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LETTER TO THE EDITOR

An xps study of the nitrogen-implanted $Zr_{76}Fe_{24}$ metglass

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Abstract. *In situ* nitrogen implantation has been carried out on $Zr_{76}Fe_{24}$ metglass, and the surface has been characterized by x-ray photoelectron spectroscopy. From the xps results it is concluded that the surface was enriched with Zr, leading to the formation of zirconium nitride. An attempt is made to explain Zr enrichment in $Zr_{76}Fe_{24}$ on the basis of heat of formation.

Ion implantation is a powerful technique for producing many intermetallic compounds, because it has the advantage of overcoming thermodynamic constraints to form, from insoluble components, metastable systems that could not be obtained from equilibrium processes. Nitrogen ion implantation in various metals and alloys has found many applications in metallurgy (Hirvonen 1978, Hartley 1979, Dearnaley 1982). Implantation of nitrogen improves the wear and resistance of various steels (Dearnaley 1982). Titanium alloy is found to give extreme resistance to wear and corrosion. The advantages of this technique have been brought out very clearly in our earlier publications (Sinha *et al* 1986, 1987, Badrinarayanan *et al* 1989). We present in this letter our x-ray photoelectron spectroscopy (xps) results on the $Zr_{76}Fe_{24}$ -N system. xps is ideally suited for probing the ion-implanted surface because we are dealing with a very thin layer, through which the implanted atom has to diffuse to form the desired alloy.

In general, amorphous alloys have been found useful for catalysts and electrode materials because they have corrosion resistance properties. Adsorption and chemisorption of many gases in metal surfaces occur only at ambient conditions, producing molecular or dissociative species on the surface. Molecules like N_2 do not adsorb to an appreciable extent at room temperature. Such a reaction can be induced using an ion bombardment technique.

For an alloy, it is possible to explain the surface enrichment of a constituent element on the basis of well known thermodynamic parameters, the primary driving force being the reduction of surface free energy. On the basis of a systematic study of several binary alloys, some generally applicable rules have been formulated classified as bond breaking theory; (Van Santen and Boersma 1974, Williams and Nason 1974, Bouwman *et al* 1976). These are as follows: (i) since the surface free energy is proportional to the heat of sublimation, the element with the lower heat of sublimation of the pair will migrate to

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the surface; (ii) on interaction with reactive gases, the surface will become enriched in the element that has the higher heat of formation. In the ion implantation technique, ions are accelerated and injected into solids. By controlling the energy of the ions it is possible to produce nitrides of definite composition. This technique can overcome some of the thermodynamical constraints to react with both Fe and Zr in the present case. According to the heat of formation, one should expect the surface to enrich with Zr, leading to the formation of ZrN.

Ion implantation and XPS analysis were performed on a VG Scientific ESCA-3-MKII electron spectrometer. Foils of pure $Zr_{76}Fe_{24}$ metglass were used for ion implantation. The starting material was cleaned in the preparation chamber of the spectrometer by argon ion etching until no signal arising from C 1s and O 1s was observed. The parameters for sputtering were 10^{-6} Torr argon pressure, 6 kV beam energy and 100 μ A beam current focused onto 1 cm² of the sample surface. Generally, sputtering of an alloy surface by argon ion bombardment leads to preferential enrichment in a particular element of the alloy. Hence we carried out the sputtering just to remove the carbon and oxygen, and the surface composition obtained after sputtering was taken to represent the initial composition of the metglass.

High-purity nitrogen at a pressure of 10^{-6} Torr was passed through an Ag_2 sputter ion gun for ion implantation. The energy of the N_2^+ molecules was 8 kV. The sample surface was oriented perpendicular to the beam. Implantation was terminated when the intensity of the N 1s peak reached a maximum. Al K x-ray radiation (1486.6 eV) was used to excite the photoelectrons. The base pressure of the analyser chamber was better than 10^{-10} Torr. The spectrometer was calibrated to give the Au 4f_{7/2} line at 84 eV. Resolution in terms of the full width of half-maximum of the gold 4f_{7/2} line was 1.6 eV, and the reproducibility of the energy values was within ± 0.2 eV.

The XPS valence band structure of $Zr_{76}Fe_{24}$ is shown in figure 1(A). The main features are a peak below the Fermi level at 1.3 eV and an asymmetry on the high-BE side. The region up to 2 eV is attributed to the Fe 3d and Zr 4d bands overlapping with each other. The XPS valence band spectra closely resemble that reported by Oelhafen *et al* (1980). On nitrogen implantation, an additional peak at 5.5 eV was observed, which is attributed to the N 2p level. The N 2s level (not shown in the figure) was observed at 15 eV. The valence band region approximately 6 eV below the Fermi level is built up from the metal d state and nitrogen 2p state, and the non-metal 2s state is well separated from the valence band, at about 15 eV below the Fermi level.

The following results were obtained from the core level spectra after the nitrogen implantation (figure 1(B)):

- (a) the Zr 3d level shifted to the high-BE side by 1.4 eV; no asymmetry in the line shape or any change in the spin-orbit splitting is observed;
- (b) the Fe 2p_{3/2} level binding energy remained unchanged; however, there is a reduction in the intensity after the implantation;
- (c) two N 1s levels were observed with binding energy values of 397.4 and 400 eV; the intensity of the high-BE-value peak reduced considerably on prolonged nitrogen implantation;
- (d) no O 1s level was observed in the XPS spectra before or after nitrogen implantation.

The observed chemical shift of 1.4 eV for the Zr 3d_{5/2} level is nearly the same as that of the Zr-N system (Badrinarayanan *et al* 1989). The absence of any chemical shift of the Fe 2p level combined with the shift of the Zr 3d level indicates that the species formed

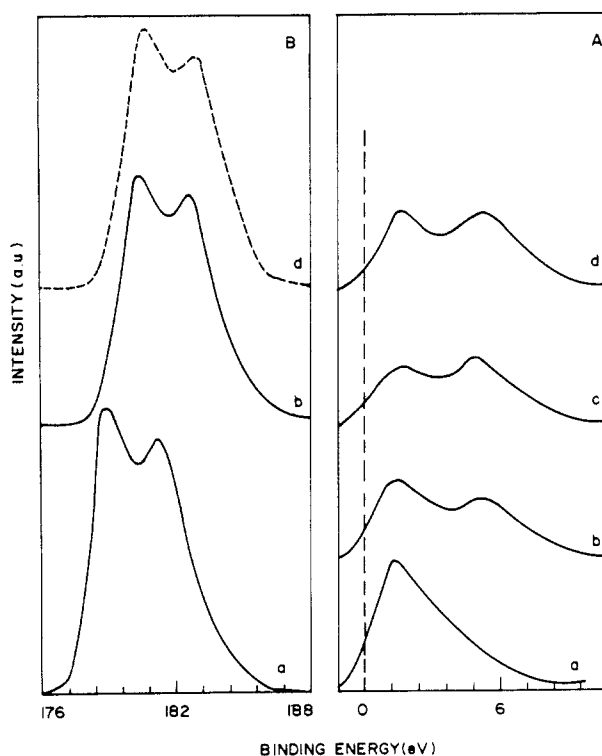


Figure 1. (A) XPS valence band spectra. (B) XPS spectra of zirconium 3d levels. (a) Clean Zr-Fe surface. (b) Nitrogen-implanted surface; 15 min. (c) Zr-Fe-N, implanted; 30 min. (d) Zr-Fe-N, implanted; 45 min.

on nitrogen implantation is zirconium nitride. From a comparison of the binding energy values of various nitrides (Lancaster and Rabalais 1979), it can be concluded that the nitrogen inserted into the metal forms the corresponding metal nitride.

Using the peak intensities of the Zr $3d_{5/2}$, N $1s$ and Fe $2p_{3/2}$ levels, the ratios of the number of Zr atoms to N atoms and Zr to Fe atoms are calculated using the relationship (Steiner *et al* 1980)

$$n_{Zr}/n_N = (I_{Zr}/I_N)(\sigma_N/\sigma_{Zr})(E_N/E_{Zr})^{0.71} \quad (1)$$

where I is the XPS peak intensity, σ is the photoelectron cross section and E is the kinetic energy of the photoelectron. In a similar manner, n_{Zr}/n_{Fe} can also be calculated. The photoelectron cross section values were taken from the literature (Scofield 1976).

Bouten and Miedema have proposed a theory for calculating the heat of formation for various metal nitrides (Bouten and Miedema 1979). Using the atomic concentrations calculated from equation (1) and the equations derived by Bouten and Miedema (equations (1) to (5), Bouten and Miedema 1979), it is possible to calculate the heat of formation of the Zr-N and Fe-N systems. The heat of formation of Zr-N is 1.6 eV (Badrinarayanan *et al* 1989) and of Fe₂N is 0.96 eV (Kothari *et al* 1985). Johansson and Martensson (1980) proposed a model to relate the core level binding energy of any metallic element in the pure phase (free atom) to that in the pure metal (measured

Table 1. Core level binding energies (eV) for Zr, Fe, Zr-Fe and Zr-Fe-N systems from xps measurements.

System	Zr (eV)		N (eV)		Fe (eV)	$\frac{n_{Zr}}{n_{Fe}}$
	3d _{5/2}	3d _{5/2}	1s	2s	2p _{3/2}	$\frac{n_{Zr}}{n_{Fe}}$
Zr	179.2	—	—	—	—	—
Fe	—	—	—	—	706.7	—
Zr ₇₆ Fe ₂₄	179.0	0.2	—	—	706.9	3.10
Zr ₇₆ Fe ₂₄ -N	180.5	1.3	397.4	16.3	706.9	4.10
Zr-N	180.9	1.6	397.7	16.8	—	—

relative to the Fermi level). Using an appropriate Born-Haber cycle, for Zr metal and the Zr-N system (Kothari *et al* 1985), one can arrive at an expression for the BE shift:

$$\Delta E = -E_{\text{formation}} \quad (2)$$

The chemical shift is calculated using the value of the heat of formation. The calculated value of the chemical shift for Zr-N is 1.6 eV (table 1), and the observed chemical shift is nearly equal to this value. In the absence of any chemical shift for Fe energy levels, it can be reasonably assumed that nitrogen implantation in Zr-Fe leads to the formation of Zr-N. Since the heat of formation of Zr-N is relatively large, it is expected that on interaction with nitrogen atoms the surface will be enriched with zirconium. Equation (1) is used to calculate the ratios n_{Zr}/n_N and n_{Zr}/n_{Fe} for different durations of nitrogen implantation. The calculated values are given in table 1. The ratio n_{Zr}/n_{Fe} changes from an initial value of 3.10 to 4.10, showing a segregation of Zr to the surface, leading to the formation of Zr-N.

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