SURFACE OXIDATION OF
THE AMORPHOUS ALLOY $Ni_{68}P_{18}Cr_{14}$ [1]

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ABSTRACT

The surface layer of $Ni_{68}P_{18}Cr_{14}$ amorphous alloy was studied by AES and XPS associated with ion beam sputtering. It was found that great differences existed between the surface layer and the bulk both in composition and chemical states. The dominant component elements Ni and P were of lower content in the surface layer, while Cr was enriched. Cr was drastically oxidized in the surface layer, but Ni underwent no oxidation. There was a P enriched region just below the surface oxide layer, which was supposed to enhance the surface segregation of Cr. Ni underwent no oxidation in $Ni_{68}P_{18}Cr_{14}$ amorphous alloy.

Key words: surface layer   oxidation   amorphous alloy $Ni_{68}P_{18}Cr_{14}$

1 INTRODUCTION

Amorphous alloys present an interesting class of new materials with outstanding mechanical, magnetic and chemical properties. In recent years, considerable efforts have been made in the development of amorphous alloys. Amorphous alloys can be easily prepared as ribbon by rapid quenching. A frequently used method is melt spinning. Because the preparation procedure is far from being an equilibrium process, and the ribbons also react with the atmosphere, the composition and chemical states of elements near the surface region may be different from the bulk. This fact has important consequences in the field of material science amd catalysis. Some experimental studies on surface composition and chemical states in amorphous alloys have been published[1-2].

In regards to chemical corrosion and oxidation, amorphous alloys are superior to their crystalline counterparts due to chemical homo-geneity, and the absence of grain boundaries, line and other defects[3-4]. The preceding experiments have shown that the addition of metallic elements to amorphous alloys can further improve the characteristics of the surface layer[5-7]. Hence, it seems reasonable that research of the effects of additive elements on the surface layer is a prerequisite for the further study of chemical and catalytic properties of amorphous alloys.

The main objective of the present experiment was to analyze the nature of the oxidized surface layer present on the shiny side of the amorphous ribbons and provide detailed information for chemical and catalytic studies.

2 EXPERIMENTAL

The specimens (20 μm thick, 3 mm wide) were prepared by melt spinning on a copper wheel and quenching in air. Their amorphous character was confirmed by X-ray diffraction Prior to the experiment, the specimens were

aged in air for a few years. The shiny free faces were chosen for analysis.

The samples in strips were cleaned in an ultrasonic bath using acetone before putting them into an analyzing chamber. They were then assembled one by one on a standard metal stub to form a reasonably flat surface area of 1 cm × 1 cm for XPS analysis.

The surface analyses were carried out on a RIBER-LAS surface apparatus. The base vacuum was in a $10 \sim 6$ Pa range. XPS was performed with a $Mg(K_{\gamma})$ source for which the photon energy was 1,253.6 eV. Single survey scans were carried out over a kinetic energy range 359 ~ 1,250 eV with steps of 0.1 eV, a pass energy (CAE) of 14 eV and a scan rate of 1 step / s. Ion beam sputtering (2 keV) was carried out in large area scanning.

For AES, monoenergetic electrons (3 kV) were used as the exciting source. Beam diameter and current were about 2 μm and 0.7 μA, respectively. Static ion beam etching was used for depth profiling, and the Ar^+ ion beam energy was 2.5 keV. The sputtering rate was estimated to be 10 nm / min.

3　RESULTS AND DISCUSSION

In order to get more detailed information about the elemental distributions in the surface layer, depth profiling has been conducted by a combination of AES and ion beam sputtering technique. A relative peak to peak height method was employed in calculations as illustrated in Fig. 1. The oxidized layer is completely removed after 120 s etching, corresponding to a thickness of about 20 nm. This layer is supposed to be formed by the mutual reaction of the sample with the environment during rapid quenching and afterward aging in air.

Fig. 1 gives the elemental abundances of $Ni_{68}P_{18}Cr_{14}$ amorphous alloy. Remarkable oxygen enrichment is found in the surface layer; the concentration of oxygen is almost up to 50

at.−% at the outmost surface. Cr is also bountiful in the surface layer. Ni and P are correspondingly depleted, their contents are far below the nominal stoichiometry in the bulk, whereas P seems to be enriched just below the surface oxide layer. C is slightly enriched in the surface layer.
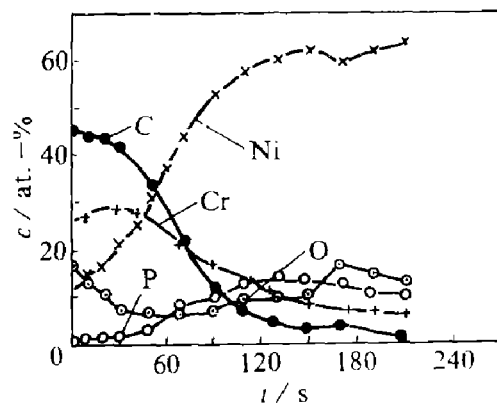

Fig. 1　Elemental abundances of $Ni_{68}P_{18}Cr_{14}$ as a function of ion sputtering time

The enrichment of oxygen in the surface layer is considered to be mainly due to oxidation. The preferential oxidation of Cr enhances the surface enrichment of O. The metalloid element P, found to be enriched in a region just below the surface oxide layer, may be the species which facilitates the surface segregation of metallic Cr. This phenomenon has also been found in Fe-B system amorphous alloys[8]. Limited C also segregates to the surface and forms a slightly C enriched layer.

With the intention of investigating the chemical states of the surface layer, XPS was employed with a $Mg(K_{\gamma})$ X-ray source. The experimental results are exhibited in Figs. 2 ~ 6. Table 1 lists the binding energies of all materials concerned.

For Ni_{2p} XPS spectra (see Fig. 2), on the native surface, no obvious Ni peaks appear (The curve was omitted), because the surface Ni content is very low. After 3 min etching, there is a peak at 852.5 eV, which represents the metallic Ni. The inner surface(after etching

for 7 min) also exhibits the metallic Ni characteristic[9].

Cr$_{2p}$ XPS spectra are shown in Fig. 3. Prior to etching, there is only one peak which is in conformity with Cr$_2$O$_3$ (5.756.7 eV)[10], the Cr on the native surface is completely oxidized to Cr^{3-}. After 3 min etching, the chemical states of Cr remain the same as in native oxidized surface. After 7 min etching, in addition to the Cr^{3-} peak, a low binding energy peak (574.0 eV) is examined as metallic Cr (574.0 eV)[11], and the quantities of metallic Cr are comparable with that of Cr^{3+}. From the results mentioned above, the preferential oxidation of Cr rather than Ni is more apparent. With appropriate addition of Cr to Ni-P amorphous alloy, Ni undergoes no oxidation in the surface layer.
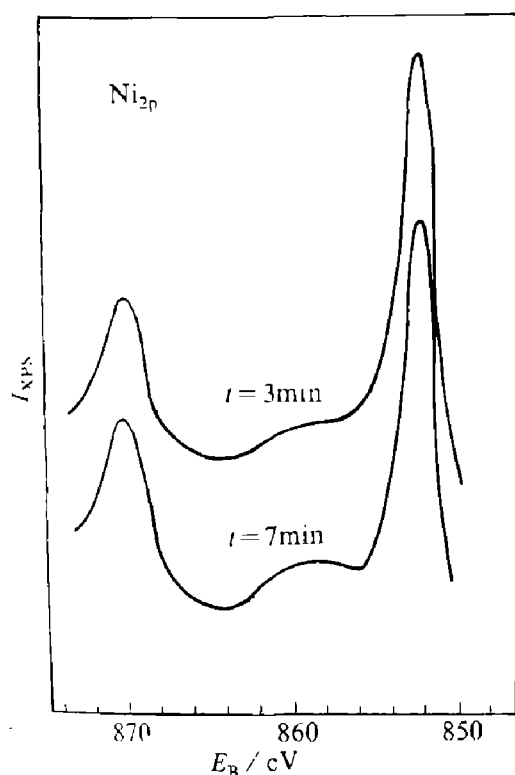

Fig. 2   XPS spectra of Ni$_{2p}$ as a
function of ion sputtering time

The additive element Cr is presumed to form a perfect passivated layer, which would block the further oxidation of the Ni-P amorphous alloy. But the great depth of the oxide layer shows no evidence for this suggestion.

The reason may be that the poor surface quality fails to form a compact Cr oxide layer. Oxygen can diffuse through the surface layer into bulk as usual.

Table 1   Comparison of the binding energies of the various elements in amorphous Ni$_{68}$P$_{18}$Cr$_{14}$ with data for pure elements, oxides and others from the literature

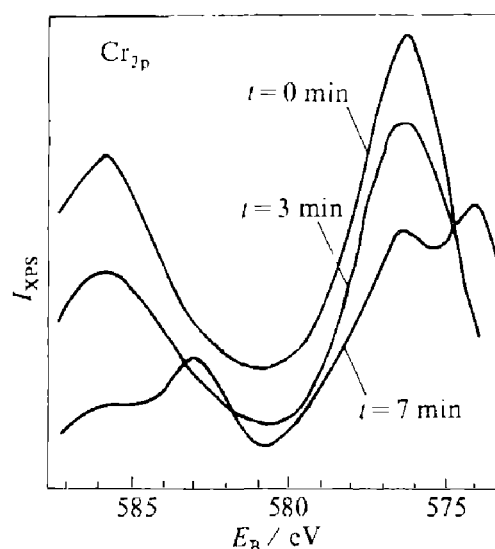| compounds level	Binding Energies eV		
	pure elements	oxides	others
Ni$_{2p}$ present results	852.4		
Ni(metallic)	852.65[9]		
Cr$_{2p}$ present results	574.0	576.5	
Cr(metallic)	574.1[11]		
Cr$_2$O$_3$		576.6[10]	
P$_{2p}$ present results	129.6	134.1	
Ref.[10]	129.45		
NiP			129.3[12]
NaPO$_3$			134.1[13]

Fig. 3   XPS spectra of Cr$_{2p}$ as a
function of ion sputtering time

The P$_{2p}$ spectra are depicted in Fig. 4. All three curves share a common peak at 129.6 eV, which represents the metalloid P(129.45 eV)[8] or NiP(129.3 eV)[12]. On the native surface, another peak appears, indicating the existence of the P chemical state, as in NaPO$_4$ etc[13]. After 3 min and 7 min etching, the existent states of P

are completely pure P or NiP, it is very hard to find any oxides.

Fig. 5 shows the XPS spectra of C_{1s}. The peak at 284.6 eV represents graphite. O_{1s} spectra (Fig. 6) is a simple one. The only peak at 530.1 eV, is Cr_2O_3, which means the existence of O_{1s} is with the prior analysis of the surface oxides. The present results are summarized in Table 1. Results from the literature are also listed.

Appreciable oxidation is very apparent here. Cr has strong affinity with O. It reacts easily with O, while Ni and P are sluggish to oxidize. Not even a slight oxidation of Ni was not found. Thus, the addition of Cr to Ni-P amorphous alloy could protect the Ni and P from oxidation.

The native oxides on NiP amorphous alloys have not attracted much attention, even though the characteristics of such oxides might shed insight into the reactivity, passivation and corrosion resistance of the alloys, but the Fe-B amorphous alloys have received much attention.
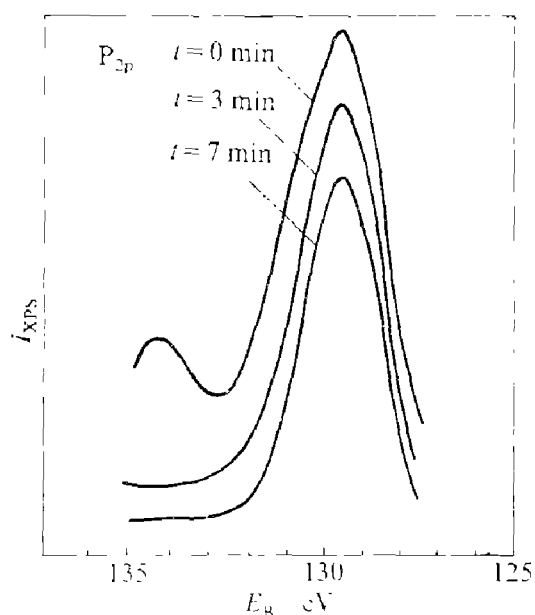
4 CONCLUSIONS

(1) The AES and XPS methods have been used to study the surface layer characteritics of amorphous alloy $Ni_{68}P_{18}Cr_{14}$. It is clear that both the composition and chemical states of the surface layer differ considerably from that of the bulk:
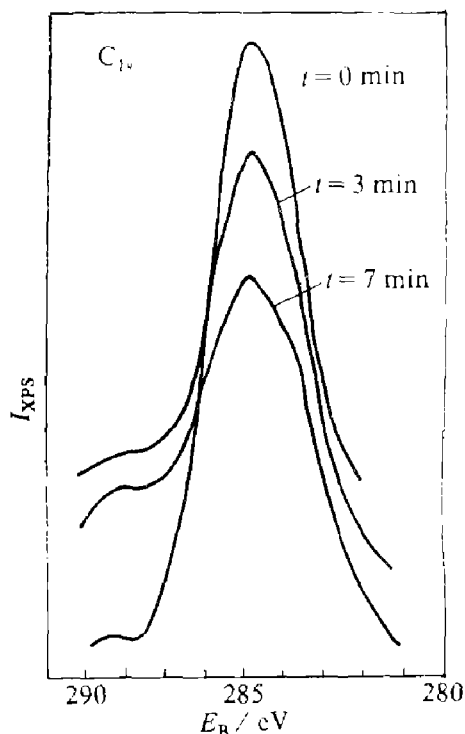

Fig. 5　XPS spectra of C_{1s} as a function of ion sputtering time

Fig. 4　XPS spectra of P_{2p} as a function of ion sputtering time
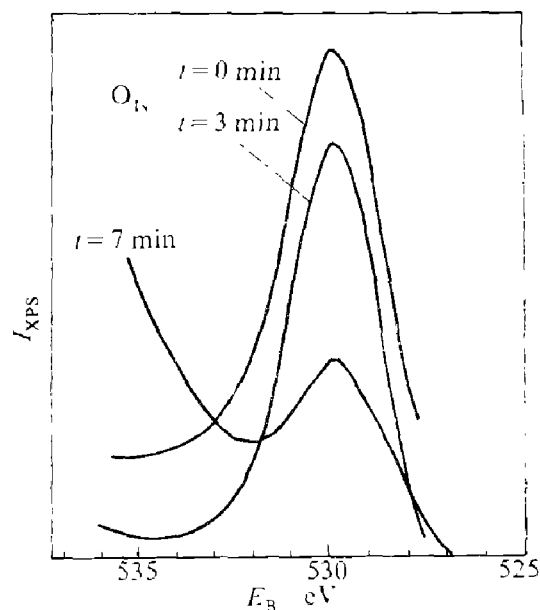

Fig. 6　XPS spectra of O_{1s} as a function of ion sputtering time

(2) The P enrichment just below the surface oxide layer is supposed to facilitate the Cr surface segregation. Concurrently, the surface segregation of C is disturbed by the active formation of the Cr oxide layer;

(3) The surface layer is rather inhomogeneous. Remarkable enrichment of O, Cr as well as a slight enrichment of C occurs in the surface layer, whereas Ni and P are correspondingly depleted. Cr is a strong oxidation element, but Ni undergoes no oxidation.

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is a couple of contradictions. Now, the following two experimental methods have be generally utilized in industry; a) shelving the assintered and ground workpiece in a storehouse for more than three months before using it; b) annealing the workpiece at a lower temperature (about 250 °C) for more than 48 h. According to the experimental data obtained in this paper, the former (natural ageing) cannot reduce the grinding residual stress. But, shelving the workpiece for a long time might be beneficial to relaxing the opposite thermal stresses which are sealed in the parts. The latter (annealing at lower temperature) can not only eliminate the thermal stress, but also reduce a portion of the grinding stress. Therefore, both theory and experimental data have confirmed the effectiveness of the above two experimental methods.

5 CONCLUSION

(1) The residual stress existing in ground surface of cemented carbide is a compressive stress, its value is about 100 to 1, 300 MPa;

(2) The stress increases with grinding feed;

(3) Natural ageing at room temperature can not obviously relax the grinding stress. but annealing at an appropriate temperature is effective for eliminating the residual stress;

(4) For the anvil workpiece used at high pressure, natural ageing for a long time and annealing at a lower temperature for a longer time may be used to eliminate the sintering thermal stress and to retain the grinding stress as much as possible for prolonging its service life.

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