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Surface Characterization of Amorphous Ni–B Films Treated with Oxygen

It has been reported that new catalysts were prepared from intermetallic compounds such as Ni–Si (*1*) and Ni–Th (*2*). These intermetallic compounds were decomposed into Ni/SiO_2 and Ni/ThO_2 in a CO + H_2 gas mixture or in oxygen. Investigations of these decompositions using X-ray photoelectron spectroscopy (XPS) were carried out for the Ni–Th system (*3, 4*). After synthesis-gas or oxygen treatments, Ni, NiO, and ThO_2 were found on the surface layers of Ni–Th intermetallic compounds. Analogous results were recognized for amorphous Fe–Ni–P–B (*5*), Pd–Zr (*6*), and Ni–Zr (*7*) alloys prepared by a rapid quenching technique. It is of great interest how the surface state of these alloys changes in such oxygen or synthesis-gas treatments.

In this investigation, the amorphous nickel boride films prepared by the RF sputtering technique (*8*) were treated by oxygen and the alterations in the surface state were examined in detail. The oxidation of the film was carried out in a constant oxygen pressure (250 Torr) at 373 K for various periods. The surface state and composition were examined by XPS at the surface and at a depth of 3 nm etched by Ar^+ ions and compared before and after the oxygen treatment, respectively. All the binding energies (BE) of XPS spectra were corrected by contaminant carbon (C1*s* = 285.0 eV).

Figure 1 and 2 show the alterations of the XPS spectra of B1*s* and Ni2*p*3/2 levels for the amorphous nickel boride films on oxygen treatment at the surface and at the etching depth of 3 nm, respectively. Two kinds of boron species appeared in the B1*s* level. The peaks at the lower and the higher BE were assigned to boron interacting with nickel (188.3 eV; B_I) and oxidized boron (192.6 eV; B_{II}; B_2O_3), respectively (*9*). In the Ni2*p*3/2 level, the main peak due to nickel metal was recognized at 853.2 eV, accompanied by a satellite peak at about 859 eV. At the surface (Fig. 1), the height of B_I and B_{II} peaks became lower and higher after the treatment, respectively. The peak due to the nickel in nickel oxide appeared at 856.5 eV after the treatment. The peak in the O1*s* level after the treatment appeared at 532.6 eV with the small shoulder around 529.5 eV due to nickel oxide. It was found that B_I and nickel metal were oxidized to B_{II} and nickel oxide, respectively, and that boron was predominantly oxidized and prevented the oxidation of nickel. At the etching depth of 3 nm (Fig. 2), the B_I peak decreased and the B_{II} peak was almost unaltered after the treatment. Nickel oxide was not observed after the treatment. It is reported that Ar^+ sputtering promotes reduction of nickel oxide in addition to the essential sputtering off the oxide layer and estimated that the effects of Ar^+ ion bombardment on nickel–oxygen surfaces are 70% sputtering and 30% reduction (*10*). The surface nickel oxide layer after the oxygen treatment is considered to be removed by Ar^+ in such a complicated process. B_{II} would not be reduced by Ar^+ sputtering because of the great affinity of boron for oxygen. In the O1*s* level, a peak appeared only at 532.6 eV without the shoulder of the low BE side. This indicates that no nickel oxide exists in the etched nickel boride films. On the other hand, the satellite peak of metallic nickel shifted toward a lower

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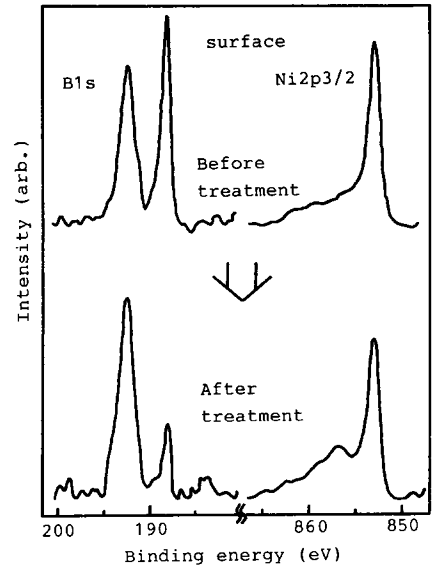

FIG. 1. X-ray photoelectron spectra of B1*s* and Ni2*p*3/2 levels at the surface of amorphous Ni–B films before and after oxygen treatment (O_2 pressure at 250 Torr, 373 K, 4 h).

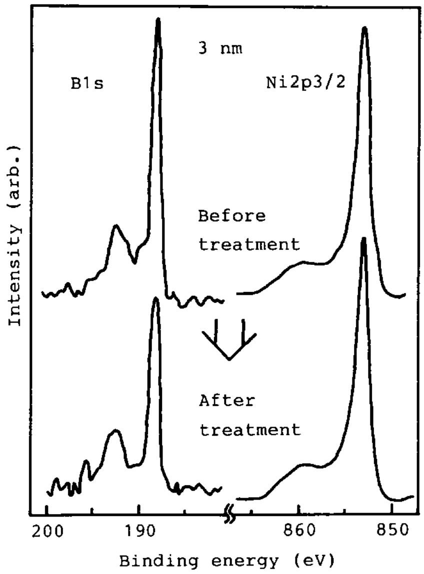

FIG. 2. X-ray photoelectron spectra of B1*s* and Ni2*p*3/2 levels at the etching depth of 3 nm of amorphous Ni–B films before and after oxygen treatment (O_2 pressure at 250 Torr, 373 K, 4 h).

binding energy, with a slight change in the spectral shape. The decrease of the B_I peak was found to be due to the enrichment of boron to the surface. Figure 3 shows the dependence of the surface composition and the surface boron/nickel (B/Ni) ratio on the oxidation time. The surface oxygen concentration increased and the boron and the nickel concentration decreased with the oxidation time. A drastic alteration of the surface composition took place in the first one hour of oxidation. The decrease of the nickel content was greater than that of the boron content. Further, the B/Ni ratio was enhanced with increasing oxidation time. These observations indicate that boron segregates to the surface by the oxygen treatment and that boron is preferentially oxidized to boron oxide. The affinity of boron for oxygen is larger than that of nickel (ΔH_f of B_2O_3 and NiO are −302.0 and −58.4 kcal/mol, respectively). Oxygen reacts predominantly with boron to form boron oxide. The surface enrichment of boron takes place in this oxidation process. These results agree with that for the oxidation of Ni–Th alloys (*4*). Because of the strong affinity of thorium for oxygen, thorium was

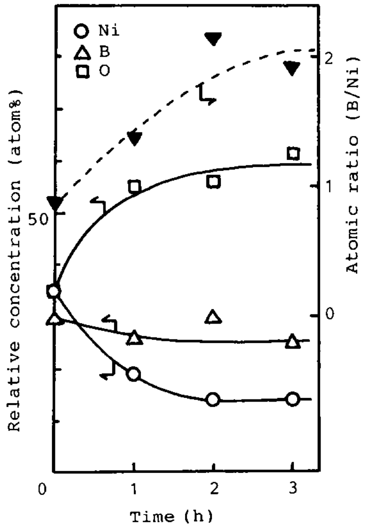

FIG. 3. Plot of surface composition and B/Ni ratio of films against oxidation time in O_2 pressure at 250 Torr, 373 K.

TABLE 1

Surface Characterization of Oxidized Amorphous Ni–B Films

Comp.	B_I[a] (%)	B_{II}[b] (%)	$B_I/Ni + B_I$	I_{sat}[c] (%)	Oxygen conc. (%)	B_{II}/O
$Ni_{74}B_{26}$	62.2	37.8	0.18	22.7	13.5	0.63
$Ni_{81}B_{19}$	57.9	42.1	0.12	23.6	10.6	0.68
$Ni_{82}B_{18}$	46.8	53.2	0.09	24.3	15.4	0.53
$Ni_{88}B_{12}$	0	100	0	27.5	19.5	0.49

[a] Fraction of B_I in total boron.

[b] Fraction of B_{II} in total boron.

[c] Satellite intensity of Ni2*p*3/2.

similarly enriched to the surface in a moderate oxidation.

The surface state of the nickel boride films has already been argued by means of the satellite intensities of Ni2*p*3/2 XPS spectra (*9*). Namely, the satellite intensity decreased from 27.0% for pure Ni to 11.7% for $Ni_{11}B_{89}$ with increasing boron concentration in the films. The decrease of the satellite intensity indicates the reduction of the number of *d* holes in the Ni 3*d* band. It was found that the electron density of nickel increased with increasing boron concentration because of the electron donation from boron to nickel. The alterations in the surface state of the nickel boride films by the oxygen treatment were evaluated for the films etched in the XPS chamber. The films with various B_I/B_{II} ratios containing 12–26 atom% of boron were obtained by treating the nickel boride films with oxygen in the different conditions. The influence of boron oxide on the electron density of nickel was examined by the change in the satellite intensity. Table 1 lists the XPS data for the films with the various B_I/B_{II} ratios. The satellite intensity increased with decreasing B_I concentration. This indicates that the electron density of nickel decreased because of the enhancement of the satellite intensity. The XPS satellite intensity for the film without B_I was 27.5% and similar to that for pure nickel. This reveals that boron oxide does not affect the electron density of nickel. The satellite peak of nickel metal would not be prevented by the nickel oxide peak because nickel oxide does not exist in the etched films. The changes in the satellite intensity is accurate enough for the above discussion. The B_{II}/O ratio was lower than the atomic ratio for B_2O_3 (0.67). The excess oxygen is attributed to adsorbed oxygen and water since O1*s* BE is 532.6 eV.

In conclusion, it was found that boron concentrated to the surface to form boron oxide and prevented the oxidation of nickel. In addition, the electron density of nickel was decreased by the oxygen treatment because of decrease of boron interacting with nickel. Boron oxide did not influence the electron density of nickel.

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