Microstructural evolution of ion-beam-mixed Al-Fe multilayers for the formation of quasicrystalline or amorphous homogeneous alloys

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Al and Fe multilayers thermally evaporated on sapphire substrates have been mixed by irradiation with 800-keV Xe⁺ ions at two different temperatures (liquid-nitrogen temperature and 493 K) and with fluences ranging from 2×10^{15} to 3×10^{16} ions/cm². The structural evolution of the irradiated samples has been followed using complementary characterization techniques such as transmission electron microscopy and conversion-electron Mössbauer spectroscopy. Homogeneous amorphous or quasicrystal-line phases are obtained at doses of 3×10^{16} ions/cm² at 77 K or 8×10^{15} ions/cm² at 493 K, respectively. Different evolutions with ion dose are observed in both cases involving combinations of various sites that tend to final states with dominant local environments characteristic of amorphous or quasicrystalline phases.

I. INTRODUCTION

Since the discovery by Schechtman $et al.^1$ of the icosahedral phase in a rapidly quenched $Al_{86}Mn_{14}$ sample, various alloys,²⁻⁶ preparation techniques (sputter-ing,^{7,8} ion-beam mixing,^{9,10} solid-state diffusion,^{11,12}...) and structural studies^{13,14} have been developed in order to study the phase. These alloys exhibit a long orientational order giving rise to sharp diffraction patterns, but they lack periodic translational order. In particular, Al-transition-metal (TM) alloys have been intensively studied.^{15,16} The composition of this phase has been determined in the range of about 20 at. % TM. One of the basic problems that needs to be answered is whether icosahedral symmetry induces any special and distinctive features in the physical properties of quasicrystals. Furthermore, since quasicrystals may be regarded as materials situated between regular crystals and completely disorder systems, their fundamental physical properties are expected to exhibit exotic features found neither in crystalline nor in amorphous materials. In previous works, we studied optical, electrical, and magnetic properties of AlMn (Refs. 17 and 18) and AlFe (Ref. 19) homogeneous quasicrystalline or amorphous alloys prepared by ion beam mixing. These properties are probably much influenced by the local environment of the TM atoms. The first ⁵⁷Fe Mössbauer spectroscopy experiments on icosahedral alloys with the composition $Al_6(Mn_{0.85}Fe_{0.15})_{1.03}$ performed by Swartzendruber et al.²⁰ confirmed this assertion. In our case, we have chosen to study by careful microstructural analysis, sim-

ply binary AlFe alloys to complete our previous works on phase properties. In this context, the capability of local environment study of conversion-electron Mössbauer spectroscopy (CEMS) is interesting using ⁵⁷Fe atoms as a local probe. Samples were prepared by ion beam mixing as it has been first reported by Knapp and Follstaedt,⁵ which allows us to obtain amorphous or quasicrystalline single-phase samples for the same concentration at well determined irradiation temperatures and doses. Careful study of phase formation as a function of ion dose with respect to the ion-beam mixing process was performed to underline the microstructural evolution of AlFe alloys using complementary CEMS and transmission electron microscopy (TEM) measurements. The investigation of local order and long-range effects from the early stage of mixing at the interfaces in the multilayer to the final homogeneous phase is reported and discussed with regards to the specific properties of the formed alloys.

II. EXPERIMENTAL PROCEDURE

The original Al-Fe multilayers were deposited by thermal evaporation on sapphire and NaCl substrates at room temperature under ultrahigh vacuum conditions. The deposits investigated here were of three bilayers with a thickness of 29 nm for Al and about 4.5 nm for Fe, giving a total thickness of the film of about 100 nm. Aluminum, which presents a better behavior than iron facing oxidation, was always at the top of the stacks. Thicknesses mentioned above were adjusted to obtain the desired composition: $Al_{82}Fe_{18}$. The thickness of the films is first measured during evaporation with an in situ quartz oscillator system and after using Rutherford backscattering spectrometry (RBS) with 2 MeV α particles. The stacks were then submitted to irradiation with a 800 keV Xe⁺-ion beam to fluences ranging from 3×10^{14} to 3×10^{16} ions/cm². Taking into account our experimental conditions, the mean range of the Xe⁺ ions in the samples (multilayer+substrate) is about 180 nm, which means that they are implanted in the substrate. That avoids any contamination of the metallic alloy by the rare gas atoms. The compositions before and after mixing, the impurity contents and the mixing efficiencies were checked using RBS analysis. The mixing temperature was 77 or 493 K depending on the nature (amorphous or quasicrystalline, respectively) of the phase to synthesize. After irradiation, the metallic films on NaCl substrates were floated off allowing the observation of these films in a Philips EM 300 transmission electron microscope. The samples on sapphire substrates were used for the studies by CEMS. In this case, the CEMS spectra were recorded at room temperature using a helium-flow proportional counter in which the sample was placed in backscattering geometry (i.e., the γ rays were at normal incidence). The Mössbauer source was a 100-mCi ⁵⁷Co in a rhodium matrix mounted on a constant acceleration triangular motion velocity transducer. The velocity scale and all the data are referred to a metallic iron absorber at room temperature. CEMS probes only the surface layer of the samples, at the depth of about 100-150 nm, which is well adapted to our experiments. It is very sensitive to the local environment of the iron probe with a content of resonant isotope (⁵⁷Fe) as low as $\sim 10^{15}$ ⁵⁷Fe/cm² (equivalent to ~ 1 monolayer). In our case, the use of natural iron in the multilayers, the enrichment of which with ⁵⁷Fe isotope is about 2% was convenient for the CEMS studies. A standard least-squares minimization routine was used to fit the Mössbauer spectra assuming Lorentzian shape for the lines in order to determine the hyperfine parameters such as isomer shifts (IS) and quadrupole splittings (QS). However, for the alloys obtained by ion-beam mixing, the use of discrete components to fit the Mössbauer spectra is not completely satisfying taking into account the iron site distribution and the irradiation defects. The broadening of the lines composing the Mössbauer spectra confirms this assertion. For these reasons, the spectra were fitted in a second step using a method which takes into account hyperfine parameter distributions around their mean values, deduced from the first fitting method. The calculation code developed by Lecaer and Dubois²¹ from the method elaborated by Hesse and Rubartsch²² has been used. This program assumes a linear relation between IS and QS (IS = α QS + IS₀, where IS₀ is taken as the mean value found by the first adjusting method) and a distribution of quadrupole splittings P(QS).

III. RESULTS

Figures 1 and 2 show the CEMS spectra obtained with samples irradiated at 77 and 493 K, respectively, with ion doses ranging from 3×10^{14} to 3×10^{16} ions/cm². The

quadrupole splitting distributions P(QS) obtained from the fit using Lecaer method mentioned previously (Sec. II) corresponding to each spectrum are also presented. The hyperfine parameters characteristic of the distributions are given in Table I for all samples studied. Figure 3 shows the electron diffraction patterns obtained with samples mixed at 77 and 493 K with the lowest and the highest ion doses for which a single phase is observed.

From the usual description of the mixing processes,²³⁻²⁵ two stages can be identified: a ballistic stage which is athermal and which can be described using pure collisional models like the TRIM code,²⁶ followed by a temperature-dependent diffusional stage enhanced by the presence of high concentrations of irradiation defects. In our experiments, a first measurement at a very low dose $(3 \times 10^{14} \text{ ions/cm}^2, \text{ Fig. 16})$ has been performed at 77 K to underline the first stage of the ion-beam mixing process, especially the ballistic stage which could be the only one efficient at this low temperature. The corresponding CEMS spectrum in Fig. 1(b) is described by the superposition of two components: the characteristic sextet of metallic iron and a quadrupole doublet due to an Al-Fe alloy. That means that for such a low mixing dose the multilayer structure is conserved and only interfacial regions have been mixed. By evaluating the relative surface of each component, it is possible to estimate the iron fraction which has been mixed: we found about 15% of the total iron quantity $(1.14 \times 10^{17} \text{ Fe atoms/cm}^2)$ has been ion-beam fixed at this step; whereas the TRIM ballistic simulation gives 13%. Note that the RBS analysis²⁷ corresponding to this mixing step confirms that the multilayer is not yet completely homogenized.

The disappearance of the magnetic sextet due to pure metallic iron and the complete appearance of the characteristic doublet due to a paramagnetic phase are observed in CEMS spectra of Figs. 1(c) and 2(a) corresponding to samples mixed with 2×10^{15} Ke⁺/cm² at 77 and 493 K, respectively. However, the TEM diffraction patterns obtained at the same stage [Figs. 3(a) and 3(c)] show a mixture of different intermediate phases such as the F phase identified by Knapp and Follstaedt⁹ in AlMn alloys. Note also that the quadrupole splitting distributions [Figs. 1(c') and 2(a')] are rather different for the two samples. For irradiation at 77 K the QS distribution exhibits three more probable sites (see QS values in Table I), whereas at 493 K, two dominant sites appear at different QS values.

These results emphasize the difference microstructures obtained as a function of temperature. With increasing ion doses, these sites subsist for samples irradiated at low temperature but their relative intensities are modified as it is shown in Figs. 1(d') 1(e'), 1(f') and Table I, up to the final stage when the homogeneous amorphous phase is obtained [Figs. 1(f') and 3(b)]. For samples irradiated at high temperature, the QS distribution tends to a unique site which is well observable in Fig. 2(d') corresponding to the highest dose $(8 \times 10^{15} \text{ ions/cm}^2)$. TEM measurements indicate that an quasicrystalline phase is obtained at 493 K for a dose of $6 \times 10^{15} \text{ ions/cm}^2$, but the double ring in the electron diffraction pattern characteristic of the icosahedral phase is not well resolved at this stage. A

better resolution is observed for a dose of 8×10^{15} ions/cm² [Fig. 3(d)]. Concurrently the width of the corresponding quadrupole splitting distributions decreases, in a good agreement with the TEM observations. Finally, for irradiation at 77 K, the homogeneous amorphous phase is obtained for a dose of 3×10^{16} ions/cm² with a corresponding quadrupole splitting distribution exhibiting a dominant site among three sites. We observe a different local environment of the transition metal in the homogeneous quasicrystalline phase obtained at 493 K for a mixing dose of 8×10^{15} ions/cm².

IV. DISCUSSION AND CONCLUSION

Our results show that there exists a difference between spatial homogenization emphasized by RBS²⁷ analysis and homogeneous nature of the obtained phase. In fact, the complete mixing at low temperature of Al and Fe atoms is deduced from the RBS measurements for a dose of $10^{16} \text{ Xe}^+/\text{cm}^2$ while a dose of $3 \times 10^{16} \text{ ions/cm}^2$ is necessary to synthesize a homogeneous amorphous phase (as confirmed by CEMS and TEM analysis). These results concerning diffusion under irradiation at low tem-



Velocity (mm/s)



FIG. 1. CEMS spectra obtained (a) with an Al¹⁸²Fe¹⁸ sample before mixing and (b) after mixing at 77 K with a dose of 3×10^{14} , (c) 2×10^{15} , (d) 5×10^{15} , (e) 1×10^{16} , and (f) 3×10^{16} Xe⁺/cm². The RBS spectrum measured after the mixing stage at 3×10^{14} Xe⁺/cm² is reported in (b'). The quadrupole splitting distributions *P*(QS) deduced from the fits of the spectra (c), (d), (e), and (f) are reported in (c'), (d'), (e'), and (f'), respectively. Parameter α which allows to describe the linear relation between IS and QS (see Sec. II) is indicated on *P*(QS) diagram.



FIG. 2. CEMS spectra obtained with an $Al_{82}Fe_{18}$ sample after mixing at 493 K with a dose of (a) 2×10^{15} , (b) 4×10^{15} , (c) 5×10^{15} , (d) 6×10^{15} , and (e) $8 \times 10^{15} \text{ Xe}^+/\text{cm}^2$. The quadrupole splitting distributions *P*(QS) deduced from the fits of the spectra (a), (b), (c), and (d) are reported in (a'), (b'), (c'), and (e'), respectively.

perature can be analyzed using the temperatureindependent model proposed by Johnson,²⁸ taking into account the chemical affinities between the different species. When the energy density ε in the cascade is high enough (which is the case of our experiments: $\varepsilon = 2.15$ keV/nm obtained from TRIM calculations²⁶), it becomes possible to use the thermal spike concept²³ to determine the mixing efficiency. A large number of metallic systems have given an experimental support²⁹ of this approach. For our Al₂₈Fe₁₈ alloys, using the heat of mixing (ΔH_m) and the cohesive energy (ΔH_{coh}) of the order of -28kJ mol⁻¹ and -340 kJ mol⁻¹, respectively, we obtain a diffusion length of about 9.8 nm for a dose of 10¹⁶ Xe⁺/cm². This value is coherent with the characteristic

lengths to cover in our multilayers to reach the complete homogenization. However, as mentioned previously, the corresponding dose of $1 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ is in agreement with the homogenization at the RBS point of view. At this stage crystalline phases are still observed and the homogeneous amorphous phase appears at higher dose $(3 \times 10^{16} \text{ Xe}^+/\text{cm}^2)$. For $3 \times 10^{16} \text{ Xe}^+/\text{cm}^2$, a much larger diffusion length of 17 nm is obtained.

Concerning the phase formation, using the very sensitive CEMS method to the local order, different behavior have been observed with respect to the temperature of irradiation: a single more probable site appears in the quasicrystalline phase, probably characteristic of the icosahedral symmetry, while three more probable sites

TABLE I. Characteristic parameters deduced from the fits of the CEMS spectra.

| $\frac{\text{Mixing dose}}{(Xe^+/cm^2)}$ | Mixing temperature 77 K | Corresponding CEMS spectrum and QS distribution Figs. 1(c),1(c') | Position of characteristic site on the QS distribution (mm/s) ^a | | | Relative intensity for each site (%) | | |
|--|-------------------------------|---|--|-------|------|--|----|-------|
| | | | 0.19 | 0.42 | 0.76 | 18 | 66 | 16 |
| 5×10^{15} | | Figs. 1(d),1(d') | 0.23 | 0.49 | 0.83 | 35 | 58 | 7 |
| 1×10^{16} | | Figs. 1(e),1(e') | 0.31 | 0.59 | 0.95 | 33 | 61 | 6 |
| 3×10^{16} | | Figs. $1(f), 1(f')$ | 0.16 | 0.47 | 0.81 | 8 | 80 | 12 |
| 2×10^{15} | 493 K | Figs. 2(a),2(a') | 0.25 | 0.46 | 0.96 | 37 | 57 | 6 |
| 4×10^{15} | | Figs. $2(b), 2(b')$ | 0.25 | 0.44 | 0.78 | 34 | 59 | 7 |
| 6×10^{15} | | Figs. $2(c), 2(c')$ | 0.30 | 0.45 | | 69 | 31 | |
| 8×10^{15} | | Figs. 2(d),2(d') | 0.32 | • • • | | 100 | | • • • |



8x1015 Xe+/cm²



FIG. 3. TEM diffraction patterns obtains for samples irradiated at 77 K with doses of (a) 2×10^{15} (b) 3×10^{16} Ke⁺/cm² and at 493 K with doses of (c) 2×10^{15} and (d) 8×10^{15} Ke⁺/cm². Rings corresponding to different phases are identified: Aluminum (---), iron (\rightarrow), F phase (-), and icosahedral phase (I).

exist in the amorphous phase. These different environments of the iron atoms in the amorphous phase and the quasicrystalline one are probably at the origin of the different transport properties reported elsewhere²⁷: different electronic structures are deduced from optical spectra as well as different magnetic behaviors deduced from magnetoresistance measurements at low temperature.

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