# X-ray photoemission study of $Fe_{40}Ni_{40}B_{20}$ metallic glass

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**Abstract.** X-ray photoelectron spectroscopic (XPS) study of the valence band and the core levels of amorphous $Fe_{40}Ni_{40}B_{20}$ are presented. The oxides which formed at the surface of as-received sample are due to oxidation of iron and boron. For etched samples, the presence of oxide is not discernible, and the chemical environment is predominantly iron–boron-like, while nickel remains unassociated. The valence band has a high density of states at Fermi levels of amorphous $Fe_{40}Ni_{40}B_{20}$ are presented. The oxides which formed at the surface of $B\,2s$ and $Fe\,3d$ states, and metalloid $s$-states respectively.

**Keywords.** Metallic glass; electron spectroscopy; valence band; shake-up satellite.

## 1. Introduction

Electron spectroscopy can yield information related to the surface properties of glassy alloys like corrosion resistance, segregation, catalysis, etc. (Oelhafen 1983). Depending on the energies of the escaping electrons from the surface, information from a depth between 5 and 30 Å (escape depth) can be used in the study of diffusion of surrounding gases, since these samples are very often vulnerable to oxidation.

A number of studies (Fusy and Pareja 1987; Myhra *et al* 1988; Roos and Vanwyk 1992) on metallic glasses were recently carried out to clarify the role of amorphous structure and chemical composition in the oxidation of surface of the alloy. In this work we examine the oxidation of amorphous $Fe_{40}Ni_{40}B_{20}$ alloy using XPS at room temperature. Examining the relevant core-level spectra of Fe, B and Ni, partial oxidation of boron and iron has been observed in unetched sample, while no such evidence is found for Ni. However, below the surface layer the chemical environment in the alloy is such that boron is more strongly bonded to iron than nickel.

## 2. Experimental procedure

The glassy sample of $Fe_{40}Ni_{40}B_{20}$ was in the form of thin ribbon and the sample kept at room temperature (300 K) under ordinary desiccation is referred to as as-received one. The XPS analysis was carried out in a VG ESCA MK II spectrometer interfaced to a VG 3040 data system which permitted data to be stored and the quantification of peaks. After pumping the spectrometer down to a pressure of $10^{-8}$ torr, spectra were obtained with $AlK_\alpha$ radiation (1486·6 eV) at a constant analyser energy of 50 eV (20 eV for narrow scan) and a take-off angle of 45° relative to the sample surface. For each specimen a survey spectrum (0–1000 eV), and high-resolution electron spectra of the major elements present in the sample (C $1s$, O $1s$, Fe $2p_{3/2}$, Ni $2p_{3/2}$ and B $1s$) were recorded. In the figures, however, only the high-resolution spectra of Fe$2p_{3/2}$ Ni$2p_{3/2}$ and B$1s$ are given. Besides, the valence band spectrum in

the region of 0–20 eV binding energy were also recorded, since it is the valence electrons which determine the magnetic and electrical properties of metallic glasses. Since the samples were mounted on stubs with double-sided adhesive polymer tapes, charging of the samples may have taken place. The C $1s$ peak at 284·6 eV from hydrocarbon has been used for calibration.

Since the samples were exposed to atmosphere, as-received specimens are expected to be dirty. After cleaning the surface by argon-ion etching at 6 kV 10 μA for 10 min, the XPS examinations were repeated again.

## 3. Results and discussion

The glassy metal $Fe_{40}Ni_{40}B_{20}$ has been studied before and after argon-ion etching. The surface of the as-received sample is very dirty with the result that very strong signals from C $1s$, O $1s$ are obtained in the wide-band spectrum, while iron and nickel signals are very weak (figures not shown).

In the as-received sample C $1s$ peak is located at 285·2 eV while it is expected at 284·6 eV. This is due to charging of the sample and a correction of 0·7 eV was applied to all the peaks that occur in the spectra, whenever necessary. In order to expose a clean layer buried underneath, argon-ion etching was carried out at 6 kV 10 μA for 10 min. After etching, unwanted C $1s$ and O $1s$ peaks have almost vanished. In order to elucidate XPS peaks of the constituent elements, narrow-scan spectra were taken with pass energy of 20 eV for both as-received and etched samples.

### 3.1 *Fe 2p peak*

In the as-received unetched sample indistinct broad and feeble peaks of F $2p_{3/2}$ and $2p_{1/2}$ are obtained at 712·2 eV and 725·0 eV respectively (figure 1a). These two peaks are presumably in the form of oxides. The difference in the binding energies of $2p_{3/2}$ and $2p_{1/2}$ turns out to be 13·3 eV. Upon etching three prominent peaks located at 707·1 eV, 712·5 eV and 720·3 eV appear (figure 1b). While the first and the third peaks are strong in intensity, the middle peak at 712·5 eV is rather weak. The XPS peaks at 707·1 eV (FWHM being 2·4 eV) and at 720·3 eV (FWHM 2·46 eV) are identified as Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of iron. As $2p_{3/2}$ level in FeB is around 707·1 eV, it indicates that the local chemical environment of Fe is closer to FeB than that of metallic iron. It is gratifying to note that the spacing between the two peaks is of the order of 13·2 eV which agrees well with the values given in the literature (Wagner *et al* 1979). The broad peak at 712·5 eV is presumably shake-up satellite of iron.

### 3.2 *Ni 2p peak*

Although nickel content in the glassy alloy is as much as 40% the nickel $2p$ XPS signal from the as-received sample is extremely feeble. However, the weak peak at 852·7 eV from nickel is just discernible in unetched specimen (figure 2a) indicating the absence of nickel oxidation. On the other hand two prominent peaks appear in the narrow scan in the region 850 to 880 eV (figure 2b) for etched sample. These two peaks located at 852·8 eV and 870 eV refer to Ni $2p_{3/2}$ and $2p_{1/2}$ respectively. The
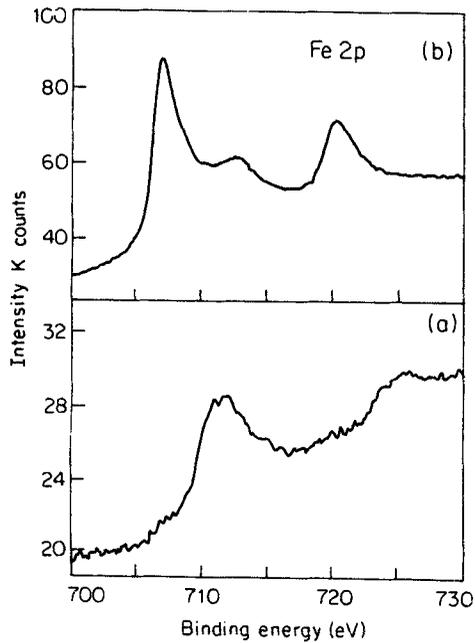
**Figure 1.** XPS spectra of Fe $2p_{3/2}$ and $2p_{1/2}$ in glassy metal of $Fe_{40}Ni_{40}B_{20}$ for **(a)** as-received sample and **(b)** argon-ion etched sample.
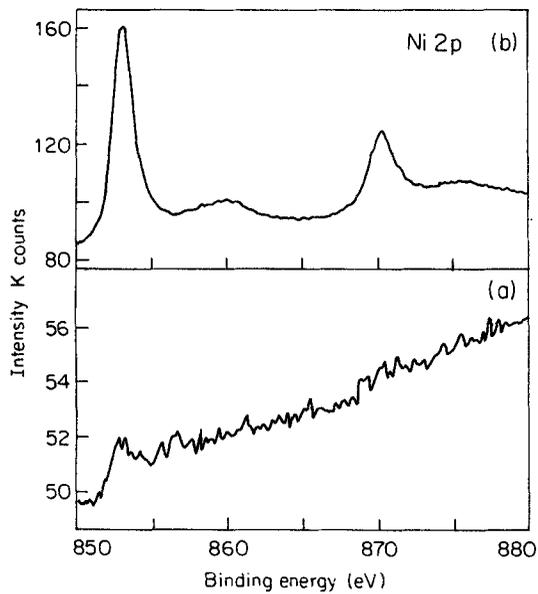
**Figure 2.** Core-level photoelectron spectra of Ni $2p_{3/2}$ and $2p_{1/2}$ in glassy metal of $Fe_{40}Ni_{40}B_{20}$ for **(a)** as-received sample and **(b)** argon-ion etched sample.
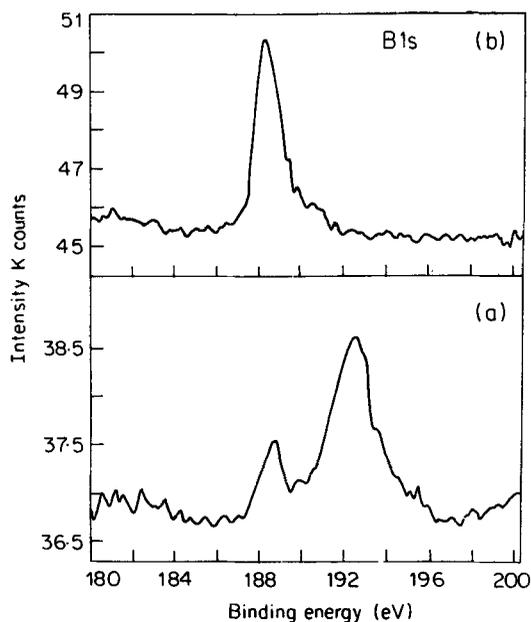
**Figure 3.** XPS spectra of B $1s$ in glassy metal of $Fe_{40}Ni_{40}B_{20}$ for (a) as-received sample and (b) argon-ion etched sample.

separation between these two peaks as obtained in our experiment is 17·2 eV which compares well with 17·4 eV quoted in the literature. A small broad peak occurring at 860 eV is reminiscent of metallic nickel (Wagner *et al* 1979).

### 3.3  *B 1s peak*

Boron being a low-atomic-number element, the XPS signal is expected to be small. Besides, surface contamination in the case of as-received sample gives rise to weak signals from B $1s$. Two peaks situated at 188·6 eV and 192·8 eV (figure 3a) are presumably due to iron-boron and oxide of boron respectively. As the normal B $1s$ peak appears at about 187 eV, the respective chemical shifts are $E_b = 1·6$ eV and $E_b = 5·8$ eV. The signal from oxide form is nearly three times stronger than the other. This result provides evidence of partial oxidation of boron located at the surface of the alloy.

After etching, the oxide peak at 192·8 eV is completely erased. The other peak is located at 188·2 eV and its FWHM is 1·5 eV. Moreover, the intensity of this peak is increased by eight-fold compared to that of the corresponding peak at 188·6 eV in as-received specimen (figure 3b). The above results support the notion that iron-boron configuration is prevalent in the amorphous state.

### 3.4  *Valence band spectra*

Prior to Ar-ion etching, XPS signals from valence electrons are feeble, broad and indistinct (figure 4a). Weak signal is partly due to the partial oxidation of metal atoms
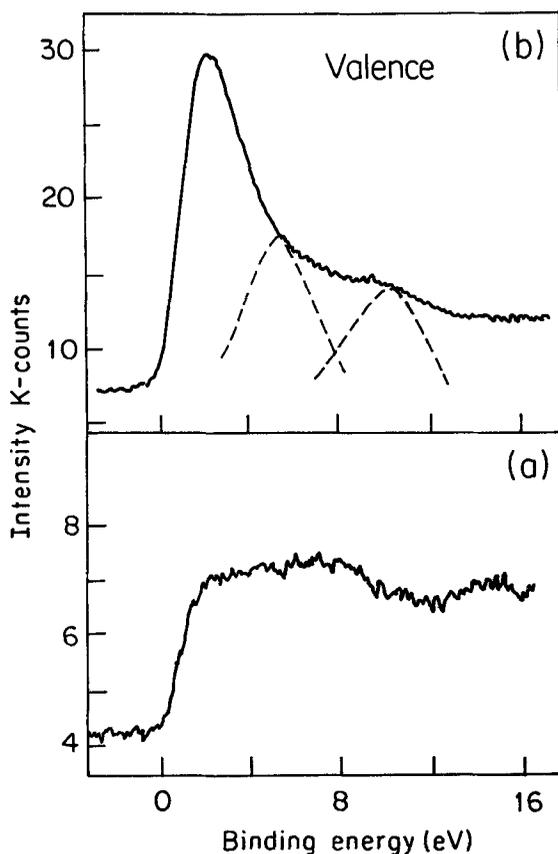
**Figure 4.** XPS ($h\nu = 1486 \cdot 6\,\text{eV}$) valence band spectra of metallic glass sample $Fe_{40}Ni_{40}B_{20}$ for (a) as-received sample and (b) argon-ion etched sample.

at the surface. After the surface of the specimen is etched, the nature of spectra undergoes a major change, and the intensity of the valence band increases ten-fold (figure 4b). As is expected for alloys the density of states rises sharply below Fermi level. With increasing binding energy, the curve shows a strong main peak at about $1 \cdot 8\,\text{eV}$. It is known that the XPS valence band spectra of pure Ni show a broad peak at about $3\,\text{eV}$ due to $3d$ states (Amamou 1980; Amamou and Krill 1980). The other major constituent in the alloy, namely Fe, is known to show two $3d$ valence band peaks around $0 \cdot 6 - 0 \cdot 8\,\text{eV}$ (Oelhafen 1983). The position of the main peak at $1 \cdot 8\,\text{eV}$ is due to the disorder in $d$ states of metal ions. In the weak disorder limit, one expects the peak at the position $E = xE_{Fe} + (1 - x)E_{Ni}$, which is $1 \cdot 85\,\text{eV}$ for this alloy. Therefore it is concluded that this peak in the valence band is the joint contribution of $3d$ states of Fe and Ni. Since $AlK_\alpha$ radiation has been used in the present study, the resolution is poor compared to UPS spectra, so that Fe and Ni $3d$ bands seem to be poorly resolved. On the higher binding-energy side, the electron spectra (figure 4b) may be resolved in two more peaks around $5\,\text{eV}$ and $9 \cdot 6\,\text{eV}$. The first one arises due to the mixing of the metalloid $p$ and Fe $d$ states, whereas the peak at higher energy is due to metalloid $s$ states. Similar conclusion about the existence of bonding states between B $2s$ and Fe $3d$ states has been substantiated by XPS studies in a series of glassy $Fe_xB_{1-x}$ alloys (Matsuura *et al* 1980).

## 4. Conclusion

The oxide state of iron and boron is completely absent in the etched sample of $Fe_{40}Ni_{40}B_{20}$, although it exists in as-received specimen. This indicates that diffusion of oxygen into the bulk is negligible. Also in the amorphous state of the sample, iron is more strongly bonded to metalloid compared to nickel. The disorder in $d$ level is found to be weak.

## Acknowledgements

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