemental phases is a useful guide to the selection of systems for SSA. The asymmetry appears to apply also in the amorphous phase which is formed, and it is this which is the focus of this paper.

In the amorphous phase the asymmetry may be essential for SSA to compete successfully against the formation of the equilibrium crystalline intermetallic compounds. The thickening of the amorphous layers may be governed by the diffusion of the fast component, whereas nucleation and growth of the crystalline phases may be limited by the diffusion of the slow component. The SSA reaction has been most studied in one system of the early/late

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transition-metal type, Ni-Zr [6]. In this system the smaller atom, Ni, is a fast diffuser in crystalline Zr, and apparently also in the Ni-Zr amorphous phase. During the reaction, the amorphous phase has a composition gradient from $\sim\text{Ni}_{50}\text{Zr}_{50}$ in contact with the Zr layers to $\sim\text{Ni}_{70}\text{Zr}_{30}$ in contact with the Ni layers [7]. The diffusivity of Ni in the amorphous phase has been estimated from the reaction kinetics [8,9], and is in agreement with direct tracer measurements [10]. The diffusivity of the slower species, Zr, has, however, not been measured. Thin film marker experiments in the amorphous phase do show a considerable asymmetry in the diffusion coefficients, and it has been estimated that the diffusivity of Zr is, at the very least, ten times lower than that of Ni [10,11]. In Section 4, preliminary results are presented on the slow species diffusion. The Zr/Hf interdiffusivity in an amorphous $\text{Ni}_{65}(\text{Zr,Hf})_{35}$ alloy is measured in order to estimate the Zr diffusivity in $\text{Ni}_{65}\text{Zr}_{35}$. This composition is chosen because it is a good glass-former in thin film deposition, and is representative of the amorphous phase during the Ni-Zr SSA reaction. The interdiffusivity is determined from the rate of homogenization of compositionally modulated thin films. This technique offers unusual sensitivity, as diffusivity values down to $\sim 10^{-27} \text{ m}^2 \text{ s}^{-1}$ can be measured [12]. Such a sensitivity may be necessary in order to measure the slow-species diffusivity, since mobility of the slow species may permit crystallization of the amorphous phase.

As described in Section 4, it is found that the diffusivity of the small atom, Ni, can be up to 10^6 times that of the larger atoms Zr and Hf. This large disparity has consequences for the analysis of diffusion in such amorphous phases. One consequence is that during diffusional transport through the amorphous phase, internal equilibrium may not be reached. The common tangent construction for the determination of the amorphous phase compositions at the interfaces with the elemental layers may not then be valid. Preliminary evidence for this is presented in Section 5, for another early/late transition-metal system, Co-Zr.

Walser and Bené [13] hypothesized that in a thin film reaction between a metal and a silicon substrate, the silicide forms from an amorphous phase at the interface. They suggested that it is the composition of the amorphous phase, presumed to be near the deepest eutectic in the system, which determines the particular silicide to form. This rule has been applied with some success. In view of the later discovery of SSA, the Walser and Bené suggestion of an amorphous phase as an intermediate reaction step seems useful. Arguably the difference between systems in which amorphization is evident and some of those in which it is not could be merely the extent of the critical layer thickness of amorphous phase before appearance of the equilibrium crystalline phases. In this way, analysis of formation of amorphous phases by interfacial reaction, and of atomic transport through the phases, may be of importance not only for SSA, but also for interfacial reactions more generally.

2. ATOMIC DIFFUSION IN AMORPHOUS ALLOYS

The mechanisms of diffusion in amorphous alloys are not well understood. It has been suggested that smaller atoms diffuse by an interstitial mechanism, while larger atoms diffuse by a substitutional mechanism mediated by vacancy-like defects [14,15]. On the other hand, unlike the behaviour found in crystalline alloys, there do not appear to be two distinct groups of solute diffusivities [16,17]. Indeed, for tracer diffusivities of a wide range of solute species (except hydrogen) a single linear correlation is found between the logarithm of the pre-exponential diffusivity and the activation energy for diffusion [18]. This correlation for amorphous alloys suggests a single mechanism involving some degree of co-operative atomic movement [18]. The diffusivities of hydrogen show a separate correlation indicating an interstitial mechanism.

For different solutes in a given amorphous alloy the variation in diffusivity may be influenced by chemical effects [19,20], but the predominant influence is that of atomic size. Although there may not be a clear distinction between interstitial and substitutional mechanisms, there is a clear correlation of smaller atomic radius with higher diffusivity in both metal-metalloid alloys [19] and alloys of early and late transition metals [10,15,20]. The correlation is stronger in the early/late transition-metal glasses [18], perhaps reflecting weaker chemical effects in those systems. In the same systems the effects of alloy composition on diffusivities have been studied. For example Hahn *et al.* [15] showed that the diffusivity of copper in Ni-Zr glasses tends to increase with decreasing Ni-content, but is not strongly dependent on

composition until the Ni-content is $\leq 35\%$. Self-diffusivities in these systems (as for amorphous alloys in general) have not been much studied, but there are some important results showing the effect of alloy composition in the Fe-Zr system [21]. In $\text{Fe}_{24}\text{Zr}_{76}$ (atomic %) the diffusivity of the smaller atom, Fe, is at most ten times greater than that of Zr, whereas in $\text{Fe}_{91}\text{Zr}_9$ it is up to 10^5 times greater [21]. The disparity in diffusivities of the small and large component species in a system of this type has not so far been directly studied in an amorphous phase composition (approximately equiatomic) relevant for SSA.

The measurement of diffusivities in amorphous alloys is difficult because of their tendency to crystallize. This problem is expected to be particularly bad for the slow species in the early/late transition-metal glasses of interest in this work. The determination of diffusivities (reviewed in [16]) has mostly been based on the measurement of composition profiles at least 3 nm deep produced by ion-implantation or diffusion from a coating. The profiles have been measured using Rutherford backscattering, nuclear reaction techniques and sputter-sectioning of samples combined with Auger electron spectroscopy, secondary ion mass spectrometry or radiotracer analysis. The measurement of self-diffusivities using radiotracers has been comparatively rare. Each of these techniques can measure diffusivities as low as $\sim 10^{-24} \text{ m}^2 \text{ s}^{-1}$ [17]. In contrast we use a technique, described in more detail elsewhere [12], based on X-ray diffraction measurement of the homogenization of deposited multilayer samples. This technique permits measurements down to $\sim 10^{-27} \text{ m}^2 \text{ s}^{-1}$. At this sensitivity a value can be obtained for a diffusivity after only one atom in five has jumped. It is possible therefore to measure diffusivities in unrelaxed samples and to detect the effects of structural relaxation of the amorphous phase on diffusivity. The multilayer technique can also reveal other effects on diffusivity, for example due to chemical gradient energy and to strain, that are not of direct interest in this work.

The major disadvantage of the multilayer technique is that it does not permit the measurement of the diffusivities of individual species, but only of interdiffusivities. The technique could still be applied to the measurement of self-diffusivity if the layers were defined by isotopic enrichment and the homogenization were detected by neutron diffraction [22]. In the present work (Section 4) X-ray diffraction is used with Hf being an isoelectronic (rather than isotopic) substitute for Zr. Hafnium and zirconium, are both in group IVb, and are chemically very similar. Like Ni-Zr, Ni-Hf also shows SSA of the multilayered polycrystalline elements [23]. That the Goldschmidt radii of hafnium and zirconium atoms are almost identical is especially important in view of the size-dependence of diffusivity discussed above. Thus there is reason to suppose that the diffusivities of Hf and Zr may be similar and that the Zr/Hf interdiffusivities determined here may provide good estimates of the Zr diffusivity in $\text{Ni}_{65}\text{Zr}_{35}$.

3. EXPERIMENTAL METHODS

Only preliminary results are reported in this paper; more complete experimental details will be given in subsequent publications [24,25]. All the thin films used in this work were deposited (at 0.2 to 0.4 nm s^{-1}) from DC magnetrons in a UHV getter sputtering system with a base pressure of $0.1 \text{ } \mu\text{Pa}$ (details elsewhere [26,27]). Substrates (of silicon, sapphire or glass) were at just above room temperature, and were rotated underneath two targets to fabricate multilayers. Alloy deposition was from composite targets. For the short periodicity multilayers used in Section 4 a constant deposition rate is vital, and control to $\sim 0.1\%$ can now be achieved [26]. Compositions of the thin films were verified using Rutherford backscattering spectrometry (RBS) and energy-dispersive X-ray spectroscopy (EDS). Amorphicity was checked using transmission electron microscopy (TEM) and X-ray diffraction (XRD). XRD was used also in Section 4 for monitoring the decay of a composition modulation by measuring the intensity of the satellite peaks near the zero-order beam. All of the XRD was performed on a Philips θ - 2θ diffractometer with $\text{CuK}\alpha$ radiation. The satellite peaks from the high quality multilayers were sharp and careful alignment (on a specially constructed stage) in the diffractometer was required for reliable intensity measurement. RBS, used particularly for the measurements in Section 5, was performed using a 2 MV Van de Graaff accelerator.

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4. Zr/Hf INTERDIFFUSION IN $\text{Ni}_{65}(\text{Zr,Hf})_{35}$

4.1. Multilayer Samples

The samples consisted of alternating layers of equal thicknesses of amorphous $\text{Ni}_{65}\text{Zr}_{35}$ and amorphous $\text{Ni}_{65}\text{Hf}_{35}$ (atomic %). The repeat distance in the multilayers (*i.e.*, the thickness of two layers) was 3.3, 1.6 or 0.78 nm. The total deposited thickness was $\sim 0.5\ \mu\text{m}$, containing a few hundred repeat distances. The XRD from these samples shows the expected amorphous halos at large angle, while at small angles near the zero-order beam there are satellites due to the imposed composition modulation. In amorphous samples these are the only peaks to arise from the modulation; they are at angles found by substituting the repeat distance into the Bragg equation. As outlined in Section 2, the intention is to estimate the Zr-diffusivity in $\text{Ni}_{65}\text{Zr}_{35}$ by measuring the Zr/Hf interdiffusivity in these samples. To ensure that homogenization of the samples, and consequent decay of the X-ray satellites, involved only Zr/Hf interdiffusion, the Ni-content throughout was made as uniform as possible.

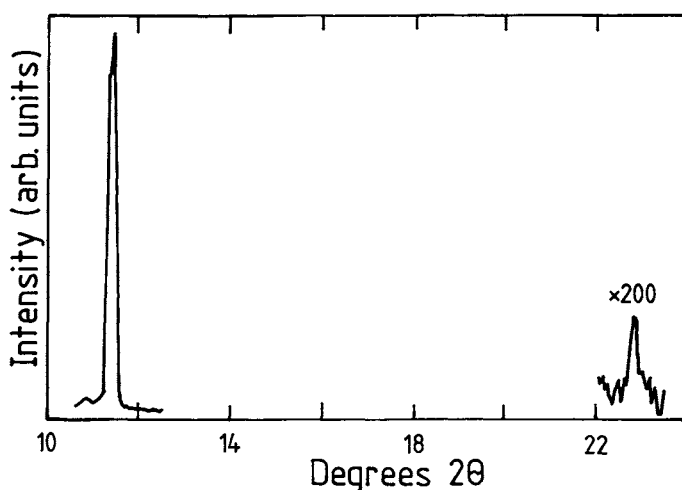


Figure 1: X-ray diffractometer trace using $\text{CuK}\alpha$ radiation from an amorphous $(\text{Ni}_{65}\text{Zr}_{35})/(\text{Ni}_{65}\text{Hf}_{35})$ multilayer with 400 repeat distances of $\lambda = 0.78\ \text{nm}$.

Figure 1 shows the satellite peaks found for the $\lambda = 0.78\ \text{nm}$ multilayer. In larger- λ samples satellite peaks up to fifth order were observed, but even in this small- λ sample the second order satellite is present, implying an interfacial roughness of $\sim 0.11\ \text{nm}$. Such low values of interfacial roughness in amorphous films are due not to high surface mobility of the atoms during deposition, but to the flattening effect of bombardment by neutral atoms reflected from the sputtering target [26]. Such bombardment is promoted by having a low sputtering pressure. With a target-substrate distance of 35 mm, we have used the lowest pressure possible in our system, $\sim 0.4\ \text{Pa}$.

4.2. Diffusion Measurements

Anneals to partially homogenize the multilayered samples were carried out in the range 553 to 663 K. Below 598 K oxidation of the samples appears to contribute significantly to the

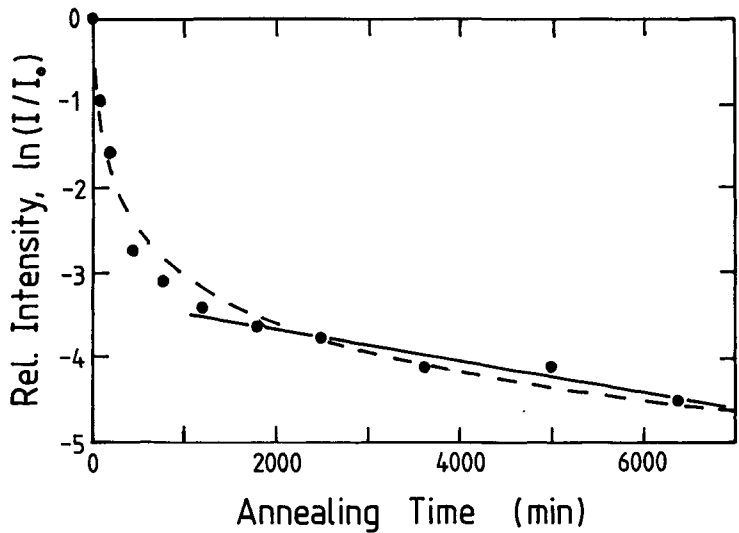


Figure 2: Decay of intensity of the first order X-ray satellite from an amorphous (Ni₆₅Zr₃₅)/(Ni₆₅Hf₃₅) multilayer with $\lambda = 1.6$ nm annealed at 633 K. The negative gradient is proportional to the Zr/Hf interdiffusivity.

observed satellite decay, and consequently diffusion coefficients are extracted only from the results of annealing at higher temperatures. Figure 2 shows a typical data set: the decay of the first order satellite intensity for a $\lambda = 1.6$ nm film annealed at 633 K. In such a plot the negative gradient is proportional to the interdiffusion coefficient \bar{D} .

$$\frac{d}{dt} \left[\ln \left(\frac{I}{I_0} \right) \right] = - \frac{8\pi^2}{\lambda^2} \bar{D} \quad (1)$$

Here I is the time-dependent intensity of the X-ray satellite, and I_0 its initial intensity [12]. It can be seen that the interdiffusivity is at first high and then settles down to an approximately constant value. The initial fast decay could be due to a contribution from Ni-diffusion, or to a general relaxation of the amorphous structure. The Ni diffusion coefficient at this temperature, estimated from data in [9], is so high ($\sim 7 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$) that it should not affect for long the decay shown which, after the initial transient, corresponds to an interdiffusivity of only $\sim 2 \times 10^{-25} \text{ m}^2 \text{ s}^{-1}$. If, on the other hand, the time-dependent behaviour is due to structural relaxation, it is expected that, in accordance with observed linear increases in viscosity [28], $1/\bar{D}$ would increase linearly. The dashed line in fig. 2 is a fit assuming this behaviour, and indicates that the decrease in \bar{D} is consistent with structural relaxation of the amorphous phase.

This relaxation complicates attempts to determine an activation energy for the interdiffusion, since different degrees of relaxation may be attained in diffusion anneals at different temperatures. Isoconfigurational measurements to permit extraction of meaningful activation energies are possible using carefully chosen annealing sequences. In the present work a $\lambda = 1.6$ nm sample was annealed at 633 K until a reasonably constant \bar{D} was attained. The same sample was annealed at lower temperatures 618 K and 598 K to determine the \bar{D} -values. Finally the sample was annealed again at 633 K to verify that the \bar{D} at that temperature had not increased further due to relaxation at the lower temperatures. Since the additional relaxation due to the lower temperature anneals was found to be negligible, the \bar{D} -values at the three temperatures can be taken to be isoconfigurational. They are found to have an Arrhenius

temperature dependence with an activation energy of 1.1 eV atom⁻¹ and a pre-exponential of $\tilde{D}_0 = \sim 10^{-16}$ m² s⁻¹. This value of Zr/Hf interdiffusivity may still be somewhat higher than that in a fully relaxed sample.

Interdiffusivity measurements in multilayers of small repeat distance are subject to gradient energy effects [12]. For homogenizing samples the effective \tilde{D} is reduced from its ideal, ∞ - λ value at low λ . In the present case there is preliminary evidence for such an effect as diffusivities were found to be somewhat higher for $\lambda = 3.3$ nm than for $\lambda = 1.6$ nm. Unfortunately, attempts to quantify the effect failed because the \tilde{D} -values measured for the $\lambda = 0.78$ nm films were necessarily for unrelaxed structures.

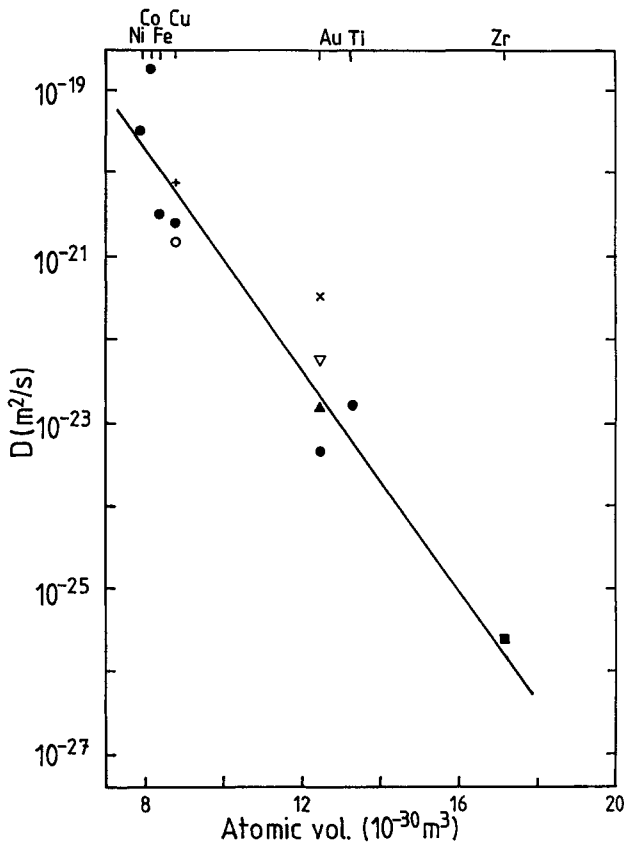


Figure 3: A survey of reported diffusion coefficients [15,35,36] for various species in amorphous Ni-Zr (with Ni-content 50 to 65 atomic %) at 573 K. The datum for Zr is the Zr/Hf diffusivity determined in the present work.

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4.3. Correlation of Diffusivity with Atomic Size

As outlined in Section 2, there is evidence that the tracer diffusivity of solutes in Ni-Zr amorphous alloys is not strongly dependent on the alloy composition unless the Ni-content is $\leq 35\%$. Accordingly it is possible to compare published diffusivity values for a wide range of solutes in Ni-Zr amorphous alloys of slightly differing compositions. Figure 3, showing D-values at 573 K, is a compilation of data for alloys with 50 to 65% Ni. The correlation of D with atomic volume (calculated from Goldschmidt radii) is clear. If this correlation is extrapolated to the atomic volume of Zr and Hf (only 2% different) it is consistent with the value of Zr/Hf interdiffusivity measured in this work. The large disparity (a factor of $\sim 10^6$) between the Ni-diffusivity and the Zr/Hf-interdiffusivity (presumed to be a reasonable estimate of the Zr-diffusivity) appears to be a natural consequence of widely different atomic size. (In Ni-Zr amorphous alloys with Ni-content $\leq 35\%$, D still depends on atomic size, but much less strongly [24].)

The linearity of the plot in fig. 3 is suggestive of an explanation based on the free volume theory for diffusive transport in amorphous systems [29]. In the theory the diffusion coefficient D is given by

$$D = g a u \exp[-\gamma v^* / v_f] \quad (2)$$

where g is a geometric factor (usually $1/6$), a the molecular diameter, u the gas kinetic velocity of the molecules, γ an overlap factor (0.5 to 1), v^* the critical free volume for a diffusive rearrangement of molecules, and v_f is the average free volume per molecule. If the assumption is made that the critical free volume fluctuation v^* for a particular diffusing atom is proportional to that atom's volume, then a correlation of the type shown in fig. 3 will result. However, the pre-exponential in the measured correlation does not match the theory, presumably reflecting the inadequacy of the simple theory in describing the free volume distribution in an amorphous phase composed of two types of atom with widely differing size.

5. COBALT DIFFUSION INTO AMORPHOUS Co-Zr

5.1. Introduction

The system Co-Zr, like Ni-Zr, is of the early/late transition metal type, and exhibits SSA [30]. The aim in this work was to determine the composition of the amorphous Co-Zr phase which would be in equilibrium in contact with crystalline elemental cobalt, that is, the composition which would be given by the common tangent construction on a free-energy composition diagram. To this end, trilayer thin film samples were deposited, consisting of ~ 30 nm Co, ~ 40 nm amorphous $\text{Co}_{50}\text{Zr}_{50}$ (atomic %) and ~ 30 nm Co. The experiment was to anneal this trilayer and monitor the Co-content of the amorphous layer using RBS. The experiment showed some effects attributable to the diffusional asymmetry discussed in Section 4.

5.2. In-Diffusion Results

Annealing experiments were carried out in the range 653 to 743 K. On annealing the trilayers the Co-content of the amorphous phase increased as was expected from thermodynamic estimates showing the common tangent composition to be more Co-rich than the initial $\text{Co}_{50}\text{Zr}_{50}$ composition. Within the resolution of the measurement, the Co-content in the amorphous layer at any stage was uniform. Figure 4 shows the variation of the amorphous layer composition with annealing time at different temperatures. Clearly, higher annealing temperatures lead to more Co-indiffusion: the diffusion is faster and the Co-content saturates at a higher level. Following some of the anneals, ion irradiation with Xe^+ at 500 keV to a dose of 10^{15} cm^{-2} was carried out. As shown in fig. 4, this does enable further indiffusion to take place in subsequent anneals.

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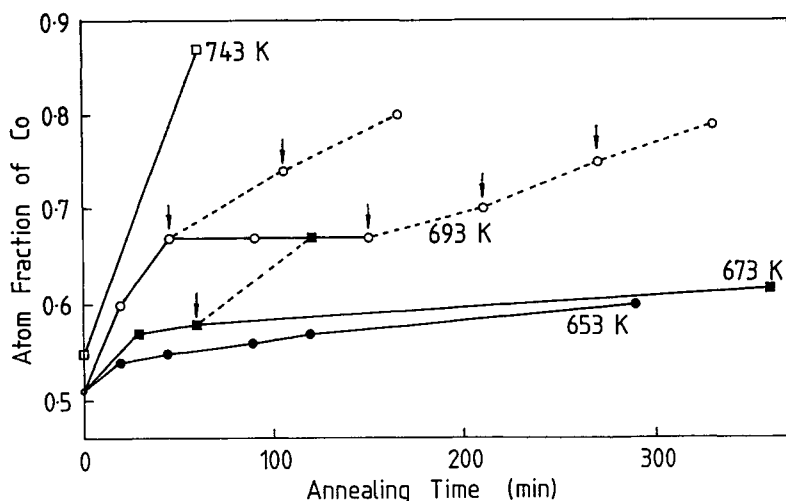


Figure 4: Effects of annealing at selected temperatures on the Co-content of an amorphous Co-Zr layer sandwiched between elemental Co layers. Ion-irradiation was carried out at the points marked by arrows.

5.3. Discussion

The lack of a detectable composition gradient in the amorphous phase during Co-indiffusion suggests that diffusion in that phase is not rate-controlling. This is consistent with the high mobility of Co in the amorphous phase. Presumably the rate of indiffusion is controlled by the dissolution reaction at the interfaces of the amorphous phase with the Co-layers.

The apparent saturation of the Co-content in lower temperature anneals is not easily reconciled with diffusional or interface reaction control. It is also not expected that the common tangent composition would be strongly dependent on temperature, so that such an effect is not a likely explanation of the observed behaviour. A possible explanation is provided by the marked diffusional asymmetry, presumably similar to that found in Ni-Zr. Given such an asymmetry, the Co will diffuse into a Zr-matrix which is essentially immobile. The matrix does not relax in the way that would be necessary for the amorphous structure to be in internal equilibrium at its composition, or for further Co-indiffusion up to the true equilibrium value to be possible. Ion-irradiation of the type used cannot cause long-range diffusion, but may change some local configurations in the Zr-matrix. In this way some further Co-indiffusion may take place in the partially relaxed matrix. The Zr-matrix may of course also relax thermally. This is presumably the case in higher temperature anneals (if crystallization does not set in), and may be happening even at the lower temperatures as suggested by the slow upward drift of the "saturation" values of Co-content in fig. 4. Ion-irradiation can enhance diffusion in amorphous phases [31], but it is important to note that this is not the relevant effect here: neither the rate of Co-indiffusion nor the saturation Co-content is controlled by diffusion as is evident from the lack of composition gradients in the amorphous layers.

6. DISCUSSION

In Section 5.3 it has been suggested that one of the consequences of the diffusional asymmetry in amorphous alloys is that an amorphous alloy changing composition may not remain in internal equilibrium. As the more mobile species diffuses in or out, the other species