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Investigation of Composition and Chemical State of Elements in Iron Boride by the Method of X-Ray Photoelectron Spectroscopy

V. G. ALYOSHIN, A. I. KHARLAMOV, AND V. M. PROKOPENKO

Institute of Metal Physics, Academy of Sciences of Ukrainian SSR, and Institute for Materials Science Problems, Academy of Sciences of Ukrainian SSR, Kiev, USSR

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The composition and chemical state of iron and boron in the surface layer of iron boride under different kinds of pretreatment of samples have been investigated by the method of X-ray photoelectron spectroscopy. It has been found that in the initial sample there is oxygen chemically combined with iron and boron atoms. Upon heating (450°C) in hydrogen, in argon, and *in vacuo* there occurs removal of oxygen only from iron atoms (no pure iron was found to be formed). Boron oxidizes and there probably appears a new surface combination of boron with oxygen in which the bonding energy of 1*s* electrons is higher than that in B_2O_3. Treatment of the iron boride surface with argon ions and with protons ensures uniform removal of oxygen from iron and boron atoms. It has been found that thermal treatment of iron boride leads to depletion of iron atoms from the sample surface layer, and pickling with argon ions and with protons leads to strong enrichment. Iron boride samples subjected to Ar^+ and H^+ bombardment tend to undergo significant oxidation when subsequently exposed to air at room temperature.

Introduction

The method of X-ray photoelectron spectroscopy (XPS) (*1–2*) has been acquiring wider and wider use in research concerning complicated physical and chemical processes occurring on the surface of a solid. This is especially true when we study the composition and chemical state of the elements in the surface layer of the substance in dependence upon the methods of treatment and upon the nature of the reacting gaseous medium. It has been found that under hydrogen treatment the surface layer of alloys Pt–Sn, Pt_3–Sn (*3*), Ni–Al (*4*), and Pd–Al (*5*) becomes enriched in the second component. In cases of two-component oxidizable systems having homogeneous and heterogeneous areas there were also differences in surface and volumetric composition (*6–8*).

Bombardment of alloys by inert gas ions gives rise to a segregation, resulting in enrichment of thin surface layers of the alloys in one of their components (*9–12*).

In metal oxides subjected to bombardment with Ar^+ ions an ion-induced formation of oxides was detected (*12*). In one study (*13*) reduction of metals in thin oxide films on the metal surface was observed when specimens were heated to 300–400°C in a vacuum of 10^{-9} Torr produced by oil-diffusion pumps. Oxide films on metals have been found to be reduced much more easily than bulk oxides. In some instances, oxide films on metals

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(such as iron) were reduced, whereas for the bulk oxide Fe_3O_4 no reduction was observed.

The fundamental study (*14*) of the chemical state of atoms in transition metal borides established the dependence of the degree of oxidaton of metal and boron atoms on the time passed after the preparation of specimens, on the type of metal, and on the crystalline structure of the compound.

For refractory alloys there have been no studies on the influence of different kinds of treatment on the composition of the surface layer.

In this work the composition and the chemical state of boron and iron in the surface layer of iron boride under different kinds of thermal treatment and under ionic pickling of the surface have been studied by the method of XPS.

Experimental Procedure

Iron boride, FeB, was synthesized from iron and boron powders in argon atmosphere at a temperature of 1100°C.

Investigation of the photoelectron spectra of iron boride was carried out with an electron spectrometer, VIEE-15. $K\alpha$ emission of magnesium (1253.6 eV) was taken as the source of photons. Photoelectron spectra were obtained with a resolution of 1.5 eV under vacuum in the spectrometer of (*1–3*). A vacuum of 10^{-7} Torr in the spectrometer was achieved by means of titanium turbomolecular and electromagnetic discharge pumps. The sample, in the shape of a thin dispersed powder, was inserted into the corrugated surface of a copper cylinder and placed in a working chamber of the spectrometer. This camera was equipped with a cylindrical heater and had a system of electrodes for ionic pickling of the sample surfaces. Sample heating was effected *in vacuo* under a chamber pressure of 5×10^{-7} Torr, or in an atmosphere of spectroscopically pure hydrogen and argon at a pressure of 10^{-2} Torr. Both the sample heating in hydrogenargon and the bombardment by argon ions and by protons (with energy 1–1.5 keV) were carried out under continuous evacuation of gases. Photoelectron spectra of the core electrons of boron, iron, and oxygen were obtained in the following way:

I—in the initial state at room temperature;

II—after 1-hr sample heating in hydrogen argon or *in vacuo* at a temperature of 450°C, as well as after bombardment with ions of argon and hydrogen;

III—after sample exposure to air for 10 sec, 24 hr, 48 hr, 10 days, 1 month.

Each kind of treatment was carried out on a new sample. Calibration of the original sample (at room temperature) was effected according to the C 1*s* (285.0 eV) line of the hydrocarbon layer which is on the sample surface. On heating of the samples of iron boride a disparity between the bonding energies of the shell electrons and the initial state was observed. In Ref. (9) a supposition is put forward that at high temperatures hydrocarbons interact with the sample surface, which leads to a shift of the C 1*s* line. Therefore, it is not reasonable to carry out a calibration of the electron spectra with a C 1*s* line under heating. In this connection we had to calibrate the spectra (after sample heating) with respect to line $2p_{3/2}$ of the electrons of iron combined with boron.

Results and Discussion

Photoelectron spectra of the shell electrons of iron, boron, and oxygen in the initial iron boride are shown in Figs. 1–5 from which it follows that Fe and B are in their main and oxidized states on the surface of FeB. The bonding energy (E_{bnd}) of the $2p_{3/2}$ electrons of iron combined with boron (Fe_B) is 707.6 eV, and E_{bnd} of the

TABLE I

CHEMICAL COMPOSITION OF THE SURFACE LAYER OF IRON BORIDE AT DIFFERENT KINDS OF TREATMENT (at. %)[a]

Treatment	Fe_B (0.47)[b]	B_{Fe} (3.04)	Fe_O (11.83)	B_O (10.68)	O_2 (73.9)	Fe/Fe_O (0.04)	B_{Fe}/B_O (0.3)	Fe_{tot}/B_{tot} (0.9)	Fe_B/B_{Fe} (0.15)
Sample I									
Heating in hydrogen	6.1	3.8	0.06	27.3	62.6	102.0	0.14	0.2	1.6
Oxidation 10 sec	5.0	0.9	0.1	30.4	63.4	42.0	0.03	0.16	5.41
Oxidation 24 hr	0.9	2.1	4.0	27.6	65.4	0.2	0.07	0.16	0.44
Oxidation 48 hr	0.8	2.0	4.1	21.7	71.3	0.2	0.1	0.2	0.42
Oxidation 10 days	0.9	1.1	4.8	18.2	72.2	0.2	0.05	0.3	0.8
Oxidation 1 month	0.3	0.5	5.9	15.4	78.0	0.04	0.03	0.38	0.5
Sample II									
Heating in argon	10.9	0.3	0.15	25.0	63.7	72.3	0.01	0.4	36.2
Oxidation 10 sec	6.9	0.6	0.24	27.5	64.7	28.9	0.02	0.25	11.2
Oxidation 24 hr	1.0	1.3	3.8	24.2	69.7	0.26	0.05	0.2	0.8
Oxidation 48 hr	0.9	1.5	5.3	24.2	68.2	0.16	0.06	0.84	0.6
Oxidation 10 days	0.7	0.6	4.3	33.3	61.0	0.15	0.01	0.14	1.15
Oxidation 1 month	0.46	0.3	5.8	19.1	74.3	0.07	0.01	0.3	1.7
Sample III									
Heating *in vacuo*	10.6	2.5	0.13	27.6	59.1	81.44	0.09	0.85	0.15
Oxidation 10 sec	8.9	0.02	0.35	26.7	61.6	25.4	0.001	0.34	4.45
Oxidation 24 hr	2.9	1.4	3.0	26.3	66.5	0.95	0.05	2.0	2.0
Oxidation 48 hr	1.1	0.8	4.6	25.8	67.7	0.24	0.03	0.2	1.4
Oxidation 10 days	0.7	1.0	5.7	26.5	66.0	0.12	0.03	0.2	0.7
Oxidation 1 month	0.2	0.85	11.0	13.6	74.3	0.01	0.06	0.8	0.2
Sample IV									
Pickling with argon ions	39.3	4.9	4.8	6.5	44.4	8.3	0.74	3.85	8.0
Oxidation 10 sec	1.5	1.6	19.7	7.5	69.6	0.07	0.2	2.3	1.0
Oxidation 10 days	0.01	8.0	0.9	44.9	46.1	0.01	0.2	0.01	0.001
Oxidation 1 month	0.2	1.3	13.9	5.5	79.0	0.01	0.2	2.1	0.12
Sample V									
Pickling with protons	41.9	2.1	2.8	7.6	45.6	14.8	0.3	20.1	20.1
Oxidation 10 sec	2.25	1.31	22.62	7.38	66.41	0.09	0.17	2.86	1.71
Oxidation 24 hr	0.57	0.81	16.15	5.03	77.63	0.03	0.16	2.86	0.7
Oxidation 48 hr	0.54	0.4	17.89	5.53	73.61	0.03	0.07	3.1	1.35
Oxidation 10 days	0.54	0.25	16.48	4.48	78.32	0.03	0.05	3.61	2.16
Oxidation 1 month	0.07	0.07	6.09	3.56	90.19	0.01	0.019	1.69	1.0

[a] Table data were obtained by way of chemical analysis of iron boride by the method of X-ray photoelectron spectroscopy (*1, 2, 15–17*).

[b] Initial state in parentheses.

$2p_{3/2}$ electrons of iron combined with oxygen (Fe_O) equals 711.0 eV. The Bonding energy of the 1*s* electrons of boron combined with iron in iron boride (B_{Fe}) equals 187.6 eV; in combination with oxygen (B_O) 191.0 eV. The bonding energy of the 1*s* electrons of oxygen chemisorbed on the surface of FeB is 531.6 eV.

Comparison of the intensities of integral lines of Fe_B, Fe_O and of B_{Fe}, B_O (see Table I) testifies to significant oxidation of iron atoms with respect to boron atoms. Also, it testifies to an approximately equivalent Fe_{total}/B_{total} ratio in the surface layer of the initial iron boride. The bonding energy of the $2p_{3/2}$ electrons of iron is higher in FeB than in pure iron, and the values of the bonding energy is the $1s$ electrons of boron in iron boride and in free boron practically coincide.

FeB heating in an atmosphere of hydrogen (sample I) (Fig. 1) leads to substantial changes in the electron spectra of iron, boron, and oxygen. In the electron spectrum of iron there is only one line of Fe_B; i.e., removal of oxygen occurred. Formation of pure iron in the surface layer of iron boride was not observed. In the electron spectrum of boron, along with the lines of B_{Fe} and B_O characteristic of the initial iron boride, there appeared a new, high-energy line with bonding energy 194.8 eV. Taking into consideration that the E_{bnd} of B $1s$ electrons in B_2O_3 is 193.5 eV, we suggest that in the process of thermal treatment of iron boride with hydrogen removal of oxygen from iron atoms is followed by formation of an anomalous oxygen combination with boron (B_XO_Y). The electron line of O $1s$ has become narrower and shifted in the direction of higher bonding energies. Comparison of the intensities of the electron lines (Table I) of boron and iron chemically combined with each other and with oxygen shows that on heating of the iron boride in hydrogen, reduction of the surface oxygen combination of iron and oxidation of boron take places with simultaneous depletion of iron from the surface layer of FeB. One may suggest that reduced atoms of iron diffuse into subsurface layers of the iron boride, and oxygen, which becomes free upon disruption of the Fe–O bond, oxidizes the boron of the surface layer.

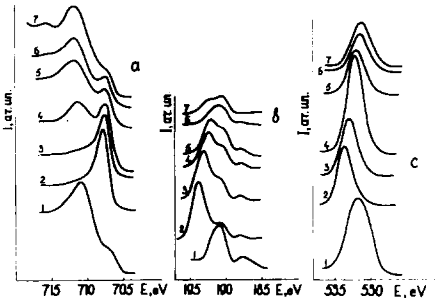

FIG. 1. X-Ray photoelectron spectra of iron (a), boron (b), and oxygen (c) in iron boride: (1) in the initial state; (2) after sample heating in hydrogen; (3) after 10-sec air exposure; (4) after 24-hr air exposure; (5) after 48-hr air exposure; (6) after 10-day air exposure; (7) after 1-month air exposure.

Air exposure of iron boride, subjected to treatment I, leads to gradual oxidation of the iron with an increase of the intensity of the maximum with E_{bnd} 191.0 eV and reduction of the intensity of the maximum with E_{bnd} 194.8 eV. With increase of exposure time this maximum shifts in the direction of lower bonding energies, coinciding with the low-energy line characterizing the state of boron in combination with oxygen in the initial sample of iron boride. When two maxima characterizing different valence states of the atoms of iron with oxygen coincide, there appears a new maximum having an intermediate value of the bonding energy. Such a process illustrates the possibility of changing the energy level of the electron lines of one and the same element depending upon the degree of homogeneity of its valence state. Increase in the air exposure time of sample I leads to slight enrichment of the surface layer with iron.

FeB heating in an atmosphere of argon (sample II) (Fig. 2) and *in vacuo* (sample III) (Fig. 3) leads, on the whole, to the same changes in the electron spectra of iron, boron, and oxygen as treatment I. The line of $1s$ electrons of oxygen becomes narrower and shifts in the direction of higher bonding energy values. In the electron spectrum of iron there is only one line characterizing the bonding energy of $2p_{3/2}$ electrons of iron in combination with boron (removal of oxygen from iron atoms in boride takes place in this case). In the

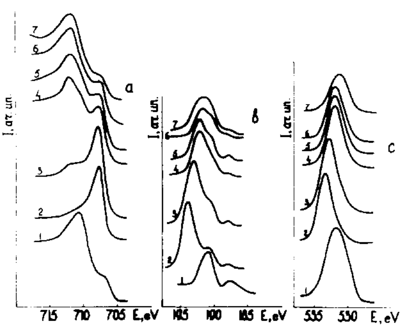

FIG. 2. X-Ray photoelectron spectra of iron (a), boron (b), and oxygen (c) in iron boride: (1) in the initial state; (2) after sample heating in argon; (3) after 10-sec air exposure of the sample; (4) after 24-hr air exposure of the sample; (5) after 48-hr air exposure of the sample; (6) after 10-day air exposure of the sample; (7) after 1-month air exposure of the sample.

electron spectrum of boron there is a maximum corresponding to the bonding energy of the 1*s* electrons of boron in combination with iron (low-energy), oxygen (intermediate and high-energy maxima). The high-energy maximum apparently characterizes the bonding energy of 1*s* in the anomalous surface oxygen combination with boron (B_XO_Y). As under treatment I, after treatments II and III the surface layer of FeB becomes enriched with oxidized boron.

On air exposure of samples II and III there may be observed fast oxidation of iron and coincidence of the two maxima in the electron spectrum of the boron "responsible" for the combination with oxygen, as well as simultaneous shifting of the common maximum in the direction of lower energy. The 0 1*s* line widens and shifts to the low-energy side. The surface layer of sample II becomes enriched with iron, and that of sample III is depleted of iron with increase of air exposure time.

Pickling of the FeB surface with protons (sample IV) (Fig. 4) leads to removal of oxygen from both iron and boron atoms. In this case, the degree of iron reduction in combination with oxygen is higher than that of boron reduction in combination with oxygen. There may be observed significant enrichment of the surface layer of FeB with iron (see Table I); therefore the ratio Fe_{total}/B_{total} becomes equal to 4.6. The electron spectrum of boron there are two maxima corresponding to the bonding energy of the 1*s* electrons of boron combined with iron in FeB and with oxygen in the anomalous combination (B_XO_Y). Consequently, both on thermal heatings I–III and on pickling of iron boride with protons, there forms

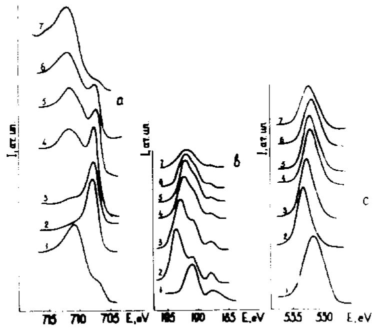

FIG. 3. X-Ray photoelectron spectra of iron (a), boron (b), and oxygen (c) in iron boride: (1) in the initial state; (2) after sample heating *in vacuo*; (3) after 10-sec air exposure of the sample; (4) after 24-hr air exposure of the sample; (5) after 48-hr air exposure of the sample; (6) after 10-day air exposure of the sample; (7) after 1-month air exposure of the sample.

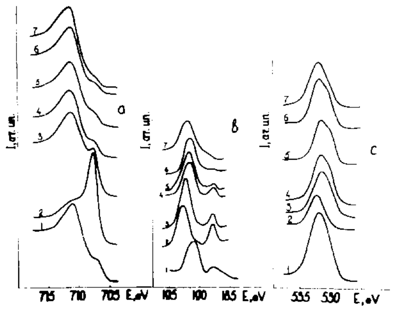

FIG. 4. X-Ray photoelectron spectra of iron (a), boron (b), and oxygen (c) in iron boride: (1) in the initial state; (2) after pickling with protons; (3) after 10-sec air exposure of the sample; (4) after 24-hr air exposure of the sample; (5) after 48-hr air exposure of the sample; (6) after 10-day air exposure of the sample; (7) after 1-month air exposure of the sample.

on its surface an oxygen combination of boron (B_XO_Y) in which the bonding energy of the core electrons of boron is much higher than in B_2O_3.

Unlike thermal treatments I–III, on treatment IV the electron line of 0 1*s* practically does not change its energy position, though the amount of oxygen in the surface layer (as follows from Table I) becomes 1.5 times lower than in the initial sample.

Iron boride subjected to proton bombardment (see Fig. 4 and Table I) quickly oxidizes on air exposure. This is particularly true with respect to iron atoms in boride. Even during the first 10 sec of air exposure, iron combines practically completely with oxygen. In the process of oxidation of sample IV iron depletion of the FeB surface layer takes place, and after 1-month air exposure the ratio Fe_{total}/B_{total} equals 1.7. In the electron spectrum of boron the increase of air exposure time of sample IV makes the maximum B_O shift in the direction of the low-energy side. In the electron spectrum of oxygen the increase of exposure time leads to no maximum energy state changes, but there appears significant peak from the low-energy side. We may suggest that, on the cleaned surface of sample IV, adsorption of oxygen occurs at the expense of a new ionic bond with transference of the electron charge to the oxygen atoms. The proportion of negatively charged oxygen in the total amount of oxygen in the surface layer of sample IV was found to be significant, which leads to widening of the 0 1*s* line in the electron spectrum of oxygen (Fig. 4b), and in some cases to splitting of this line.

FeB pickling with argon ions (sample V) (Fig. 5) leads to more uniform (in comparison with treatment IV) removal of oxygen from iron and boron atoms. The surface layer of iron boride becomes enriched with iron combined with boron. It is necessary to mention that, unlike samples I–III, in samples IV and V oxygen is removed from iron atoms (in iron boride) to a lesser degree.

In the electron spectrum of oxygen in sample V (see Fig. 5c) the electron line maximum, unlike samples I–IV, is shifted to lower bonding energies. The amount of oxygen in sample V, as compared with the initial sample of FeB, is lowered more than 1.5 times.

On air exposure of sample V, atoms of iron are oxidized faster than atoms of boron. From Fig. 5 and from Table I we can see that practically complete oxidation of iron occurs within 10 sec with simultaneous iron depletion of the sample surface layer. It is necessary to mention that after 10-day air exposure of sample V the surface layer of iron boride contains an extremely small amount of iron. On further exposure of sample V, the amount of iron on the surface of FeB increases and after 1-month exposure the ratio Fe_{total}/B_{total} becomes equal to 2.1.

In the electron spectrum of boron the maximum of B_O shifts to the side of lower bonding energies with increase of boron oxidation, and after a 10-day exposure of sample V the energy level of this maximum coincides with the position of the maximum of B_O in the initial sample of FeB. In the

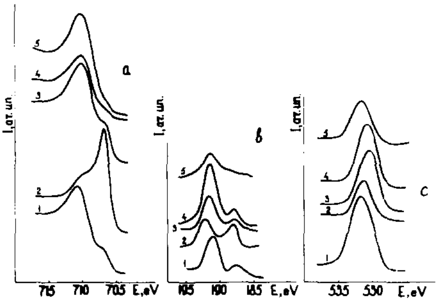

FIG. 5. X-Ray photoelectron spectra of iron (a), boron (b), and oxygen (c) in iron boride: (1) in the initial state; (2) after pickling with argon ions; (3) after 10-sec air exposure of the sample; (4) after 10-day air exposure of the sample; (5) after 1-month air exposure of the sample.

electron spectrum of oxygen the increase of air exposure time of sample V leads to shifting of the line of 0 1*s* to the side of higher bonding energies.

Comparison of the electron lines of iron, boron, and oxygen and correlation of the integral intensities of these lines under different kinds of treatment allows one to come to the following conclusions concerning the changes of composition and chemical state of the elements in the surface layer of FeB.

1. All kinds of thermal treatment of iron boride and pickling of its surface with argon ions and with protons lead to removal of chemically combined oxygen from the iron atoms. No formation of pure iron was found in this case.

2. On thermal treatments boron in the surface layer of FeB becomes oxidized. There probably occurs formation of a new surface anomalous combination of boron with oxygen (B_XO_Y) in which the bonding energy of the 1*s* electrons of the boron is higher than in B_2O_3. After pickling of the iron boride surface with argon ions and with protons, the amount of boron combined with iron increases in comparison with boron combined with oxygen.

3. Thermal treatments of iron boride lead to iron depletion of the surface layer, but methods of pickling lead to strong enrichment.

4. On air exposure of samples subjected to thermal treatment *in vacuo* and in hydrogen, the surface of FeB becomes enriched with iron, but in the other cases it becomes depleted.

5. Samples of iron boride subjected to pickling become strongly oxidized on further air exposure.

Thus, the composition of the surface layer and the chemical state of the elements in iron boride are not constant, both in the case of alloys and in the case of compound oxides, but depend upon the method of sample treatment.

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