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Fe-Ti metastable-phase formation by ion-beam mixing

R. Brenier, T. Capra, P. Thevenard, A. Perez, M. Treilleux, J. Rivory,
J. Dupuy, and G. Guiraud
Département de Physique des Matériaux, Université Claude Bernard (Lyon I), 43 boulevard du 11 Novembre 1918,
69622 Villeurbanne CEDEX, France

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The glass-forming ability of the Fe-Ti system by ion-beam mixing of multilayers at 300 K is investigated at three compositions: $Fe_{83}Ti_{17}$ (close to eutectic), and Fe_2Ti and FeTi (compositions of the equilibrium compounds). The formation of bcc $Fe_{83}Ti_{17}$ is shown whereas an amorphous state is obtained at Fe_2Ti and FeTi compositions. A good qualitative interpretation of the experimental results is given in the framework of metastable enthalpy curves and correlations with the equilibrium phase diagram are discussed. Rutherford-backscattering spectrometry of α particles has been used to characterize the mixing efficiency. X-ray diffraction at glancing incidence and conversion-electron Mössbauer spectroscopy have been performed to investigate the short-range order in the glassy state.

I. INTRODUCTION

The formation of Fe_xTi_{100-x} amorphous alloys has been investigated during these last few years with different success. Hirvonen *et al.*[1] have observed the formation of an amorphous single-phase state by ion-beam mixing (IBM) in the narrow compositional range ($\sim Fe_{50}Ti_{50}$) which seems to be the most favorable one with regard to thermodynamics. On the other hand, sputtering technique[2,3] gives amorphous phases within the range $25 \leq x \leq 80$ and bcc solid solutions outside this domain. All these phases have been widely characterized by x-ray diffraction and Mössbauer spectroscopy, and it can be useful to compare them to the IBM ones.

We have recently been able to obtain glassy alloys by IBM of Fe-Ti multilayers at 77 and 300 K in a wide compositional range ($29 \leq x \leq 67$).[4] The aim of the present paper is, on the one hand, to report series of experiments performed to study the glass-forming ability (GFA) of the Fe-Ti system by IBM at room temperature as a function of composition: $x = 83$ very close to an eutectic point and $x = 67$ and $x = 50$ compositions of the equilibrium compounds. In the last two cases we have followed the sequence of phase formation versus the irradiation dose. The role played by carbon and oxygen impurities from residual atmosphere and the influence of silicon contamination results from the possible mixing between the metallic layers and the silicon substrate are discussed. We make an attempt to interpret our results in the framework of the thermochemical properties of the observed metastable phases. On the other hand, we also discuss the chemical short-range order (CSRO) in the glassy state as it can be studied by conversion-electron Mössbauer spectroscopy (CEMS) and x-ray diffraction. Rutherford-backscattering spectrometry (RBS) of 2-MeV α particles has been used to measure the film compositions and irradiation doses. The detection angle of the α particles was 160°.

II. EXPERIMENTS

Iron and titaniuim multilayers of total thickness 200 nm have been deposited by electron-gun evaporation onto silicon substrate, under ultrahigh-vacuum conditions (10^{-9} Torr). The deposition rate (0.2 $nm\,s^{-1}$) and thickness of each film ($\sim$ 10 nm) were monitored by quartz oscillators. The RBS analysis for film control and the mixing process using 800-keV Xe^+ ions have been performed *in situ*. The fluence range extended from 0.8 to 3.6×10^{16} $Xe^+\,cm^{-2}$ with an ion flux of 3×10^{11} $Xe^+\,cm^{-2}\,s^{-1}$. The substrate temperature did not exceed 300 K during bombardment. Figure 1 shows the RBS spectra of the Fe_2Ti sample before and after mixing at a dose of

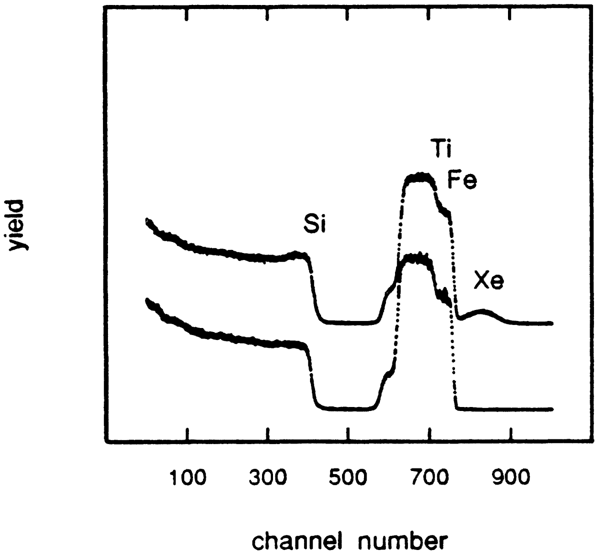

FIG. 1. RBS spectra of the Fe_2Ti sample before mixing (bottom spectrum) and after mixing at a dose of 1.7×10^{16} $Xe^+\,cm^{-2}$ (top spectrum).

TABLE I. Phases obtained after the different mixing doses for the three multilayer compositions studied.

Composition	Dose (10^{16} Xe^+ cm^{-2})	Phases
$Fe_{83}Ti_{17}$	1.7	bcc sol. sol. (91%)+α-Fe (9%)
Fe_2Ti	1	a-(Fe-Ti) (42%)+bcc sol. sol. (58%)
	1.7	a-(Fe-Ti) (75%)+bcc sol. sol. (25%)
	2.4	a-(Fe-Ti) (100%)
FeTi	0.8	a-(Fe-Ti)
	3.6	a-(Fe-Ti)

1.7×10^{16} Xe^+ cm^{-2}. The measured projected range of the xenon distribution is 120 nm so that the ballistic damage distribution is approximately centered in the middle of the multilayer.

X-ray diffraction patterns have been recorded using Cu $K\alpha$ radiation at glancing incident (2.5°). CEMS have been performed at room temperature using the helium flow proportional counter technique[5] and a ^{57}Co source in a rhodium host. Isomer shift values are given with respect to metallic iron at 300 K.

III. RESULTS

The phases identified after mixing are listed in Table I for the different compositions and irradiation doses.

The x-ray diffraction pattern of the Fe-richest sample ($Fe_{83}Ti_{17}$) in Fig. 2 shows the presence of a bcc solid solution with a lattice parameter $a_0=0.293$ nm. The main component (91%) of the Mössbauer spectrum (Fig. 3) is a wide-line sextet, so the hyperfine interaction between the ^{57}Fe nucleus and its environment is a magnetic one (Zeeman effect). Hence at room temperature the bcc $Fe_{83}Ti_{17}$ phase is magnetically ordered. The hyperfine field (HF) and the isomer shift (IS) of this sextet are a HF of 260 kOe and an IS of 0 mm s^{-1}. Moreover, a second sextet in the spectrum, with a HF of 330 kOe and an IS of 0 mm s^{-1} reveals the presence of a small amount of unmixed iron (~9%).

In Figs. 4(a)–4(c) the three Mössbauer spectra of the Fe_2Ti sample mixed with the respective irradiation doses 1, 1.7, and 2.4×10^{16} Xe^+ cm^{-2} are presented. At the highest dose (2.4×10^{16} Xe^+ cm^{-2}) the alloy is in a glassy state as it has been previously reported.[4] The presence of a wide-line doublet (average isomer shift IS of -0.15 mm s^{-1} and a quadrupole splitting QS of 0.33 mm s^{-1}) in the Mössbauer spectrum [Fig. 4(c)] shows that the ^{57}Fe nuclei are submitted to an electric field gradient (Stark effect) in the glass. Hence this amorphous state is paramagnetic at room temperature with a large distribution of the ^{57}Fe atomic sites. At intermediate doses (1 and 1.7×10^{16} Xe^+ cm^{-2}) the Mössbauer spectra [Figs. 4(a) and 4(b)] are composed of a superposition of a wide-line doublet and two sextets. The average parameters of the doublet are an IS of -0.19 mm s^{-1} and a QS of 0.31 mm s^{-1}, so that the chemical composition of the corresponding amorphous phase is close to $Fe_{50}Ti_{50}$. As for the two sextets, they are identical to those previously attributed to the bcc magnetic phase and to a small amount of unmixed iron. In the same way the x-ray diffraction pattern gets evidence for both the amorphous and the bcc phase.

The multilayer of global composition $Fe_{50}Ti_{50}$ transforms into a single amorphous phase under an irradiation

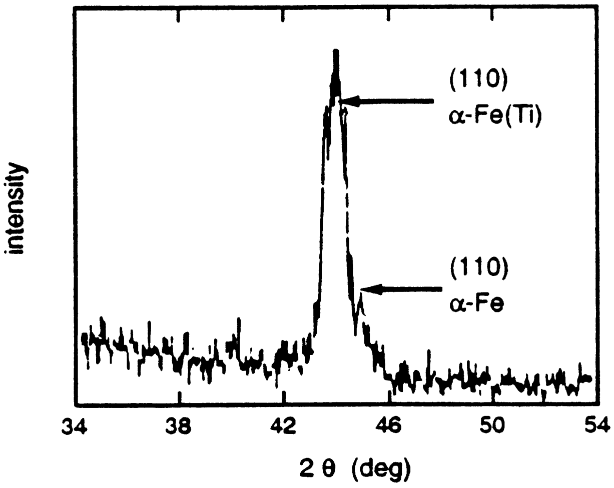

FIG. 2. X-ray diffraction pattern at glancing incidence of the mixed $Fe_{83}Ti_{17}$ sample.

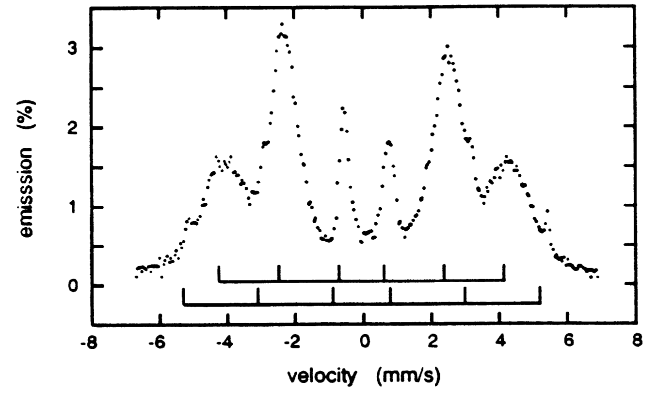

FIG. 3. Conversion-electron Mössbauer spectrum at 300 K of the mixed $Fe_{83}Ti_{17}$ sample.

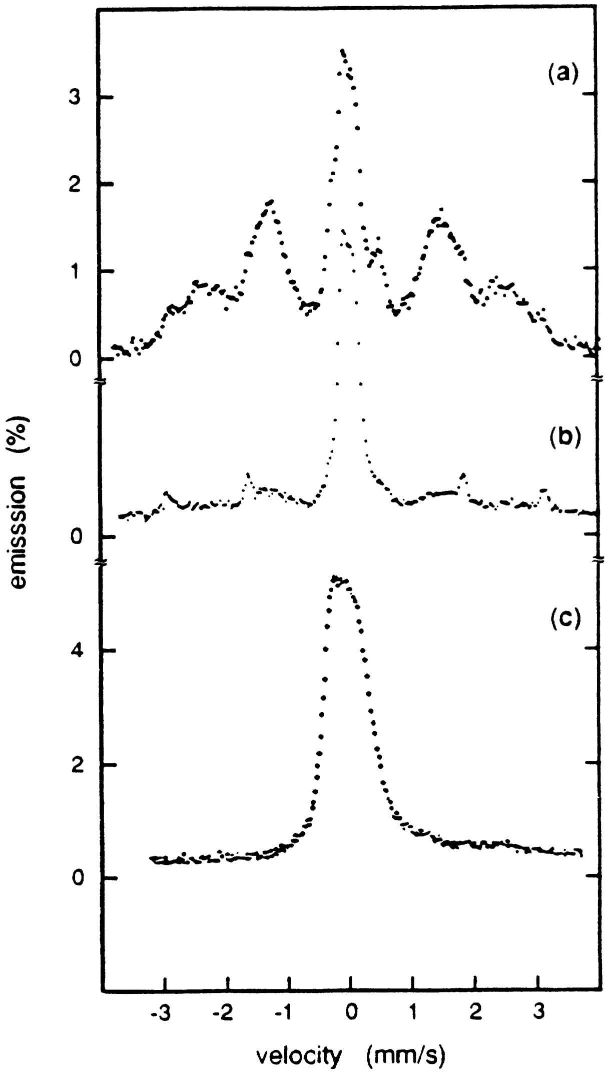

FIG. 4. Conversion electron Mössbauer spectra of the Fe_2Ti sample after different mixing doses: (a) 10^{16} $Xe^+\,cm^{-2}$, (b) 1.7×10^{16} $Xe^+\,cm^{-2}$, and (c) 2.4×10^{16} $Xe^+\,cm^{-2}$.

dose of 0.8×10^{16} $Xe^+\,cm^{-2}$ as reported in Ref. 4 and remains in this state up to a dose of 3.6×10^{16} $Xe^+\,cm^{-2}$ without any modification in the Mössbauer spectrum or in the x-ray diffraction pattern. The average isomer shift and quadrupole splitting of this doublet are -0.20 and $0.32\ mm\,s^{-1}$, respectively.

IV. DISCUSSION

A. Short-range order in Fe-Ti amorphous alloys

The average isomer shift and quadrupole splitting deduced from the fitted quadrupole doublet distributions of the Mössbauer spectra are reported in Figs. 5(a) and 5(b) as a function of the glass composition. Figure 5(c) shows the corresponding variation of the averaged interatomic distance d in the first coordination sphere, as it can be estimated from the x-ray diffraction patterns using

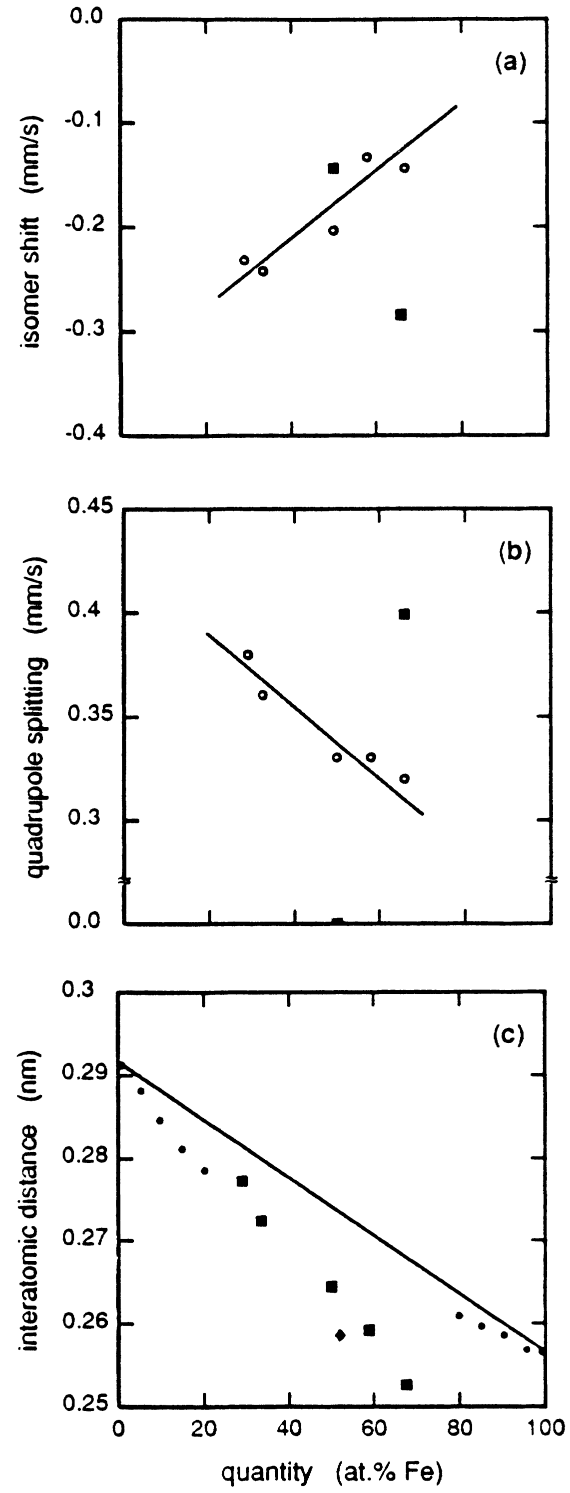

FIG. 5. Variations vs the glass composition of (a) isomer shift (open circles) [values for crystalline compounds are also reported (solid squares)], (b) quadrupole splitting (open circles) [values for crystalline compounds are also reported (solid squares)], and (c) average first interatomic distance (squares). The distances between the first neighbors in the crystalline Fe-Ti compound (solid rhombuses) and in the bcc solid solutions (circles) are also reported. The solid line represents the linear interpolation between Fe and Ti Goldschmidt diameters.

Erhenfest's relation $dq = 1.23 \times 2\pi$.

The IS is closely related to the density of s electrons on the ^{57}Fe nucleus. In transition-metal alloys the electronic density of states DOS results from hybridization between s and d states. The number of electrons having true s type depends on the alloy composition x and hence IS varies with x.

The QS value decreases from 0.38 to 0.32 mm s^{-1} when the iron content increases from 29 to 67 at. %. QS is related both with the principal component of the electric field gradient (EFG) on the ^{57}Fe nucleus and with the asymmetry parameter η. In general these two contributions can only be separated when the local symmetry is known. However, the variation of η $(0 \leq \eta \leq 1)$ could by itself explain a QS variation of 0.048 mm s^{-1} at most, but not 0.06 mm s^{-1}. So it is reasonable to admit that the EFG continuously varies over the studied compositional range.

Moreover, the EFG depends on the local atomic environment around the ^{57}Fe atoms, and not on the electronic distributions. This can be concluded because the former contribution is nearly independent of temperature, while the latter one is not. Indeed we have experimentally found that QS is temperature independent between 77 and 300 K.[4]

If we suppose that the coordination number is constant whatever the glass composition is (about 12 as it is in the crystalline compact structures), the size difference between Fe and Ti atoms would expend and deform the first coordination sphere when the Ti content increases from 33 to 71 at. %. The consequence would be an enhancement of the EFG and *a fortiori* of QS. A dilatation is actually observed as evidence is get from Fig. 5(c): the average interatomic distance d increases in the same as as QS does.

We can also compare this distance d to the distance d' interpolated between the Goldschmidt diameters of Fe and Ti. At any given composition d is much shorter than d' which is a consequence of an alloying effect in addition to a purely geometrical effect. Such a contraction in the glass is compatible with a CSRO. In Ni-Ti glass obtained by sputtering technique, the existence of a CSRO had been suggested by Moine *et al.*[6] on the basis of the same argument, and further proved by Ruppersberg *et al.*[7] by x-ray and neutron scattering measurements. However, according to Rodmaq *et al.*[8] the CSRO in the Fe-Ti glasses obtained by sputtering technique is expected to be weak. Therefore we can conclude that the Fe-Ti glasses are more chemically disordered than the Ni-Ti glasses though they are not totally disordered.

B. Feasibility of metastable phases

The GFA is drastically affected by the contamination level of the layers. Indeed the results of the mixing process of $Fe_{50}Ti_{50}$ multilayers we have reported in Ref. 9 are very different from the above-mentioned one for the same global composition. The major difference between the two series of experiments is the carbon and oxygen impurity content in the Ti layers before mixing. In the former ones the [O]/[Ti] and [C]/[Ti] ratio is about 100%, while in the latter ones it is less than 1% (less than the sensitivity threshold of RBS analysis when it is performed on samples deposited on berylium substrates[4]). The spatial mixing of Fe and Ti species is so much reduced at high contamination content that a dose of at least 10^{16} Xe^{+} cm^{-2} is required to produce a detectable effect in the RBS spectra, while the homogenization of the low contaminated multilayers is well achieved at such a dose.

Therefore layers of very stable compounds such as carbide or oxide act as diffusion barriers against ballistic mixing. Moreover, the formation of amorphous phase is inhibited. Such impurity effects had previously been reported by Hirvonen *et al.*[1]

The substrate-film interface does not exhibit Si-metal compound formation or any measurable interdiffusion (Fig. 1) unlike in the mixing experiment on Fe-Si or Ti-Si bilayers reported in the literature.[10] The distance $R_D - x$ between the silicon-metal interface and the maximum of the ballistic damage distribution (assuming a Gaussian shape) is probably responsible for this difference. Indeed the damage density at the interface

$$\rho = \exp\left[-\frac{(R_D - x)^2}{2\,\Delta R_D^2}\right]$$

is about 1% in our case and 90% in Ref. 10 according to Trim calculations.[11] Therefore silicon contamination of the metallic layers is not expected to influence the metastable phase formation in our case.

The correlation between the GFA and Fe-Ti equilibrium phase diagram leads to the following remarks.

(i) The existence of an eutectic point at $Fe_{84}Ti_{16}$ composition seems to have no beneficial influence on the GFA by ion-beam mixing at room temperature. This feature is common to the vapor-quenching methods but unlike the liquid-quenching ones.[12]

(ii) We never observe the formation of the Fe_2Ti compound ($MgZn_2$) structure) probably because of too long a nucleation time with respect to the time scale (10^{-10} s) of the thermal spike surrounding the xenon trajectory. This is not the case for the bcc structure owing to its very simple unit cell.[13] Therefore we can make the assumption that kinetic conditions are fulfilled for bcc and amorphous phase formation by IBM of Fe-Ti multilayers at room temperature and the thermodynamics determines the metastable phase formation.[14]

An enthalpy diagram can be calculated for the main phases: liquid, glass, and bcc solid solution (Fig. 6). The enthalpy curves of the bcc sol-sol and the liquid are derived from extrapolations at $T = 0$ K of the recent thermodynamic data on the Fe-Ti system given in Ref. 15. These curves show that the bcc sol-sol is more stable than the liquid all over the compositional range Fe_xTi_{100-x}. Therefore approximating the glass enthalpy by the liquid one cannot account for our results. However, in some metallic alloys the glass enthalpy is lower than the liquid one owing to structural relaxation.[16] According to Loeff and Weeber[17] a better estimation for the glass enthalpy can be given.

On one hand the CSRO is greater in the amorphous

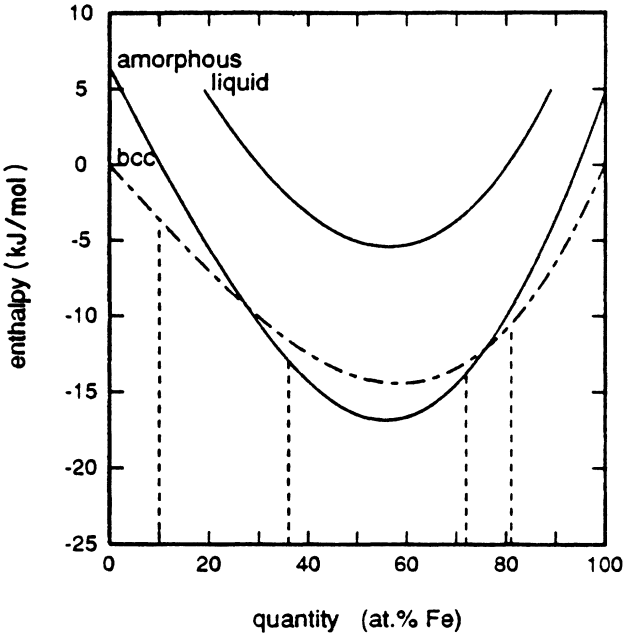

FIG. 6. Enthalpy curves of the liquid, the glass, and the bcc solid solution. Vertical dotted lines show the phase-stability limits given by the common tangent rule (see text).

state than it is in the liquid state so that the chemical part ΔH^{chem} of the mixing enthalpy ΔH^{mix} is reduced in the glass with respect to the liquid by ΔH^{ord}:

$$\Delta H_l^{\text{mix}} = \Delta H^{\text{chem}} ,$$

$$\Delta H_g^{\text{mix}} = \Delta H^{\text{chem}} + \Delta H^{\text{ord}} < \Delta H^{\text{chem}}$$

with

$$\Delta H_{\text{ord}} = -x(100-x)\delta[C_{\text{Fe}}(C_{\text{Fe}}C_{\text{Ti}})^2 \Delta H_{\text{sol}}^{\text{Fe in Ti}} + C_{\text{Ti}}(C_{\text{Fe}}C_{\text{Ti}})^2 \Delta H_{\text{sol}}^{\text{Ti in Fe}}] ,$$

where C_{Fe} and C_{Ti} are the surface concentrations of the elements[18]

$$C_{\text{Fe}} = \frac{xV_{\text{Fe}}^{2/3}}{xV_{\text{Fe}}^{2/3} + (100-x)V_{\text{Ti}}^{2/3}}$$

$$C_{\text{Ti}} = \frac{(100-x)V_{\text{Ti}}^{2/3}}{xV_{\text{Fe}}^{2/3} + (100-x)V_{\text{Ti}}^{2/3}}$$

with V_{Ti} and V_{Fe} atomic volumes.

δ is a free parameter lying between 0 (totally chemically disordered case) and 8 (totally ordered equiatomic compound). according to Weeber[19] $\delta = 5$ for amorphous alloys including Ni-Ti glasses. It follows from the above discussion on the CSRO in Fe-Ti glasses that assuming $0 < \delta < 5$ is reasonable. Indeed the best choice to rationalize our experiments is $\delta = 2$.

On the other hand, taking the crystalline state of the pure elements as the reference state, an enthalpy term must be added to the chemical contributions in order to get the total enthalpy of the liquid and the glass. Such a term is the melting enthalpy for the liquid and the crystalline-amorphous transition enthalpy for the glass:

$$\Delta H_l^{\text{Tr}} \simeq R\overline{T_m} = 8.3\overline{T_m} ,$$

$$\Delta H_g^{\text{Tr}} \simeq C\overline{T_m} = 3.5\overline{T_m} ,$$

where R is the gas constant, C a fit parameter,[17] and $\overline{T_m}$ is the average melting temperature. Hence one gets for the glass enthalpy ΔH_g:

$$\Delta H_l = \Delta H^{\text{chem}} + 8.3\overline{T_m} ,$$

$$\Delta H_g = \Delta H^{\text{chem}} + \Delta H^{\text{ord}} + 3.5\overline{T_m} ,$$

$$\Delta H_g = \Delta H_l + \Delta H^{\text{ord}} - 4.8\overline{T_m} .$$

In the frame of this semiempirical model the amorphous phase is more stable than the bcc sol-sol within the range $27.5 < x < 75.5$; this range is in rather good agreement with the vapor-quenching method experiments.[2–12] The lack of stability of the bcc sol-sol with respect to the amorphous one around the central part of the compositional range is to be related to the (positive) lattice strain energy included in the bcc-phase enthalpy as pointed out by Von Allmen.[20] Indeed the maximum enthalpy difference between the glass and bcc phases is 2.4 kJ mol^{-1} which is smaller than the maximum elastic energy of the bcc structure (7.2 kJ mol^{-1}).

Applying the classical tangent rule between the amorphous and the bcc enthalpy curves leads to three domains of composition:

(1) A single glassy state for $36 < x < 72$.

(2) A two-phase alloy (glass and bcc sol-sol) for $10 < x < 36$ and $72 < x < 81$.

(3) A single bcc sol-sol for $x > 81$ and $x < 10$.

Such phase stability limits are in agreement with our experimental results at $Fe_{50}Ti_{50}$, Fe_2Ti mixed with 2.4×10^{16} Xe^+ cm^{-2}, and $Fe_{83}Ti_{17}$ compositions, and with the results on the Ti-rich compositions reported in Ref. 21.

V. CONCLUSION

By ion-beam mixing of Fe-Ti multilayers at 300 K an extension of the Fe-rich terminal solid solution and a single- or two-phase state (amorphous plus bcc) have been obtained according to composition and/or irradiation dose.

The thermodynamics of the glassy state considered as a phase more stable than a purely extrapolated liquid at low temperature on one hand and the thermodynamics of the highly strained bcc structure on the other hand, lead to phase-stability limits compatible with our experimental results. Nevertheless, the phase evolution at Fe_2Ti composition as a function of the irradiation dose requires a kinetic treatment.

The study of the short-range order in the glassy state is not presently well achieved. Measurements of the electronic density of states in the amorphous Fe_xTi_{100-x} alloys could be useful to understand the isomer-shift variation as a function of composition. The variations of the average first interatomic distance and quadrupole splitting with respect to composition do not show any discontinuity and suggest both a continuous compositional change and deformation of the first coordination sphere. Nevertheless, the derivation of the three partial pair-correlation functions from diffraction measurements is necessary to better interpret our Mössbauer results and to determine the chemical order parameter in the glass. This would lead to a fruitful comparison between the Fe-Ti glasses obtained by IBM and by sputtering methods.

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