

Iron self-diffusion in chemically homogeneous multilayers

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Abstract. Iron self-diffusion measurements in amorphous and nanocrystalline chemically homogeneous multilayers (CHM) of FeZr/⁵⁷FeZr, (with nm range periodicity) have been studied with neutron reflectivity technique. It has been found that both the activation energy for diffusion and the pre-factor were significantly smaller as compared with bulk alloys. Effect of compressive stress on self-diffusion reveals a significant dependence on the activation energy as a function of applied stress. On the basis of the obtained results the diffusion mechanism in amorphous and nanocrystalline CHM of FeZr/⁵⁷FeZr is reviewed in this paper.

1 Introduction

Atomic diffusion in amorphous (*a*) and nanocrystalline (*n*)-alloys has been a subject of great interest as changes in the structure of these alloys and their relation to physical properties are of primary interest from the point of view of their technological applications and stability against external environment [1,2,3,4]. Generally, these alloys are metastable, and at elevated temperatures various atomic rearrangements take place [5], which leads to a strong need for an understanding of the self-diffusion behaviour in *a* and *n*-alloys. In most of the studies performed on self-diffusion, profiling and sectioning techniques such as radiotracer techniques, secondary ion mass spectroscopy (SIMS), Rutherford backscattering, Auger electron spectroscopy etc. were used. The depth resolution available with the profiling and sectioning techniques is of the order of a few nm, which gives a lower limit for probing diffusion lengths. It is known that the crystallisation temperature in the *a*-alloys is around 700 K and in order to study self-diffusion and structural relaxations at lower temperatures (~400 K) in a reasonable time, a technique with greater sensitivity is required. Further, the crystallisation temperature in nm range thin films and multilayers (ML) is even lower as compared to bulk alloys; a technique with sub nanometer resolution is essential for studying self-diffusion and structural relaxation in thin films and ML. Neutron reflectivity (NR) is a non-destructive technique which can be used for studying self-diffusion in a CHM with a resolution as small as 0.1 nm. Due to the fact that scattering length density of neutrons is different for isotopes of an element, a significant contrast for neutrons gives a possibility of studying diffusion in a CHM, while for X-rays the whole ML structure is like a single layer. In an earlier study A. L. Greer *et al* [6] have demonstrated the application of neutron reflectivity technique for measuring self-diffusion in *a*-NiZr ML. In the present work, we have measured self-diffusion of iron in chemically homogeneous *a* and *n*-ML of FeZr/⁵⁷FeZr. Effect of compressive stress on self-diffusion has also been studied to determine the associated diffusion mechanism.

2 Experimental

CHM of FeZr/⁵⁷FeZr were prepared using magnetron and ion beam sputtering techniques. The chemical composition of the deposited layers was determined with X-ray photoelectron spectroscopy technique and the chemical contrast between the layers was investigated with X-ray reflectivity (XRR). The thermal stability of the ML was studied with X-ray diffraction (XRD) conversion electron Mössbauer spectroscopy (CEMS). The self-diffusion measurements were

performed using neutron reflectivity technique at the reflectometer AMOR [7] at SINQ, PSI in the time of flight mode using two different angular settings.

3 Results and discussion

3.1 a -Fe₆₇Zr₃₃/⁵⁷Fe₆₇Zr₃₃ ML: Two different CHM with composition: [^{natural}Fe_{67±3}Zr_{33±3}/⁵⁷Fe_{67±3}Zr_{33±3}] were prepared using magnetron and ion beam sputtering techniques and self-diffusion measurements were performed using NR. Fig.1 shows a typical XRR pattern obtained from the ML. The featureless decay of the XRR confirms absence of any chemical contrast between the natural and ⁵⁷FeZr layers. The XRD and CEMS measurements of the ML reveal that for a temperature <573 K, the ML remains in the a -state and above this temperature the crystallization process starts [8]. The self-diffusion measurements were carried out in the temperature range of 373-523 K to avoid influence of crystallization on the diffusion process. Fig. 2(a) shows the NR pattern of the ML in the as-deposited state and after annealing at 373K for various periods of time. As can be seen, after an annealing time of 22 hours the Bragg peak has completely vanished indicating that the whole layer stack has been diffused. In addition, at initial times a shift of Bragg peak towards higher q_z values was observed. This shift of the Bragg peak towards higher q_z mean a reduction in the bilayer period and can be related to annihilation of free volume as a result of structural relaxation during annealing. A similar decay of the Bragg peak has been observed at other annealing temperatures too. The decay of the Bragg peak intensity can be used to calculate the diffusion coefficient using the expression [6]:

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

Where I_0 is the intensity of the n^{th} order Bragg peak at time $t=0$; D is the diffusivity at the annealing temperature T , and d is the bilayer periodicity. The height of the Bragg peak was determined after subtracting the background due to Fresnel reflectivity by multiplying the data by a factor of q_z^4 , where q_z is the momentum transfer. Fig. 2(b) shows a dependence of diffusivity as a function of annealing temperature which follows the Arrhenius type behaviour given by $D=D_0 \exp(-E/k_B T)$; where D_0 , E and T are the pre-exponential factor, the activation energy and the annealing temperature respectively and k_B is the Boltzmann constant. The calculated values of D_0 and the activation energy E are $5 \times 10^{-18 \pm 1} \text{ m}^2 \text{ s}^{-1}$ and $(0.38 \pm 0.05) \text{ eV}$, respectively.

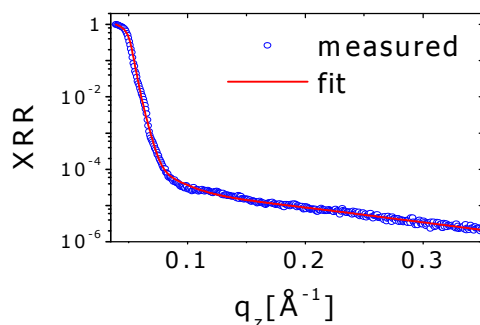


Fig.1: X-ray reflectivity pattern measured using Cu-K α X-rays and standard θ - 2θ geometry of the [FeZr (9 nm)/⁵⁷FeZr(5 nm)]₂₀ ML.

Self-diffusion measurements in an a -ML [Fe₆₇Zr₃₃ (3 nm)/⁵⁷Fe₆₇Zr₃₃(4 nm)]₁₀ prepared by ion-beam sputtering were also performed using nuclear resonance reflectivity (NRR) at ESRF [9]. Since the chemical composition of the alternate layers is identical, there is no contrast due to the electronic scattering, and the only contrast comes due to different number density of ⁵⁷Fe nuclei. Around the nuclear resonance, the nuclear contrast strongly depends upon the energy of the incident photon. The reflectivity of the ML can be calculated using Parratt's formalism [10], by coherently summing the reflected amplitudes over the energy width of the incident radiation [11]. It is interesting to see that the values of E and D_0 obtained with NR and NRR are similar within experimental errors (Fig.

2b). There has been a lot of discussion in the literature regarding the effect of preparation techniques on the diffusivity. For example, in a number of studies [12,13] diffusivity of a number of impurities like Au, Cu, Fe, Ti has been measured for *a*-films of NiZr produced by co-evaporation. In these films no variation of the diffusivity was observed with structural relaxation. The authors attributed this to the fact that the evaporation produced well relaxed samples. Further, Faupel *et al* [14,15] found a significant isotope effect in the diffusivity of Co in melt-spun *a*-Co_{76.7}Fe₂Nb_{14.3}B₇ while in sputter deposited *a*-Co₅₁Zr₄₉ no isotope effect was observed. This difference was again attributed to a difference in the structure of as prepared melt-spun and sputter deposited *a*-alloy. In this context it is interesting to observe that, the films produced by two different techniques, namely magnetron sputtering and ion beam sputtering have similar diffusivity, suggesting that they are similar in structure.

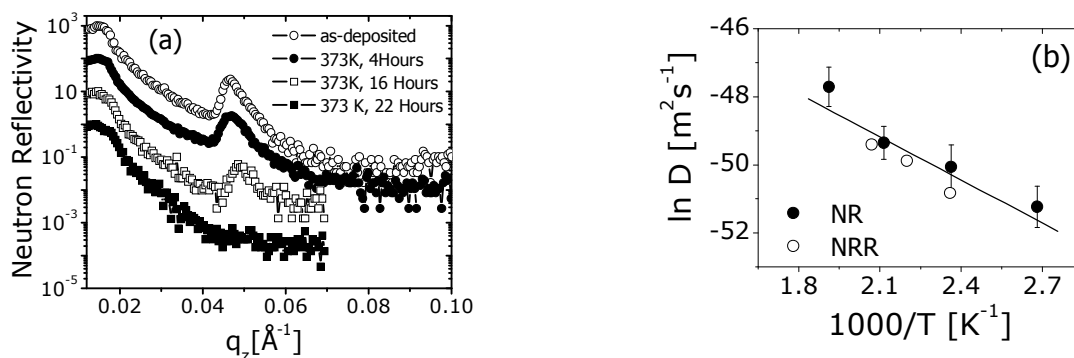


Fig.2: NR pattern in the as-deposited state and after annealing at 373 K for different periods of time (a). Arrhenius behaviour of the diffusivity measured with NR and NRR (b). The solid circles represent the diffusivity measured with NR and open circles with NRR.

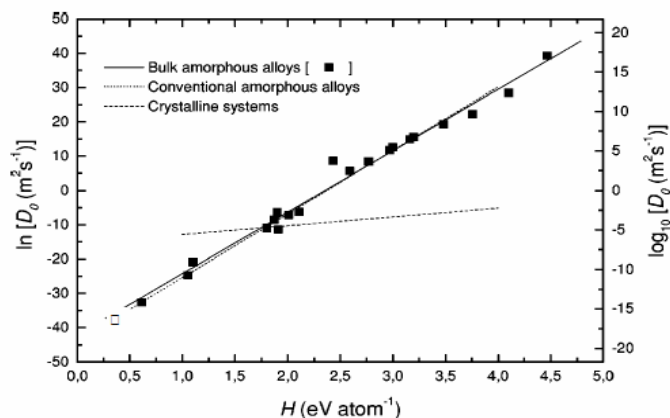


Fig.3: Correlation between D_0 and E for amorphous and crystalline alloys (taken from [1]). The open square (\square) corresponds to the present study.

On the other hand, the values obtained in the present case follow the well-known correlation between D_0 and E for self and impurity diffusion in conventional and bulk *a*-alloys [16,17]. This relationship has a universal character as it has been observed not only for self and impurity diffusion in *a*-alloys but also in nanocrystalline and crystalline alloys [17]. The relationship between D_0 and E is known as isokinetic relation and is given by [18]: $\ln D_0 = \ln A + E/B$, Where A and B are constants. Taking the data point from the present study and comparing it with the studies done on bulk *a*-alloys (Fig. 3) the values for A and B are equal to 2×10^{-20} and 0.056, respectively, which are very close to the values obtained for diffusion in *a*-alloys and interdiffusion in chemically inhomogeneous metallic ML. With the values obtained from isokinetic relation, the entropy term for diffusion can be calculated [19]. The entropy term ΔS for the present sample would be about $7k_B$, which is much smaller as compared to bulk *a*-alloys (20-60 k_B) and close to the value obtained for

interdiffusion in chemically inhomogeneous ML. This value would roughly correspond to a cluster of about 7 atoms taking part in diffusion, which is considerably smaller as compared with bulk α -alloys. This would mean that diffusion in the CHM is not highly collective but involves a relatively small group of atoms, indicating a much faster diffusion as compared with that of bulk α -alloys.

3.2 Effect of compressive stress in nano-composite $\text{Fe}_{75}\text{Zr}_{25}/^{57}\text{Fe}_{75}\text{Zr}_{25}$ ML: In order to get further insight into the diffusion mechanism in the CHM, structures with different applied stresses were prepared [20]. It is known that pressure/stress dependence of diffusivity is the key for determination of the associated diffusion mechanism [21]. For the case when diffusion takes place via defects in thermal equilibrium, one expects an activation volume of the order of the size of a defect i.e. one atomic volume for a single jump vacancy diffusion. For a diffusion process without thermally generated defects, the activation volume should be nearly vanishing [22]. The ML with nominal structures $[\text{Fe}_{75}\text{Zr}_{25}(25 \text{ nm})/^{57}\text{Fe}_{75}\text{Zr}_{25}(12 \text{ nm})]_{10}$ were deposited on Si (100) substrates which are bent to different curvatures using a 3 point bending device, during deposition. A release of bending causes a uniaxial compressive stress in the deposited ML. The self-diffusion of iron in these ML has been studied by annealing all the ML together in the temperature range of 373–533 K, where a nano-composite structure is formed. The decay of the intensity at the Bragg peak positions was measured as a function of annealing time and temperature. Fig 4 shows a typical decay of the Bragg peak intensity for a sample prepared without any stress and with an applied stress of 46 GPa. In all the samples the logarithm of diffusivity and inverse of temperature follows the Arrhenius type behaviour giving E and D_0 for diffusion.

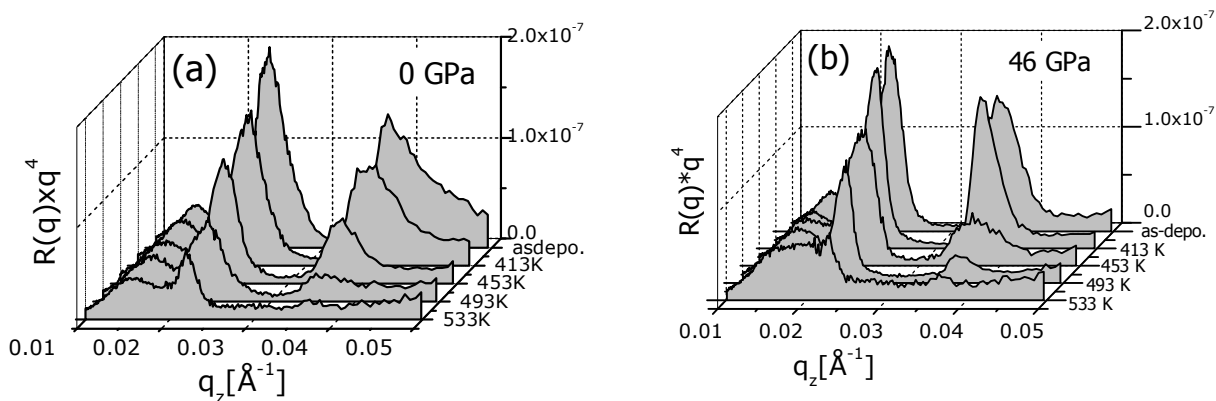


Fig.4: NR pattern of the $[\text{Fe}_{70}\text{Zr}_{30}(10\text{nm})/^{57}\text{Fe}_{70}\text{Zr}_{30}(20 \text{ nm})]_{10}$ ML prepared without any applied stress (a) and with an applied stress of 56 GPa (b) as a function of annealing time at 473 K.

The activation energy without any applied stress was found to be 0.25 eV, while with an applied uniaxial stress of 27 and 46 GPa it increases to 0.31 and 0.51 eV, respectively (Fig.5 a). It may be noted that for a highly collective diffusion mechanism the activation volume available for diffusion should be vanishing or close to zero. Our results clearly indicate a significant variation in the activation energy with the applied stress. Since the stress applied in the present case is only uniaxial, the exact values of activation volume could not be computed. However qualitatively, the measurements indicated a non vanishing activation volume. As it is evident from the results obtained with isokinetic relation, the diffusion mechanism in the chemically homogeneous ML is not highly collective and involves only a small group of atoms, thus a non vanishing activation volume as obtained with uniaxial stress dependence is not surprising.

3.3 a, $n\text{-Fe}_{85}\text{Zr}_{15}/^{57}\text{Fe}_{85}\text{Zr}_{15}$ ML: Self-diffusion of iron ^{57}Fe was also studied in $\text{Fe}_{85}\text{Zr}_{15}$ alloy deposited by ion-beam sputtering. It was found that the crystallization of the amorphous film starts at relatively low temperatures and occurs in two steps, in the first step which starts at 473 K, bcc-Fe precipitates out and a nano-composite phase is formed. The microstructure of the system consists of nanocrystalline grains of average size 12 nm, embedded in the grain boundary region of the remaining amorphous phase. In the second step at 673K, the remaining amorphous phase transforms

into Fe_2Zr . The self-diffusion measurements of iron in the n -state and in the parent a -state has been carried out using SIMS depth profiling and NR techniques, respectively. Fig. 5(b) shows the measured values of the diffusivity in the n - and parent a -state. It is interesting to note that even in the amorphous phase the diffusivity lies along the same line as that for the diffusion in the n -state which means that in the present case the, *diffusivity in the n -state is similar to that in the parent a -state* [23]. This is in contrast to the situation found in finemet type $n\text{-Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy, in which Fe self-diffusion shows an enhancement over that in the parent a -state by a factor as high as 14 [24,25]. The enhanced diffusivity in the n -state has been attributed to rapid Fe diffusion in the FeSi nanocrystals. Though Fe diffusivity in the FeSi nanocrystals is a few orders of magnitude higher than that in the a -phase, the fact that the nanocrystals are separated from each other by the grain boundary phase and thus do not form a connected path, makes the diffusivity in the nanocomposite to be limited by the diffusivity in the a -grain boundary phase. In the present case, the nanocrystals consist of bcc-Fe in which the volume diffusion is orders of magnitude lower than that in the $a\text{-Fe}_{85}\text{Zr}_{15}$. This information combined with the fact that the grain boundary region forms a percolating path through the sample, implies that atomic diffusion in $n\text{-Fe}_{85}\text{Zr}_{15}$ should occur exclusively through the amorphous grain boundaries. This conjecture is supported by the fact that the diffusivity in a -phase is similar to that in the $n\text{-Fe}_{85}\text{Zr}_{15}$.

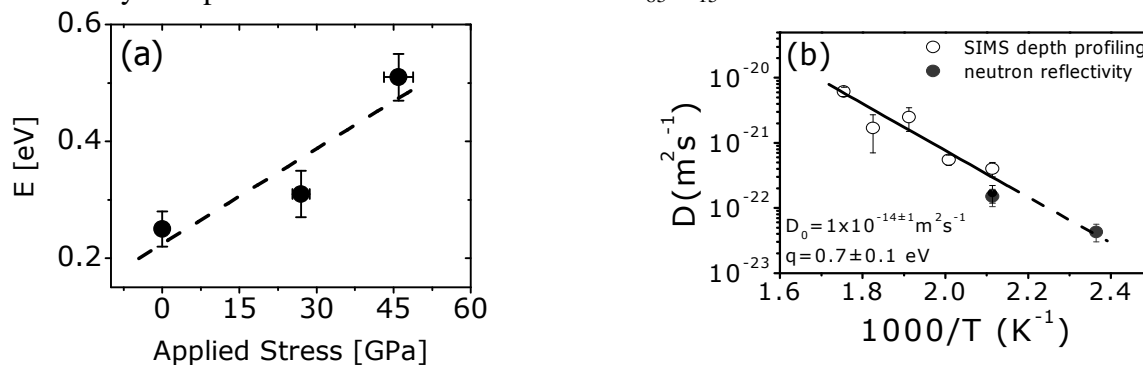


Fig. 5: Variation of activation energy with the applied stress. The dashed line is a guide to the eye (a). Arrhenius behaviour diffusivity in $\text{Fe}_{85}\text{Zr}_{15}$ alloy obtained with SIMS and NR measurements (b). The straight line represents a fit to the data in the n -state and the dashed line show an extrapolation for the parent a -phase.

4 Summary

It has been found that iron self-diffusion in $a\text{-Fe}_{67}\text{Zr}_{33}$ alloy is significantly different as compared with bulk a -alloys. A collective diffusion mechanism governs diffusion in a -alloys, while in the case of CHM a diffusion mechanism involving rather a small number of atoms was observed. In case of $n\text{-Fe}_{85}\text{Zr}_{15}$ alloy, it was found that diffusion occur exclusively through the grain boundary region, in contrast to the mechanism of atomic diffusion in another n - alloy of similar class- $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$, where $n\text{-FeSi}$ grains provide a fast diffusion path and therefore, an enhancement of diffusivity takes place on nano crystallization. The mechanism of the diffusion in this case was found similar to that in compacted n -metals.

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