

# MICROSTRUCTURAL STUDY OF $\text{Fe}_{1-x}\text{Ti}_x$ ALLOYS FORMED BY ION BEAM MIXING

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## ABSTRACT

Microstructure of the Fe-Ti system by ion beam mixing of multilayers at 300 K and 77 K has been studied in a wide composition range. The ion bombardment was carried out using  $\text{Ar}^+$  ions at 80 keV. Using grazing angle x-ray diffraction, we find that the lattice parameters of these bcc solid solutions are very close to that of  $\alpha$ -Fe. Extended x-ray absorption fine-structure spectroscopy have been performed to investigate the short-range order in the ion-beam-mixed state. The structure parameters, such as the interatomic distance and the coordination number, are estimated from the Fe  $K$ -edge Fourier filtered EXAFS spectra. The interatomic distance is independent of the alloy concentration, and it is almost constant. The study of x-ray absorption near-edge structure gives information on the individual  $p$  components of the partial density of states of the conduction band of the Fe and Ti. We also find that a charge transfer from Ti to Fe atoms takes place.

## 1. INTRODUCTION

Ion Beam Mixing (IBM) has the advantage that some metastable compositions and structures can be produced, which do not exist in the equilibrium state<sup>(1,2)</sup>. Recently, studies of Fe-based binary alloys produced by IBM indicate that Fe forms amorphous and metastable crystalline phases with 3d transition metals such as Ti and V<sup>(3,4)</sup>. Ion beam mixed  $\text{Fe}_{1-x}\text{Ti}_x$  alloys are typical example of metal-metal alloys. Under equilibrium condition, solids containing Fe and Ti exist as crystalline intermetallic compounds ( $\text{FeTi}$  and  $\text{Fe}_2\text{Ti}$ ) and low solubility (a few percent) alloys<sup>(5,6)</sup>. R. Brenier *et al.* have recently obtained glassy alloys by IBM of Fe-Ti multilayers at 77 K and 300 K in a wide compositional range ( $0.33 \leq x \leq 0.71$ )<sup>(7)</sup>. On the other hand, sputtering technique gives amorphous phases within the range  $0.2 < x < 0.75$  and bcc solid solutions outside this domain<sup>(8)</sup>. Depending on the composition the properties change from ferromagnetic at the Fe-rich side of  $\text{Fe}_{1-x}\text{Ti}_x$  alloys and reveal an invar type thermal expansion anomaly<sup>(9)</sup>. In these respects, it is interesting to study the structure of  $\text{Fe}_{1-x}\text{Ti}_x$  alloys as a function of alloy concentration.

We report in this paper x-ray diffraction (XRD) at glancing incidence and X-ray absorption spectroscopy (XAS) measurements on ion-beam-mixed Fe-Ti thin films in wide compositional range ( $0.1 < x < 0.7$ ) in order to investigate the short-range order and electronic structure in the ion-beam-mixed state. In the past, transition metal *K*-edge XAS measurements have proved to be a useful tool in identifying the atomic and electronic structure changes<sup>(10)</sup>. In x-ray absorption near-edge spectra (XANES), spectral intensity of a *1s* to *4p* transition will be shown to evidence a charge transfer to Fe from Ti in this system. The extended x-ray absorption fine structure (EXAFS) spectroscopy results are shown to be well agree with the structural results of XRD on ion-beam-mixed Fe<sub>1-x</sub>Ti<sub>x</sub> alloys.

## 2. EXPERIMENT

Iron and titanium multilayers in wide composition range ( $0.1 \leq x \leq 0.7$ ) were deposited onto a SiO<sub>2</sub>/Si substrate by electron beam evaporation in a high vacuum ( $\sim 10^{-7}$  Torr). The relative thickness of the each metal layer (Fe or Ti) was adjusted so that the average film composition was equal to a pre-determined value. The total thickness of the multilayers, roughly 900 Å, was designed to match the mean projected range of the 80 keV Ar<sup>+</sup> ions. The deposition rate and evaporated thickness of each element were monitored and controlled by a vibrating quartz-crystal deposition monitor. Ion beam mixing was carried out with 80 keV Ar<sup>+</sup> ions at sample substrate temperature of 300 K and 77 K in a vacuum of  $2 \times 10^{-7}$  Torr. To avoid heating due to ion bombardment the sample holder was glued to a large copper block, and ion currents were maintained below  $1.5 \mu\text{A}/\text{cm}^2$ . The ion fluence ranged between  $1.5 \times 10^{16} \text{ Ar}^+/\text{cm}^2$  and  $2 \times 10^{16} \text{ Ar}^+/\text{cm}^2$ .

The microstructure of the ion beam mixed Fe<sub>1-x</sub>Ti<sub>x</sub> phases formed as a function of composition has been studied by XRD, EXAFS and XANES. X-ray diffraction patterns were collected on a SINTAC (Model XDS 2000) diffractometer with a Cu *K*<sub>α</sub> source ( $\lambda = 1.54 \text{ \AA}$ ). Data were collected from  $2\theta$  value of  $20^\circ$  to  $70^\circ$  using a step size of  $0.05^\circ$ . The XAS measurements of Fe and Ti *K*-edges were made on beam line X19A of National Synchrotron Light Source (NSLS) in the Brookhaven National Laboratory. The measurements were made at room temperature in fluorescence mode using a Si(220) double crystal monochromator.

## 3. RESULTS AND DISCUSSION

Using grazing angle x-ray diffraction method, the formation of bcc solid solution of the samples with  $x < 0.3$  is ascertained. The lattice parameters of these bcc alloys are very close to that of  $\alpha$ -Fe. In addition mixed crystalline bcc  $\alpha$ -Fe,  $\beta$ -Ti and amorphous Fe-Ti phases coexist within ion-beam-mixed films in the composition range  $0.4 < x < 0.7$ .

Fig. 1(a) and 1(b) show the XANES spectra of the Fe and Ti *K*-edge of  $\text{Fe}_{1-x}\text{Ti}_x$  alloys. These spectra were background-subtracted by fitting the pre-edge background with a least square fitting method. All spectra were normalized to unity step in the absorption coefficient from well below to well above the edge. The zero of energy is assigned to the first inflection point of each spectrum. The main feature at about 20eV above the Fe *K* edge indicated by the label B in Fig. 1(a) is an atomic-like transitions from *1s* core to empty *4p* states. This transitions also produce multiple peaks (feature A) in the near-edge energy region. The multiplicity of these features is governed by the solid-state splittings of the *4p* levels and by replication of *4p* features associated with different *3d* configuration state. The continuous change of main peak indicates a continuous mixing of the electron states of Fe and Ti atoms above the Fermi energy level. The clear decrease of feature B with increasing Ti concentration represents the gradual filling of Fe *4p* band.

On the other hand, Fig. 1(b) shows the substantial increase of feature B, which is proportional to the number of the empty states near the Fermi energy with *p* symmetry at Ti site, with Fe concentration. The *K*-edge results indicate that the number of *p*-symmetry empty states about Ti site increases with Fe concentration. This observation is consistent with a gradual filling of Fe *4p* band. Taking into account the Pauling's electronegativities for Fe (1.8) and Ti (1.5), we can expect a charge transfer from Ti to Fe atoms. Electronic state density calculations performed by Papaconstantopoulos for the crystalline FeTi compound indicate a transfer of 0.18 electron towards Fe with the relative fractions of 2/3 and 1/3 for *d* and *s* states respectively<sup>(11)</sup>. The fact that the charge transfer is observed at the *K*-edge suggests

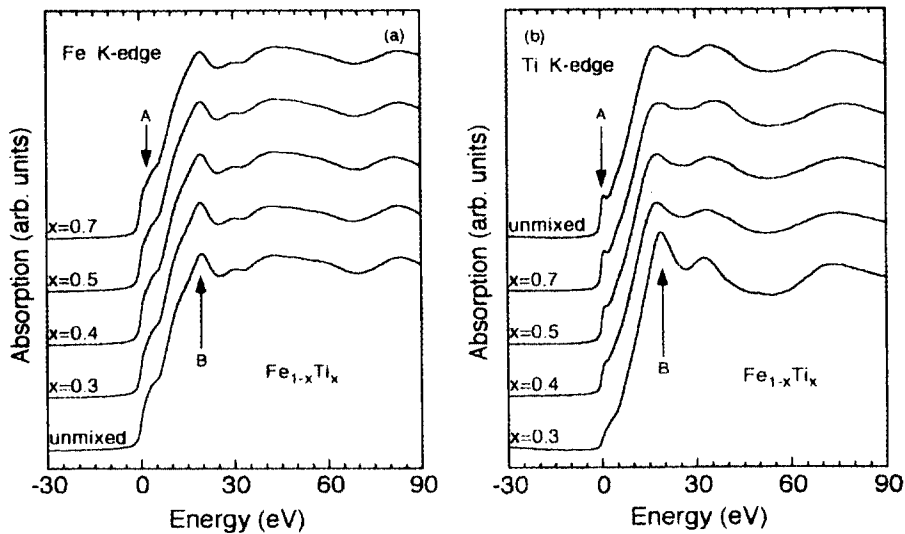


Fig. 1 (a) Fe *K*-edge and (b) Ti *K*-edge XANES spectra of ion-beam-mixed  $\text{Fe}_{1-x}\text{Ti}_x$  alloys.

that electron energy bands crossing the Fermi level must involve the hybridization of  $d$  band with  $p$  band.

Next we turn to the analysis of the EXAFS data. The structure parameters, such as the interatomic distance, the coordination number, are estimated from the Fe  $K$ -edge Fourier filtered EXAFS spectra. Measurements were made at the Fe  $K$ -edge for the ion-beam-mixed  $\text{Fe}_{1-x}\text{Ti}_x$  alloys. EXAFS spectra show no significant change in the alloy concentration. EXAFS interference function  $\chi(k)$  was extracted from the measured absorption data using standard techniques<sup>(12)</sup>. Fig. 2 shows Fourier transforms of  $k^3\chi(k)$  for pure Fe,  $x = 0.1, 0.5,$  and  $0.7$ . (The  $k$  range for the transforms is  $2.0 \sim 15.0 \text{ \AA}^{-1}$ .) The Fourier transforms of the Fe  $K$  spectra for IBM  $\text{Fe}_{1-x}\text{Ti}_x$  alloys exhibits a peak at  $4.45 \text{ \AA}$ , which is typical of a bcc structure. The presence of this peak confirms that the local order in the ion-beam-mixed state is bcc. The nearest-neighbor EXAFS contribution has been isolated by Fourier filtering the peak between  $1.5$  and  $3.0 \text{ \AA}$  in  $R$  space. The resulting single shell data were analyzed using the ratio method. The interatomic distances of first and second shells are nearly independent of the alloy concentration, and those are almost constant. This result agrees with XRD measurements. In addition, we find that the interatomic distance of alloys mixed at  $300 \text{ K}$  is longer than that of alloys mixed at  $77 \text{ K}$ . Simulations indicate that the coordination number of first and second shells decreases with increase in  $x$ .

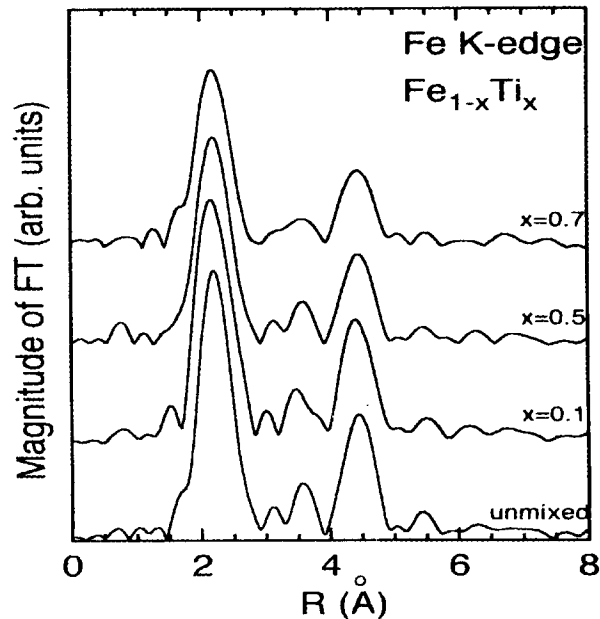


Fig. 2 Magnitudes of the Fourier transforms of  $k^3\chi(k)$  obtained from Fe  $K$ -edge measurements in ion beam mixed  $\text{Fe}_{1-x}\text{Ti}_x$  alloys.

## 4. CONCLUSIONS

$\text{Fe}_{1-x}\text{Ti}_x$  alloys over a wide composition range of  $0.1 \leq x \leq 0.7$  have been made by ion beam mixing at 300 K and 77 K. In the Fe-Ti ion-beam-mixed alloys, up to 30 at. % of Ti, the bcc solid solution structure is sustained, and at above 40 at. % of Ti mixed crystalline bcc  $\alpha$ -Fe,  $\beta$ -Ti and amorphous Fe-Ti phases coexist within ion beam mixed films. However, we do not find any signature of intermetallic compounds FeTi (CsCl structure) and  $\text{Fe}_2\text{Ti}$  ( $\text{MgZn}_2$  structure). We suggest that the state of the ion-beam-mixed Fe-Ti system is equivalent to that at about 1800 K in equilibrium. As seen in the phase diagram, solubility can be stabilized over the entire composition range at this temperature. Therefore, ion-beam-mixing promotes alloying through both collisional mixing and thermal spike mixing as well as a reduction in the driving force for thermal segregation once alloyed mainly due to the negative value of heat of formation.

The XANES of Fe and Ti *K* edges directly probes the local density of *p*-like symmetry for the conduction band of IBM Fe-Ti system. In particular the spectral intensity of a *1s* to *4p* absorption feature proves that charges are transferred to the Fe site from Ti and contributed to the filling of the empty *p*-states of Fe. These charge transfer may occur through *d-p* hybridization upon alloying. The formation of local chemical bonds between transition metals affects the occupancy or hybridization of *d* states, and this change can be revealed in the transition to the empty *4p* states. The results of EXAFS data at the Fe *K* edge show that the structure of the Fe is largely unaffected by the addition of Ti. The EXAFS fits show that the Fe-Fe distance is 2.48-2.50 Å, close to that of bulk bcc Fe.

## ACKNOWLEDGMENTS

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