Changes in the Chemical State and Composition of the Surface of Iron Oxides due to Argon Ion Sputtering

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XPS has been used for investigating the influence of argon ion sputtering on the chemical state and composition of the surface of three iron oxides, Fe_2O_3, Fe_2NiO_4 and Fe_2ZnO_4. XPS spectra of these oxides were measured, while bombardment by argon ions of 3keV were interrupted. The chemical state of the surface of these oxides was found to change from Fe^{3+} to Fe^{2+} by argon ion bombardment, suggesting the reduction of the surface of these oxides. This behavior was attributed to a decrease of the oxygen composition of the surface of these oxides. Then, particular attention should be paid in analysis of a layered structure of oxides formed on the iron and steel surface.

1. Introduction

Various oxide layers are formed on the surface of iron and steel by annealing under an atmosphere with oxygen at high temperatures [1]. The surface of iron oxides has been analyzed by XPS so far [2-6]. By combination with ion bombardment, a depth profile of an oxide layer is often investigated. The depth profile may be converted to the quantitative chemical composition as a function of depth of the oxide layers, by correcting the elemental sensitivity and sputtering rate. This data processing takes no account of preferential sputtering of any element. However, it has been pointed out that preferential sputtering in some compounds leads to deviation from real chemical composition and state [7-11]. Thus, sputtering characteristics of elements in iron oxides should also be studied, in order to evaluate a real quantitative depth profile of oxide layers formed on the iron surface.

Thus, the objective of this work is to study the influence of argon ion sputtering on the chemical composition and state of the surface of three typical iron oxides, Fe_2O_3 (corundum), Fe_2NiO_4 and Fe_2ZnO_4 (spinel). XPS spectra of these oxides are measured, while argon ion bombardment is interrupted. Based on these results, characteristic features in sputtering of the iron oxides are discussed.

2. Experimental

Pellets of Fe_2O_3, Fe_2NiO_4 and Fe_2ZnO_4 of 3mm in thickness were prepared by pressing of oxide powders and subsequently heating them at 1473K for 10h and at 773K for 72h. Small rods of 2mm square and 6mm length were cut from the pellets. Their cleaved surfaces were analyzed by XPS.

XPS analysis with incident X-ray of Al Kα was carried out to evaluate the chemical state and composition of the surface of these oxide samples. XPS spectra of O 1s, Fe 2p, Ni 2p, Zn 2p and Zn LMM Auger spectra were mainly measured. A neutralizer by electron gun was applied to measurement of non-conductive Fe_2O_3. Ion bombardment, by the rate was about 0.02 nm/s for Fe_2O_3, was performed by argon ions of 3keV.

3. Results and Discussion

3.1 Changes in the chemical state

Figures 1 (a), (b) and (c) show O 1s XPS spectra from cleaved Fe_2O_3, Fe_2NiO_4 and Fe_2ZnO_4, respectively The position and shape of these spectra are similar, and no change was observed by ion bombardment.

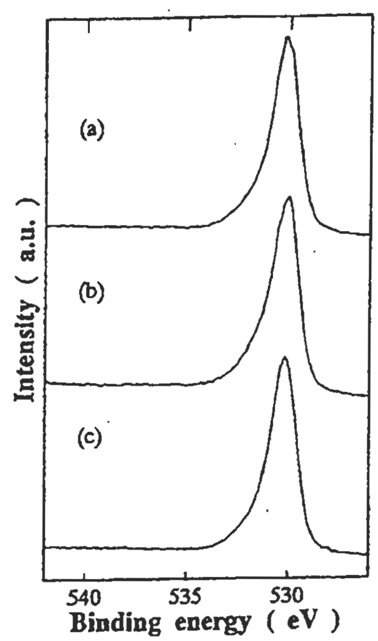

Fig.1 O 1s XPS spectra from cleaved (a) Fe_2O_3, (b) Fe_2NiO_4 and (c) Fe_2ZnO_4.

On the other hand, XPS spectra of metallic elements were influenced by argon ion bombardment, as follows. Figures 2 (a), (b), (c) and (d) describe Fe 2p XPS spectra from Fe_2O_3 sputtered for 0s, 30s, 60s and 300s, respectively. These spectra show that iron in the surface of cleaved Fe_2O_3 is Fe^{3+}, and argon ion bombarding induces the reduction of Fe^{3+} to Fe^{2+} [11]. Such reduction behavior was also observed in Fe_2NiO_4 and Fe_2ZnO_4.

Characteristic changes by argon ion bombardment were also found in Ni XPS spectra. Figures 3(a), (b), (c), (d) and (e) show Ni 2p XPS spectra from Fe_2NiO_4 bombarded by argon ions for 0s, 30s, 60s, 150s and 300s, respectively. By argon ion bombardment, a new peak appears at about 853eV. This peak corresponds to the formation of metallic nickel.

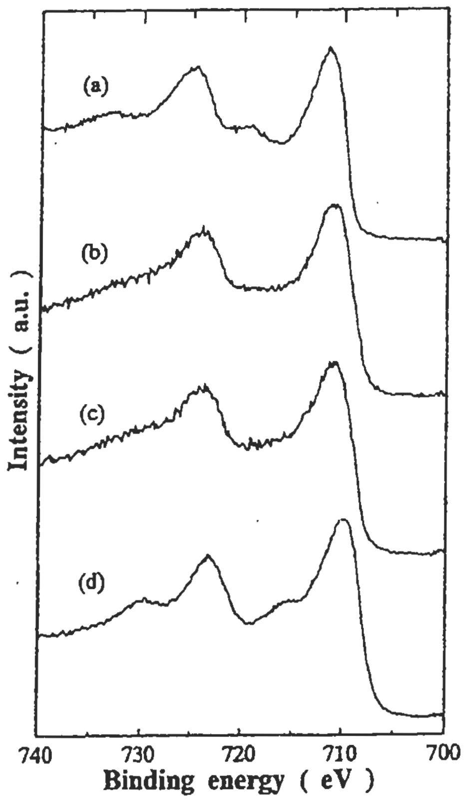

Fig.2 Fe 2p XPS spectra from Fe_2O_3 bombarded for (a) 0s, (b) 30s, (c) 60s and (d) 300s.

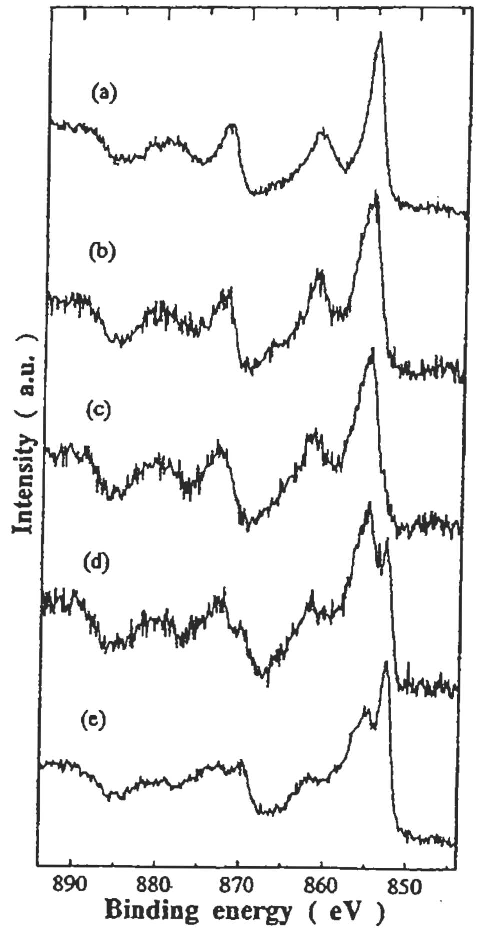

Fig.3 Ni 2p XPS spectra from Fe_2NiO_4 bombarded for (a) 0s, (b) 30s, (c) 60s, (d) 150s and (e) 300s.

However, little characteristic change by argon ion bombardment was found in Fe_2ZnO_4, as shown in Figs. 4(a) and (b), which show Zn 2p XPS spectra from Fe_2ZnO_4 bombarded by argon ions for 0s and 300s, respectively. Significant chemical change in Zn is known to reveal in Auger spectra of Zn. Figure 5(a) and (b) show Zn LMM Auger spectra from Fe_2ZnO_4 bombarded by argon ions for 0s and 300s, respectively. In spite of these different measurements, significant spectral changes by argon ion bombardment are not detected.

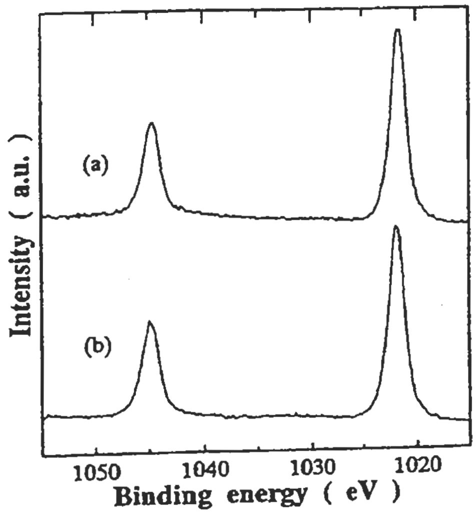

Fig.4 Zn 2p XPS spectra from Fe_2ZnO_4 bombarded for (a) 0s and (e) 300s.

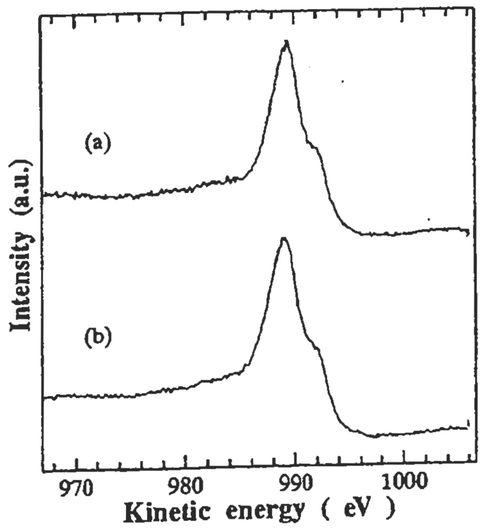

Fig.5 Zn LMM Auger spectra from Fe_2ZnO_4 bombarded for (a) 0s and (e) 300s.

3.2 Compositional changes

Variation in the chemical state of the surface of these oxides should be compared with the surface composition of the oxides analyzed by XPS. Figures 6 (a), (b) and (c) show apparent sputtered depth profiles of the Fe_2O_3, Fe_2NiO_4 and Fe_2ZnO_4 obtained by analyzing the surface of the cleaved oxides from XPS measurement while interrupting argon ion bombardment. These depth profiles clearly show oxygen in the oxides is preferentially sputtered by argon ions, while iron remains on the sample surface. In addition, argon bombardment induces to enrich the nickel component, which is consistent with changes in chemical state of nickel as shown in Fig.3. On the other hand, the zinc composition on the surface of Fe_2ZnO_4 is not largely influenced by argon ion bombardment. This corresponds to the results on the chemical state of zinc, as shown in Figs.4 and 5.

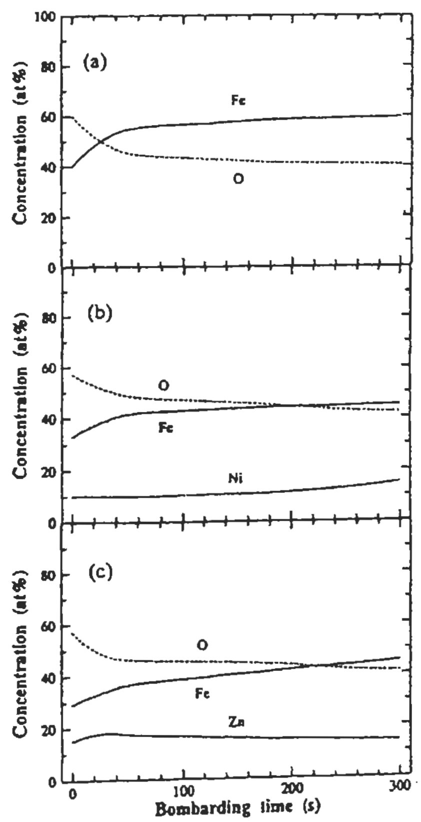

Fig.6 The surface composition of (a) Fe_2O_3, (b) Fe_2NiO_4 and (c) Fe_2ZnO_4, as a function of argon ion bombarding time.

The schematic illustration of ions in the initial surface and ion-bombarded surface of these oxides may be summarized from the results obtained in this work, as shown in Fig.7. Fe^{3+} and Ni^{2+} ions in the oxides are, more or less, reduced to Fe^{2+} and Ni^0 by argon ion bombardment, respectively. On the other hand, Zn^{2+} ions are largely unchanged. These characteristic variations in the surface of the oxides may be related to their stability. Also, it should be noted that the oxygen composition in depth profiles of the oxides is underestimated because of preferential sputtering by argon ion bombardment. This situation may be similar to depth analysis of oxide scales formed on iron and steel. Therefore, in order to obtain an accurate depth profile from measured XPS data using ion bombardment, some correction should be made. The correction should take into account changes in the chemical state and composition occurring the surface of the oxides by ion bombardment, although development of the quantitative procedure is now in progress.

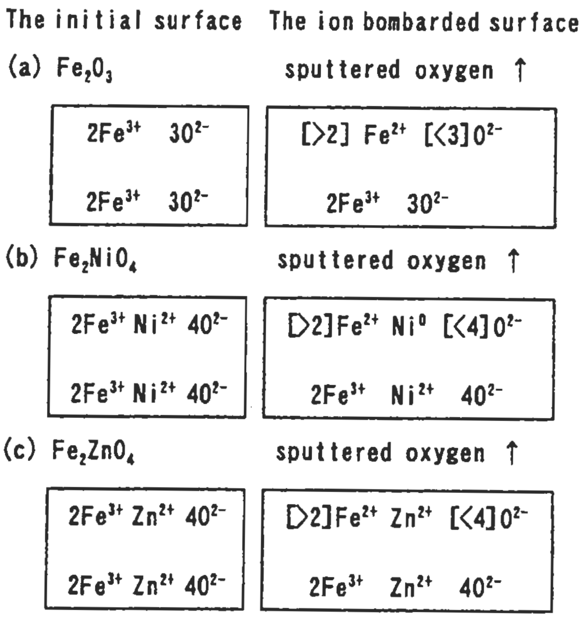

Fig.7 Schematic illustration showing distribution of ions in the initial surface and ion bombarded surface of (a) Fe_2O_3, (b) Fe_2NiO_4 and (c) Fe_2ZnO_4.

4. Concluding remarks

XPS was used for analyzing the influences of argon ion bombardment on the chemical state and composition of the surface of Fe_2O_3, Fe_2NiO_4 and Fe_2ZnO_4. The main results are as follows:

1) The chemical state of the surface of these oxides changes from Fe^{3+} to Fe^{2+} by argon ion sputtering, indicating the reduction of the surface of these oxides.
2) Ni^{2+} in Fe_2NiO_4 is changed to Ni^0 by argon ion bombardment, while Zn^{2+} in Fe_2ZnO_4 is largely unchanged.
3) These characteristic features of ions in these oxides are correlated with the decrease of the oxygen composition of the surface of these oxides.

5. References

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