Does the diffusion mechanism in thin amorphous Co$_{81}$Zr$_{19}$ films change during structural relaxation?

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Abstract. In order to clarify the diffusion mechanisms in metallic glasses we measured the time dependence and the isotope effect $E = (D_\alpha/D_\beta - 1)/\left(\sqrt{m_\beta/m_\alpha} - 1\right)$ of Co diffusion in thin 1 µm amorphous Co$_{81}$Zr$_{19}$ films during structural relaxation. To observe diffusion on a nanometre scale the radiotracer technique in conjunction with serial sectioning in conjunction with ion-beam sputtering was employed. A drop of the diffusivity by a factor of three was found during structural relaxation at $T = 573$ K, but no change in $E$ was observed. Small isotope effects of $E = 0.00(2)$ in the relaxed and even in the as-quenched states in the present alloy strongly suggest collective hopping diffusion mechanisms in the relaxed as well as in the as-quenched states. These results are in good accordance with results in thin 1 µm amorphous Co$_{51}$Zr$_{49}$ films. The results are compared to measurements in melt-spun amorphous Co$_{76.7}$Fe$_2$Nb$_{14.3}$B$_7$, where a drastic drop of $E$ during relaxation has been observed. We further discuss the results with respect to measurements in melt-spun Co$_{80}$Zr$_{11}$ ribbons to clarify the mechanism of annealing defects. The absence of any geometry effect seems to rule out annihilation of quenched-in free volume at the outer surface in thin Co–Zr glasses.

1. Introduction

Crystalline materials are characterized by a well defined three-dimensional periodic structure whereas amorphous alloys can be described as a dense random packing of hard spheres in the simplest model [1]. These alloys are also termed ‘metallic glasses’ and are non-equilibrium
systems without any long-range order but short-range order up to a few nanometres. Metallic glasses have been of great interest because of their extraordinary mechanical, electrical and magnetic properties \[2, 3\].

The production of metallic glasses requires quenching at rates of the order of $10^6 \text{ K s}^{-1}$ \[4\]. Melt-spun samples have been produced with a thickness up to $70 \mu\text{m}$ whereas thin films up to only $1 \mu\text{m}$ can be obtained, for example, by sputtering techniques \[5\]. Recently, bulk metallic glasses have been produced with low cooling rates of only $1 \text{ K s}^{-1}$ \[6, 7\]. During cooling, additional volume is quenched in from the liquid state. This so-called excess volume anneals out during annealing at elevated temperatures. The density increases \[8, 9\] and an improvement in the topological short-range order has been observed \[10\]. Moreover, an improvement in chemical short-range order has also been discussed \[11\].

This structural relaxation is reversible above the glass transition temperature $T_g$, but irreversible below $T_g$. Below $T_g$ the diffusivity decreases during relaxation until it approaches a thermodynamic metastable equilibrium state indicated by a time-independent value of the diffusivity \[12, 13\]. Nearly all physical properties are affected by structural relaxation, often it may lead to severe embrittlement, see for example \[14\].

There are still open questions concerning the mechanism of how any quenched-in excess volume anneals out during structural relaxation. Free volume changes in amorphous Zr\textsubscript{46.7}Ti\textsubscript{8.3}Cu\textsubscript{7.5}Ni\textsubscript{10}Be\textsubscript{27.5} (vitreloy 4) have been observed by positron-annihilation spectroscopy \[9\]. These measurements show a geometry effect which suggest that free volume migrates to the outer surface. On the other hand, Egami explains annihilation mechanisms based on the recombination of regions of higher and lower densities \[14\]. The annealing of excess volume arises from the anharmonicity of the interatomic potentials without involving the surface.

The stability of metallic glasses is governed by atomic transport phenomena. Therefore, structural relaxation, phase separation and crystallization are of great interest. Hence investigations on the diffusion mechanisms have been performed over the past few decades also with regard to technological applications (for reviews see e.g. \[15\]–\[17\]). While the knowledge on the diffusion mechanism in the relaxed state has increased considerably over the last few years (e.g. \[18\]) there are open questions, in particular, on the diffusion behaviour during relaxation. To get information about the diffusion mechanism in general, isotope effect measurements have turned out to provide valuable information.

The isotope effect is defined as

$$E = \frac{D_\alpha / D_\beta - 1}{\sqrt{m_\beta / m_\alpha} - 1}$$

where $D_i$ and $m_i$ are the diffusivity and mass of the isotope $i$, respectively. Measurements of self-diffusion in densely packed crystalline metals result high isotope effects of $E \approx 0.7$ \[15, 19\] and are interpreted as single atom jumps via vacancies. In contrast, in fully relaxed metallic glasses small isotope effects of $E \approx 0.0$ to $E \approx 0.1$ have been measured in amorphous layers \[18, 20\]–\[22\]. In particular, investigations in thin $1 \mu\text{m}$ amorphous Co\textsubscript{51}Zr\textsubscript{49} layers showed a drop of diffusivity but no change in the isotope effect during structural relaxation \[22\]. Small $E$ values were interpreted as resulting from a strong dilution of the mass effect through participation of some tens of atoms in the diffusion process. From this point of view, collective mechanisms have been discussed in the relaxed state. Recently, collective hopping of groups of atoms has also been proposed to govern diffusion in the strongly undercooled liquid state of the new bulk metallic glasses \[23, 24\].

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Table 1. Overview of Co diffusion data in Co$_{81}$Zr$_{19}$ at $T = 573$ K.

| Annealing time (s) | Relaxation time (s) | $\langle D \rangle$ ($10^{-21}$ m$^2$ s$^{-1}$) | $E$ |
|--------------------|---------------------|---------------------------------------------|-----|
| 8400               | 4200                | 17                                         | 0.00(2) |
| 9600               | 13 800              | 6.6                                        |     |
| 11 100             | 23 550              | 4.5                                        |     |
| 11 100             | 34 650              | 3.7                                        | 0.00(2) |

On the other hand, investigations of the isotope effect in 70 µm melt-spun amorphous Co$_{76.7}$Fe$_2$Nb$_{14.3}$B$_7$ showed a change in $E$ from $E \approx 0.5$ to low values typical of the relaxed state during structural relaxation [13], while the diffusivity dropped by a factor of three. This was explained in terms of a transition from a single jump to a cooperative mechanism during structural relaxation. The single-jump mechanism was attributed to excess volume occurring in the form of vacancy-like localized defects.

In the present paper, we report on $^{57}$Co/$^{60}$Co self-diffusion and isotope effect measurements in a 1 µm thick amorphous Co$_{81}$Zr$_{19}$ layer during structural relaxation. In this well known system diffusion mechanisms have also been discussed by Klugkist et al [25].

The question is addressed as to whether a drop in diffusivity can be observed during structural relaxation even in amorphous Co$_{81}$Zr$_{19}$ layers, as seen in Co$_{51}$Zr$_{49}$ layers [22] and in 50 µm thick melt-spun Co$_{89}$Zr$_{11}$ ribbons [26] and as to whether the isotope effect $E$ changes during structural relaxation as observed in the metal–metalloid system Co$_{76.7}$Fe$_2$Nb$_{14.3}$B$_7$ [13]. Due to the onset of crystallization, penetration depths are restricted. Hence, the measurements were performed with a well established radiotracer technique in combination with serial sectioning by sputtering.

2. Experimental procedure

In order to observe the structural relaxation, all experiments have been performed on one sample. A 1 µm layer of Co$_{81}$Zr$_{19}$ was prepared by means of triode magnetron sputtering onto a carefully polished and cleaned single crystals of sapphire in an ultrahigh vacuum (UHV) chamber as described by Troche et al [5]. The exact concentration was determined by electron microprobe analysis. For the diffusion measurements the sample was fixed on a copper heating plate in an UHV chamber (pressure < 10$^{-6}$ Pa). As radiotracer a mixture of $^{57}$Co and $^{60}$Co isotopes, handled as $^{57}$CoCl$_2$ and $^{60}$CoCl$_2$ in a 0.1 M HCl was used to measure the self-diffusivity in the Co–Zr alloy. The radiotracer was deposited in situ by flash evaporation in high vacuum directly after sputter cleaning the specimen with argon ions. Then annealing was performed at $T = 573$ K for different times, as seen in table 1. X-ray measurements after each experiment did not show any crystallinity before and even after the longest annealing.

Penetration profiles were obtained by serial sectioning (600 eV, 1 mA cm$^{-2}$) performed in an ion-beam sputtering apparatus similar to that described by Faupel et al [27]. The removed material was collected on a Mylar foil, which was advanced after each section by means of a computer controlled motor. The sputtering rate was calculated from the weight loss, the cross section area, the density of the samples and the sputtering time. The tracer concentration in each section was determined by use of an intrinsic Ge detector, counting the intensities of the $\gamma$ lines of $^{57}$Co and $^{60}$Co. Measurements were corrected for the $\gamma$ background and isotope lifetimes.

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Penetration profiles of $^{57}$Co diffusion in amorphous Co$_{81}$Zr$_{19}$ for $T = 573$ K and the various annealing times as indicated. The $^{57}$Co activity is plotted against the square of the penetration depth. The first data points (open symbols) are affected by surface effects and were not taken into account. The diffusion coefficient $D$ can be evaluated from the slope $m = -1/4(Dt)$ of the straight line fitted to the data points. The resolution function of the microsectioning technique is also shown.

Under these circumstances the Co concentration $c(x, t)$ is given by the thin-film solution of Fick’s second law:

$$c(x, t) = \frac{I_0}{\sqrt{\pi Dt}} e^{-x^2/(4Dt)}.$$  (2)

Here $I_0$ denotes the initial tracer concentration at $x = 0$ and $t = 0$, $t$ denotes the diffusion time, $D$ is the diffusion coefficient and $x$ is the penetration depth. The diffusion coefficient $D$ was determined from the slope $m = -1/4(Dt)$ of the straight lines fitted to the penetration profiles (see figure 1).

To obtain $E$ values, the activity ratio of $^{57}$Co and $^{60}$Co is plotted against the $^{57}$Co activity on a logarithmic scale. By means of the thin-film solution one obtains

$$\ln\left[\frac{c_\alpha(x, t)}{c_\beta(x, t)}\right] = \text{constant} - (D_\beta/D_\alpha - 1) \ln[c(x, t)].$$  (3)

$D_\alpha/D_\beta - 1$ can be taken from the slope, as seen in figure 3. The isotope effect was evaluated according to equation (1).

3. Results

The resulting penetration profiles are plotted in figure 1. The activity of the $^{57}$Co tracer is plotted against the square of the penetration depth for the different annealing times as indicated. The

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Figure 2. Isotope effect profiles of Co diffusion in Co$_{81}$Zr$_{19}$ for the structurally relaxed and as-quenched states. The activity ratio of $^{57}$Co and $^{60}$Co is plotted against the $^{57}$Co activity on a logarithmic scale.

Figure 3. Time dependence of $^{57}$Co diffusion in Co$_{81}$Zr$_{19}$ during structural relaxation. The diffusion coefficients are plotted against the relaxation time. The last data point represents the fully relaxed state (for details see discussion).

temperature was kept constant at $T = 573$ K for all experiments. The first data points were affected by surface effects and were not taken into account. The resolution function of the microsectioning technique is also shown. This function was determined by serial sectioning of a sample that had not been previously annealed. The tail at large penetration depths originate from tracer atoms that were first distributed onto components of the sputter chamber and then sputtered off again.

The measured profiles were corrected by a deconvolution of the measured profile with the resolution profile. This deconvolution did not affect diffusivities within given experimental errors. Experimental errors in the absolute diffusivity are about 30%. The major contributions originate from uncertainties in the depth calibration measurement. We would like to point out that these uncertainties do not affect the evaluation of the isotope effect $E$, which only depends on the ratio of the isotope diffusivities.
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The resulting time dependence of Co diffusion is shown in figure 3. To take into account the fact that all diffusion coefficients are time-averaged values, the calculated diffusivities were plotted against the relaxation time for each experiment. This relaxation time was calculated as the sum of half of the annealing time and the time of the preceding annealing experiments (see table 1).

Isotope effects were determined for the first and the last diffusion experiment and are also shown in figure 2. Here, the activity of $^{57}$Co/$^{60}$Co is plotted against the $^{57}$Co activity on a logarithmic scale. $E$ can be evaluated from the slope of the straight line according to equation (3).

The isotope effects and the diffusivities as well as the calculated relaxation times are summarized in table 1.

4. Discussion

The investigated isothermal time dependence of the diffusivity is shown in figure 3. The diffusivity after the last experiment is similar to the diffusivity in fully relaxed Co$_{81}$Zr$_{19}$ glasses measured by Klugkist et al [25]. The diffusivities in this thin 1 $\mu$m amorphous layer show a drop of $D$ during structural relaxation by a factor of three. This order of magnitude is similar to that measured in thin amorphous Co$_{51}$Zr$_{49}$ layers [22] and also to Co$_{89}$Zr$_{11}$ melt-spun samples of 50 $\mu$m thickness [26]. Assuming that defects migrate to the outer surface, the relaxation time should be proportional to the square of sample thickness and therefore relaxation should proceed much faster in thin layers compared to much thicker melt-spun samples. Comparing the sample thickness and the relaxation time of these thin films with those in melt-spun samples, it appears that the migration of defects to the outer surface can be excluded. The drastic drop of diffusivity in these thin layers strongly suggest that there is no influence of sample thickness on relaxation. From this point of view defects do not seem to migrate to the outer surface.

Obviously, there is also no mass dependence of diffusion in the as-quenched state. Therefore, a contribution of quasivacancies as diffusion vehicles can be excluded, because such vehicles would result in a much larger isotope effect, as seen in Co$_{76.7}$Fe$_2$Nb$_{14.3}$B$_7$ glasses [13], for example, or in crystalline materials [15, 16].

Also, in the above mentioned thin 1 $\mu$m Co$_{51}$Zr$_{49}$ layers, no change in $E$ has been measured during structural relaxation. The small values of $E$ in the relaxed and in the unrelaxed states in Co–Zr glasses seem to be independent of concentration [18, 28] and independent of degree of relaxation. This suggests that collective diffusion mechanisms occur in the as-quenched state as well as in the relaxed state. Such cooperative hopping of several atoms has also been observed in computer simulations [29, 30]. ‘Medium assisted highly cooperative hopping’ has further been suggested by an extension of the mode-coupling theory to the glassy state [31].

Taking into account the almost vanishing activation volume of 0.08 $\Omega$ ($\Omega$ being the average atomic volume) in the present alloy measured by Klugkist et al [25], the diffusion process in this thin Co$_{81}$Zr$_{19}$ layer is suggested to be collective without involving thermally generated defects.

In conclusion the present investigations show that the diffusion mechanism in the amorphous Co$_{81}$Zr$_{19}$ films does not change during structural relaxation. In the as-quenched state as well as in the relaxed state diffusion occurs via collective hopping processes.

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