Chemical effects in ion beam mixing of Fe-Al multilayers

R. Brenier, B. Canut, L. Gea, S. Ramos, P. Thevenard, C. Dubois, J. Dupuy,
G. Prudon, M. Brunel

► To cite this version:

R. Brenier, B. Canut, L. Gea, S. Ramos, P. Thevenard, et al.. Chemical effects in ion beam mixing of Fe-Al multilayers. Journal de Physique IV Proceedings, 1994, 04 (C3), pp.C3-263-C3-271. 10.1051/jp4:1994336 . jpa-00252533

HAL Id: jpa-00252533

<https://hal.science/jpa-00252533>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chemical effects in ion beam mixing of Fe-Al multilayers

R. BRENIER, B. CANUT, L. GEA, S.M.M. RAMOS, P. THEVENARD, C. DUBOIS*, J.C. DUPUY*, G. PRUDON* and M. BRUNEL**

Université Claude Bernard Lyon I, Département de Physique des Matériaux, URA 172 du CNRS, 69622 Villeurbanne cedex, France

** Laboratoire de Physique de la Matière, I.N.S.A., 20 Avenue Albert Einstein, 69621 Villeurbanne cedex, France*

*** Laboratoire de Cristallographie, C.N.R.S., 25 Avenue des Martyrs, BP. 166 X, 38042 Grenoble cedex, France*

ABSTRACT

Fe-Al multilayers have been mixed with Xe^+ ions at high temperatures. The composition depth profiles have been analyzed by secondary ion mass spectroscopy (SIMS). It is shown that SIMS reveals the Al-rich compound formation inside the initial Al layers, and that this point cannot be questioned by exaltation effect on Fe^+ or Al^+ ion intensities. Phase formation has been proved by X-ray diffraction at grazing incidence.

Introduction

The mechanisms of ion beam mixing (IBM) have widely been investigated since 10 years (1). Three contributions are believed to induce the redistribution of the target atoms : binary collisions, dense cascade collisions sometimes considered as thermal spikes, and radiation enhanced diffusion (RED). RED is efficient if the temperature is not too low ($T \geq 300$ K) and is guided by chemical potential gradients. At low temperature, binary collisions well describe the interaction of light ions with matter whereas thermal spike models are more suitable to reproduce the effects of heavy ions crossing a target of heavy atoms ($Z \approx 60$). In this last case it has been shown that the thermodynamic properties of the target such as the cohesive energy ΔE_c and the mixing enthalpy ΔH_m can greatly influence the mixing process (2) (3). Nevertheless when the atomic number of the target atoms is lower ($Z \sim 30-40$) the correlation between the mixing efficiency and the thermodynamic parameters is less accurate (4). Moreover for some low- Z metals ($Z \sim 20$) the correlation is quite questionable (5). The Fe-Al system belongs to this last category and the previous measurements of the mixing efficiency show some dispersion confirming that it is a borderline case (6, 7, 8).

In this context we have undertaken experiments to try to get evidence of chemical effects in IBM of Fe-Al multilayers ($Z \approx 20$) at different temperatures. The preliminary results presented here concerns mixing at temperatures higher than 300 K since chemical effects via RED undoubtedly exist.

Then our purpose is to test a promising but difficult method : analyzing the composition profile in irradiated Fe-Al multilayers by secondary ion mass spectroscopy (SIMS). Indeed SIMS has the advantage of high sensibility and depth resolution (9) but the drawback of matrix effects (10). Then the relation composition-ion intensities depth profiles has to be well understood. Our experiments consist in mixing Fe-Al multilayer of Al rich global composition able to lead to metastable phases such quasi-crystals (11 - 12). The Fe^+ and Al^+ ion intensity depth profile measured by SIMS are fitted using empirical exaltation coefficients and correlated to the phase formation studied by X-ray diffraction at grazing incidence.

Experiments

Multilayers composed of 3 Fe layers alternated with 3 Al layers were deposited by electron-gun evaporation onto optically polished sapphire substrate, in an oil-free vacuum system (10^{-8} torr). The top layer was of Al type. The film thicknesses were controlled in situ by a quartz micro-balance.

Ion beam mixing was performed using 800 keV Xe^+ ions. One sample series was irradiated at 220°C temperature at a fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ and a second one was irradiated at 370°C at a fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$.

The elemental composition and the layers thicknesses were measured by Rutherford backscattering spectrometry of 2 MeV alpha particles. The composition profiles were analyzed by SIMS using O_2^+ ions under an oxygen flooding at a saturation pressure of 10^{-5} torr. The phases present in the samples before and after mixing were identified by X-ray diffraction at grazing incidence of 0.5° , using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$).

Results

• As-deposited multilayers

The RBS spectrum of the as-deposited sample is shown in figure 1.a. From this spectrum the thickness of each Al layer can be evaluated to 35 nm. The 1st Fe layer has a thickness of 4 nm, and the 2 others, 5 nm. Moreover a pollution of the sample by a small amount of Cu is apparent. Therefore the global composition of the multilayers is $\text{Al}_{83}\text{Fe}_{16}\text{Cu}_1$.

In SIMS analysis (figure 2.a.) the $^{56}\text{Fe}^+$ and $^{27}\text{Al}^+$ intensities show all the individual layers. Indeed the depth resolution is about 7 nm (1). The phase identification is deduced from the X-ray diffraction pattern given in figure 3.a.. Fcc - Al and bcc - Fe are the only phases present in the sample. All layers are textured since some intense peaks are absent of the spectrum.

• Irradiated multilayers

After mixing at 220°C or 370°C , the RBS spectra (figure 1. b, c) indicate that interdiffusion has occurred in the samples. However only the SIMS technique has a high enough depth resolution to show that the multilayer have not been entirely homogenized (figure 2. b, c). The total sputtering time in spectra (b) and (c) is shorter than it is in spectrum (a) due to the differences in the primary ion intensity and in the transmittance of the spectrometer. Indeed the multilayer mixed at 220°C at the fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ presents 8 maxima on the $^{56}\text{Fe}^+$ signal in phase coincidence with 8 minima on the Al^+ signal. The relative amplitude of the modulation of the Fe^+ intensity is about 50 %. The X-ray diffraction pattern is shown in figure 3.b.. Several compounds have been formed : quasi-crystals, Al_5Fe_2 and $\text{Al}_{13}\text{Fe}_4$. the fcc phase of Al is still present in the sample.

In the multilayer irradiated at 370°C at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ the Fe^+ and Al^+ intensities show the same modulation as for mixing at 220°C at the fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$, with a lower amplitude vanishing close to the substrate. So this last region has a rather flat composition profile $\text{Fe}_{16}\text{Al}_{83}$. X-ray diffraction have not yet been performed so the phases formed are still unknown in this sample.

Discussion and conclusion

The problem is to explain the surprising number of extrema of Fe^+ (or Al^+) intensity profiles in the SIMS spectra of the mixed samples. The possible role of the main impurities Cu, O and C will first be discussed. The RBS spectra (figure 1) show that the C and O contents inside the films are lower than the sensitivity of this technique (≤ 1 at. %). Indeed this low level due to good vacuum during the metal deposition (10^{-8} torr) is not expected to have any effect in our results since Gaboriaud et al. (7) have found no difference in mixing measurements of Fe-Al multilayers evaporated in a vacuum of 5×10^{-7} or 10^{-9} torr. As well the effect of 1 at. % Cu on the interdiffusion of the main species Fe and Al is likely negligible. Concerning exaltation effects in SIMS analysis, Cu and Fe have similar behavior in Al alloys (10), so that Cu is not believed to disturb our SIMS profiles. Then two hypothesis will be examined :

1. The undulated intensity profile strictly traces the composition profile (no matrix effect in SIMS analysis). Since in the multilayer mixed at 220°C at the fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ the formation of compounds has been proved by X-ray diffraction, the compounds necessarily form inside the Al layers by Fe diffusion from initial Fe layers. So that an Fe peak ($\text{N}^\circ 1$ in figure 2.b.) is between 2 satellites ($1'$ and $1''$ in figure 2.b.). Such a compound precipitation in Al can be understood since no solid solution of Fe in Al exists in the Al-rich side of the equilibrium phase diagram. In a similar way compound precipitation could have occurred in the multilayer mixed at 370°C at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$. This last point is presently under investigation.

2. The composition profile presents only 3 Fe content maxima centered on the initial Fe layers, the extra maxima being due to matrix effects in SIMS analysis.

In the case where compound formation has been proved, the compounds are supposed to be distributed in the sample so that the Fe content monotonically decrease from initial Fe rich zone to Al rich zone without maxima. Thus we look for a matrix effect responsible for the extra maxima on Fe^+ intensity profiles.

Matrix effects in SIMS analysis have been investigated by J.L. SERAN, in the Fe-Al system, using Ar^+ primary ions under an oxygen flooding at saturation pressure (10). These conditions are closed to ours except that O_2^+ ions were used in our case.

The exaltation coefficient of Fe^+ ions in the $\text{Fe}_x\text{Al}_{1-x}$ alloy is defined as a function of x by :

$$\rho_{\text{Fe}}(x) = \frac{I_{\text{Fe}}(x)}{x I_{\text{Fe}}(x=1)} \quad [1]$$

where $I_{\text{Fe}}(x)$ is the intensity of Fe^+ ions sputtered from the $\text{Fe}_x\text{Al}_{1-x}$ alloy by the Ar^+ beam.

The measurements of $\rho_{\text{Fe}}(x)$ by SERAN in the range $0.6 < x < 1$ have been reported in figure 4.a.. Values for $0 < x < 0.6$ are "raisonnable" extrapolations supposing that a saturation effect occurs at low Fe content, as it is the case for the exaltation coefficient of Cu in $\text{Al}_x\text{Cu}_{1-x}$ alloys for example (10). Relation [1] allows to calculate $I_{\text{Fe}}(x)$ for the entire composition range. This has been done in figure 4.b. with $I_{\text{Fe}}(x=1) = 1$ for simplification.

Let's apply such an exaltation effect to calculate the Fe^+ intensity depth profile resulting from a given concentration depth profile. In our present hypothesis the interdiffusion between Fe and Al initial layers lead to concentration profile rather well represented by a complementary error function. Such a profile is reported in figure 4.c. in the case where $x_{\text{max}} = 1$. The exaltation effect induces a shift in the maximum of the

curve. But such an effect disappears if $x_{\max} \leq 0.6$ (see figure 4.d.) as expected from $I_{Fe}(x)$ (figure 4.d.).

It is then concluded that matrix effects resulting from exaltation of Fe^+ intensity in a solid solution Fe_xAl_{1-x} as in SERAN work cannot explain our experimental SIMS spectra, for 2 reasons :

- In the sample mixed at 370°C at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ (figure 2), the concentration profile is closed to the global composition $x = 0.16$, so that matrix effects must be sensitive to Fe content as low as 16 %.

- For both mixed samples the I_{Fe} profile of an Fe peak in Al must contain 3 nearly equal maxima, and not only 2.

Let's try to look for a $\rho_{Fe}(x)$ function which could qualitatively fit the SIMS spectrum of the multilayer mixed at 370°C at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$. If matrix effects are responsible for the slight modulation of I_{Fe} the exaltation coefficient $\rho_{Fe}(x)$ has to be highly increased near $x = 0.16$. Such a coefficient is reported in figure 5.a.. The calculated Fe^+ intensity depth profile resulting from a concentration profile for $20 < x < 10$ is qualitatively in good agreement with the experimental situation (figure 5.b.).

The $\rho_{Fe}(x)$ function suitable to fit the Fe^+ intensity spectrum of the sample mixed at 220°C at the fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ (figure 2.a.) can be found in the same way and is given in figure 6.a..

The I_{Fe^+} profile (figure 6.b.) qualitatively well reproduce the measurement (figure 2.a.), supposing $0.05 < x < 0.6$ to fix ideas.

It is here necessary to look for the physical meaning of the fitted exaltation coefficient $\rho_{Fe}(x)$. The abrupt enhancement of $\rho_{Fe}(x)$ around $x = 0.16$ is coexisting with the decrease of the exaltation coefficient of $\rho_{Al}(x)$, since the maxima of I_{Fe^+} occur at the same sputtering times as the minima of I_{Al^+} in the SIMS spectra of the mixed samples (figure 2). So that around $x = 0.16$ the ionization probability of Fe atoms is enhanced while the one of Al atoms is reduced. Such an effect suggests a particular local environment of Fe and Al atoms. Therefore it seems reasonable to attribute the matrix effect to one or several compounds which have been observed by X-ray diffraction.

In Fe-Al alloys an electron transfer from Al to Fe is revealed by density of states calculations (13 - 14) in agreement with Pauling electronegativity scale. Such a charge transfer should favour Al against Fe ionization, in disagreement with our SIMS spectra. However this picture is certainly far too naïve since it does not take into account for the role of oxygen. Further investigations are necessary to better understand the origin of the matrix effect.

We can deduce that in the multilayer mixed at 370°C at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ the SIMS spectrum reveals the precipitation of a compound with electronic behaviour similar to the one found after mixing at 220°C.

In conclusion it has been shown that SIMS analysis of composition depth profiles in mixed Fe-Al multilayers reveals the formation of Al-rich compounds inside the initial Al layers. This point is not questioned even if matrix effects likely exist at low Fe content.

Acknowledgements

The authors are very grateful to Y. LIMOGE for fruitful comments on the subject discussed in this paper.

REFERENCES

- (1) Y.T. CHENG, S.J. SIMKO, M.C. MILITELLO, A.A. DOW, G.W. AUNER, M.H. ALKAISI and K.R. PADMANABHAN
Nucl. Instr. and Meth. in Phys. Res. B 64 (1992) p. 38.
- (2) T.W. WORKMAN, Y.T. CHENG, W.L. JOHNSON, M.A. NICOLET
Appl. Phys. Lett., 50 (21) (1987) p. 1485.
- (3) Y.T. CHENG, G.W. AUNER, M.M. ALKAISI, K.R. PADMANABHAN, M.M. KARMAKAR
Nucl. Inst. and Meth. in Phys. Res., B59/60 (1991) p. 509.
- (4) P. BORGESSEN, D.A. LILIENFELD, H.H. JOHNSON
Appl. Phys. Lett., 57 (14) (1990) p. 1407.
- (5) P. BORGESSEN, D.A. LILIENFELD, H.H. JOHNSON, T.L. ALFORD, R.E. WISTROM
J. Appl. Phys., 68 (3) (1990) p. 1364.
- (6) R.J. GABORIAUD, C. JAOUEN, J.J. GROB, A. GROB
Appl. Phys. A41 (1986) p. 127.
- (7) R.J. GABORIAUD, J.J. GROB, F. ABEL
Nucl. Instr. and Meth. in Phys. Res. B 19/20 (1987) p. 648.
- (8) M.A. VASCONCELLOS, J.A.T. BORGES da COSTA, W.H. SCHREINER, I.J.R. BAUMVOL
Appl. Phys. Lett., 55 (5) (1989) p. 513.
- (9) C. DUBOIS, J.C. DUPUY, G. PRUDON, P. PINARD, R. BRENIER, M.F. RAVET, M. PIECUCH, M. MAURER, J.F. BOBO
Proceeding of SIMS 8, 15 - 20 Sept. 91, Amsterdam (John WILEY and Sons) 1992.
- (10) J.L. SERAN
Thèse d'Etat, Université Paris-Sud, Centre d'Orsay (1979).
- (11) B.X. LIU, G.A. CHENG, C.H. SHANG
Phil. Mag. Lett., vol. 55 N° 6 (1987) p. 265.
- (12) J.C. PLENET, A. PEREZ, J. RIVORY, O. LABORDE
Phys. Rev. B, vol. 47 (1993) p. 3021.

- (13) E. BELIN, Z. DANKHAZI, A. SADO, Y. CALVAYRAC, T. KLEIN, J.M. DUBOIS
J. of Phys. Cond. Matter., 4 (1992) p. 4459.
- (14) C.L. FU, M.H. YOO
Mater. Chem. and Phys., 32 (1992) p. 25.

Figure 1 : R.B.S. spectra of the Fe-Al samples :

- a) as deposited
- b) mixed at the fluence of $0.8 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ at 220°C
- c) mixed at the fluence of $1.5 \times 10^{16} \text{ Xe}^+/\text{cm}^2$ at 370°C

Figure 2 : S.I.M.S. spectra spectra of the Fe-Al samples :

- a) as deposited
- b) mixed at the fluence of 0.8×10^{16} Xe⁺/cm² at 220°C
- c) mixed at the fluence of 1.5×10^{16} Xe⁺/cm² at 370°C

Figure 3 : X-ray diffraction patterns at the incidence angle of 0.5° :

- a) as deposited
- b) mixed at the fluence of 0.8×10^{16} Xe⁺/cm² at 220°C

Figure 4 : (a) Exaltation coefficient ρ_{Fe} following SERAN (7) in $\text{Fe}_x\text{Al}_{1-x}$ alloy.
 (b) Fe^+ intensity as a function of Fe content.
 (c) Resulting matrix effect on the analyse of a Fe content profile for $0 < x < 1$.
 (d) Resulting matrix effect on the analyse of a Fe content profile for $0 < x < 0.6$.

Figure 5 : (a) Exaltation coefficient ρ_{Fe} necessary to qualitatively reproduce the I_{Fe} intensity as in the experimental S.I.M.S. spectrum of the sample mixed at 370°C .
 (b) Resulting matrix effect on the analyse of a Fe content profile for $0.1 < x < 0.2$.

Figure 6 : (a) Exaltation coefficient ρ_{Fe} necessary to qualitatively reproduce the I_{Fe} intensity as in the experimental S.I.M.S. spectrum of the sample mixed at 220°C.

(b) Resulting matrix effect on the analyse of a Fe content profile for $0.05 < x < 0.6$.