Characterization and Control of Aluminum Oxide Thin Films Formed on Surfaces of FeCo-V Alloys

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X-ray photoelectron spectroscopy (XPS), ellipsometry, and cathode luminescence were utilized for characterizing oxide films formed on the surfaces of FeCo-V alloys (Permendur) that contained small amounts of aluminum via annealing under a low partial pressure of oxygen. XPS spectra showed that the oxide films were composed primarily of aluminum oxide, which was a result of preferential oxidation of aluminum on the surfaces of the alloys during annealing. The thicknesses of the oxide films were estimated from XPS depth profiles coupled with the sputtering rate of a SO$_2$/Si film, and the thicknesses were compared with those of the oxide films measured via non-destructive ellipsometry. The thicknesses obtained from the depth profiles may have been overestimated because of a difference in sputtering rate between silicon oxide and aluminum oxide. As measured via ellipsometry, the thickness of the aluminum oxide thin film, which was less than 100 nm, increases with the aluminum content in the alloys. Wide XPS spectra from the sample surfaces with different roughness suggested that the aluminum oxide thin films were homogeneously formed on the smooth surfaces, whereas metallic elements in the alloy substrates were detected on the rough surfaces. Furthermore, the electrical resistivity of the alloys with the smooth surfaces increases significantly with the aluminum content, which may be attributable to the formation of the aluminum oxide thin film. These results indicate that the addition of a small amount of aluminum and surface smoothness are important for controlling formation of the aluminum oxide thin films with high resistivity in FeCo-V alloys by annealing under a low partial pressure of oxygen.

Keywords: FeCo alloy; Aluminum oxide; Preferential oxidation; Electrical resistivity

I. INTRODUCTION

Fe- and Co-based alloys are expected to be applied extensively to functional materials owing to their ferromagnetic properties. Among those alloys, near-equatomic FeCo alloys are known to offer high saturation magnetization and higher permeability [1, 2]. However, they are brittle at room temperature, as these binary alloys exhibit the B2-ordered structure. As the addition of a third element and heat treatments can result in ductile alloys for cold-working, the mechanical properties of FeCo alloys can be improved by modifying the chemical composition and heat treatment. It was shown that the addition of vanadium induced the disordered structure in Fe-Co alloys, making it ductile after appropriate heat treatments, thereby increasing their resistivity [1, 2]. Hence, FeCo-2V alloys, referred to as Permendur, are industrially manufactured. In addition to the soft magnetic properties of Fe-Co binary alloys, such as high saturation magnetic flux density and high permeability in FeCo-2V alloys, their magnetostrictive properties are of significant importance...
interest as well [3, 4]. To apply Fe-Co alloys to actuators and motors, their magnetic and surface properties must be improved because they are used as sheets with insulated surface films. Hence, it is necessary to manufacture alloy sheets with insulated films even though Permendur is shaped primarily as bars [5]. To achieve a high volume fraction of magnetic materials, these insulated films must be extremely thin, as exemplified in non-oriented silicon steel with coating [5].

The oxidation of a specific element at high temperature is regarded as a process to form an insulated oxide thin film on the surfaces of alloys under controlled annealing conditions [6]. Typically, aluminum oxide thin films are formed on the surfaces of Fe-Al alloys, and they are analyzed using a few techniques [7, 8]. The annealing atmosphere is changed with different partial pressures of oxygen, which are controlled by H₂O/H₂ ratios in the gas. X-ray photoelectron spectroscopy (XPS) results showed that an aluminum oxide film was formed on the surfaces of the samples annealed at high temperatures under a low partial pressure of oxygen. Secondary ion mass spectrometry depth profiles showed that the surfaces of the samples annealed at high temperatures under a low partial pressure of oxygen were covered with an aluminum oxide thin film of approximately 50 nm in thickness. These results indicate that aluminum, one of the less noble elements, is preferentially oxidized in the Fe-based alloy containing such elements annealed under a low partial pressure of oxygen. This annealing process is considered effective for fabricating aluminum oxide thin films on the surface of FeCo-V alloys, as bulk aluminum oxide is insulated.

The objective of this study is to characterize oxide films formed on the surfaces of FeCo-V alloys (Permendur) added with small amounts of aluminum by annealing under low partial pressures of oxygen. The samples with rough or smooth surfaces were prepared by lapping using emery papers or subsequent polishing. XPS, ellipsometry, and cathode luminescence (CL) were utilized to analyze oxide films, and the electrical resistivity was measured to investigate the insulation property of the surface oxides.

II. EXPERIMENTAL

A. Samples

Ingots of FeCo-V alloys (49% Co–2% V, in mass%) were cast after induction melting of raw materials. Small amounts of aluminum, i.e., 0.25, 0.50, and 0.75 mass%, were added to the alloys. These alloys are denoted as Samples A, B, and C, respectively. They were hot-forged and rolled to sheets of ~2 mm in thickness. The alloy sheets were lapped using emery paper up to #800 and were subsequently buff-polished using alumina powder. The surface roughnesses $R_{\text{max}}$ of the lapped and polished samples were measured to be 1.4 and 0.9 μm by a roughness meter (Mitutoyo Surftest SJ-301), respectively.

The alloy sheets were annealed at about 1173 K for 0.5 h under the pure hydrogen, in which the amount of residual oxygen was very low (less than ca. $10^{-13}$ Pa), to fabricate aluminum oxides on the alloy sheets by annealing. The surfaces of the annealed samples were primarily blue, which was a result of color interference by films on the substrate.

B. Measurements

XPS measurements were performed to analyze the chemical composition and states of the FeCo-V alloys surfaces using PHI-5600 and PHI Versaprobe-II, in which the incident X-ray was monochromatized Al Kα. The X-ray beam sizes of PHI-5600 and PHI-Versaprobe-II were approximately 800 and 100 μm, respectively. PHI-5600 coupled with argon ion sputtering was used for depth profiling the surface films [9]. Meanwhile, Versaprobe-II with Al Kα of 100 μm in the beam diameter was used to analyze the microscopic areas of crater edges, which correspond to specific portions of the depth profiles.

Automatic ellipsometry (Mizojiiri Co. Ltd.) was used to characterize the thickness and refractive index of the oxide films. The light of a wavelength 632.8 nm was irradiated onto the sample surface by an incident angle of 60°. The average values measured at nine points were used to determine the thickness and refractive index.

CL spectra of the samples were obtained using a customized scanning electron microscope CL (SEM-CL) system. Details regarding the SEM and acquisition of the CL spectra have been reported previously [10–14]. In brief, the CL spectra were acquired using a spectrometer (QE65Pro, Ocean Optics Inc.) by attaching an optical fiber to an SEM equipment (Mighty-8DXL, TECHNEX). The light emitted from the samples was collimated using an off-axis parabolic mirror, and the collimated light was collected using a plano-convex lens attached to the tip of the optical fiber. The acquisition time for the CL spectra was 10 s.

To characterize the electrical property of the surface oxides formed on the alloy sheets, the electrical resistivity of the surface oxide thin film was measured by sandwiching the oxide thin film of interest between the alloy substrate and a copper electrode. The contact area was usually 4 mm × 3.25 mm for samples with an oxide thin film.

Figure 1: XPS depth profiles of Sample B.
III. RESULTS AND DISCUSSION

A. XPS depth profiles

Figure 1 shows XPS depth profiles of Sample B, which was annealed under a low partial pressure of oxygen. The profiles were obtained using PHI-5600 without charge-up correction combined with the sputtering of 3 kV Ar ions, in which the sputtering rate of SiO$_2$/Si was 2.93 nm min$^{-1}$. The surface thin film comprised aluminum and oxygen, suggesting that an aluminum oxide film covered the substrate of the FeCo-V alloy. If the sputtering rate of SiO$_2$/Si is adapted in the depth profiles, then the thickness of the oxide film will be calculated from the data. In these calculations, it was assumed that the sputtering rate of Al$_2$O$_3$ was similar to that of SiO$_2$. More realistic results of the oxide film thicknesses were obtained from non-destructive ellipsometry, which will be compared later.

B. XPS spectra near the sputtering crater

Figure 2 shows a photograph of the sputtering crater of Sample B, in which the area in blue is the oxide thin film, whereas the metallic portion is the substrate obtained via sputtering. To obtain in-depth information from the crater edge, the microscopic XPS spectra were measured at points (a), (b), and (c) in small X-ray beams of approximately 0.1 mm in diameter.

The sample surface was sputtered slightly by argon ions to remove carbon contamination. Figures 3 and 4 shows O 1s and Al 2p XPS spectra, respectively, obtained from points (a), (b), and (c) in Figure 2. These depth profiles of Sample B annealed under the low partial pressure of oxygen showed that the oxide films were composed of aluminum oxide.

Figure 5(a–c) shows the V 2p$_{3/2}$ XPS spectra from points (a), (b), and (c) in the sputtering crater of Figure 2. Similarly, the Fe 2p$_{3/2}$ and Co 2p$_{3/2}$ XPS spectra of points (a), (b), and (c) in the sputtering crater of Sample B are shown in Figures 6 and 7, respectively. The binding energies of V 2p$_{3/2}$, Fe 2p$_{3/2}$, and Co 2p$_{3/2}$ in these XPS spectra are similar to those of the metallic states of V 2p$_{3/2}$ (512.8 eV), Fe 2p$_{3/2}$ (707.0 eV), and Co 2p$_{3/2}$ (778.2 eV). Furthermore, as a very thin native oxide layer was formed on the surface by exposure to air after XPS depth profiling [15, 16], additional sputtering was conducted to remove carbon contamination in microscopic XPS analysis. However, a small component of the native oxide was observed in each spectrum, which indicates that metallic elements of vanadium, iron, and cobalt were primarily present in the substrate and near the interface.

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**Figure 2**: Photograph of the sputtering crater of Sample B; points (a), (b), and (c) were analyzed by XPS with an X-ray of 100 μm in diameter.

**Figure 3**: O 1s XPS spectra of points (a), (b), and (c) in sputtering crater of Sample B. Baselines of spectra (a) and (b) are denoted as broken lines.

**Figure 4**: Al 2p XPS spectra of points (a), (b), and (c) in sputtering crater of Sample B. Baselines of spectra (a) and (b) are denoted as broken lines.

**Figure 5**: Al 2p XPS spectra of points (a), (b), and (c) in sputtering crater of Sample B. Baselines of spectra (a) and (b) are denoted as broken lines.
addition, it may be remarked that vanadium is slightly enriched at the interface between the aluminum oxide thin film and the substrate, though the chemical state of vanadium may be affected by the oxide film.

C. Ellipsometry and CL

The thickness and refractivity of the aluminum oxide thin films prepared in the present study were measured using ellipsometry. The results are summarized in Table 1. The thickness of the oxide thin films increased with aluminum content. The refractivity values were consistent with that of aluminum oxides [17, 18], although the refractivity of Sample A was lower than those of Samples B and C. This indicated that the chemical composition or density of the oxide film of Sample A deviated from that of aluminum oxide, which may arise from vanadium enrichment between the oxide film and substrate.

Figure 8 shows the thickness values of aluminum oxide films on the FeCo-V alloys measured using ellipsometry versus aluminum content. The thickness values were compared with those by XPS depth profiles combined with the sputtering rate of SiO2/Si, as plotted in Figure 8. The thickness values obtained from the XPS depth profiles were considered to be overestimated because it resulted from the difference in sputtering rate between SiO2 and Al2O3. Comparing the thickness values with those of Fe-Al alloys in previous studies [7], the present results obtained via ellipsometry appear to be reasonable.

Figure 9 shows the CL spectra from aluminum oxide films formed on surfaces of FeCo-V alloys with different aluminum contents. The shape of these spectra was similar to those of oxides formed on Fe-Al alloys in a previous study [11]. In that study, CL and X-ray emission optical luminescence images enabled us to distinguish the Al2O3 scale from other scales from the luminescent color of the Al2O3 as

| Sample | Thickness (nm) | Refractive index |
|--------|---------------|-----------------|
| A      | 47.2 ± 8.9    | 1.670 ± 0.008   |
| B      | 73.3 ± 14.6   | 1.816 ± 0.020   |
| C      | 84.9 ± 6.4    | 1.815 ± 0.004   |

Figure 6: Fe 2p XPS spectra of points (a), (b), and (c) in sputtering crater of Sample B. Baselines of spectra (a) and (b) are denoted as broken lines.

Figure 7: Co 2p XPS spectra of points (a), (b), and (c) in sputtering crater of Sample B. Baselines of spectra (a) and (b) are denoted as broken lines.

Figure 8: Thickness of the aluminum oxide films on the FeCo-V alloys versus the aluminum content. The thickness values were estimated from sputtering XPS depth profiles combined with sputtering rate of SiO2/Si (●) and the ellipsometry measurements (▲).

Figure 9: Cathode luminescence spectra from the aluminum oxide films formed on the surfaces of the FeCo-V alloys with different aluminum contents.
well as observe the surface morphology of the oxide scale. The CL intensity of a peak at 695 nm in the spectra can be used to determine the scale thickness when relatively thick Al₂O₃ films are characterized.

D. Formation conditions of aluminum oxide thin films

To understand the formation process of aluminum oxide thin films, the mechanism of oxide film formation should be discussed based on the thermodynamic properties of the elements involved. It was assumed that the preferential oxidation of aluminum in the present alloys with residual oxygen in the atmosphere occurred on the alloy surface, even though a small amount of residual oxygen remained in the hydrogen atmosphere [7], in which the partial pressure of oxygen \( p_{O_2} \) in the present annealing conditions was estimated to be \( 1 \times 10^{-13} \) Pa. The original hydrogen gas with a dew point of ca. 243 K was used in the present work, but the purity of hydrogen is influenced by adsorbed species in a gas piping line.

The Ellingham diagram of formation free energy of metallic oxides of cobalt, iron, vanadium, and aluminum is shown in Figure 10(a). Typical annealing conditions under high and low partial pressures of oxygen are denoted in this figure, where the low partial pressure of oxygen in the present annealing condition is positioned between formation free energies of vanadium and aluminum. Figure 10(b) illustrates the layered structure of these samples annealed under different conditions. When Fe-Al alloys were annealed in the high partial pressure of oxygen, aluminum was oxidized and enriched near the substrate and oxide layer [19], as illustrated in the upper-layer structure in Figure 10(b). Meanwhile, if the Fe-based alloy was annealed in a hydrogen atmosphere such as in a low partial pressure of oxygen, aluminum oxide thin films were formed, and other metallic elements were not oxidized. The cross-section of the formation of aluminum oxide thin film is shown in the lower schematic of Figure 10(b). These results are reasonable for smooth surfaces; however, it was observed that the oxidation of aluminum as a thin film did not always occur. For example, Figure 11 compares the wide XPS spectra of smooth and rough surfaces of Sample A, of which the surfaces were slightly sputtered to remove carbon contamination. The elements of vanadium, iron, and cobalt were detected in the rough surface despite the same composition of the substrate, whereas only aluminum and oxygen were detected on the smooth surface. In general, since thermal expansion is large between the oxide and alloy, it is considered that the aluminum oxide thin film formed on the rough surface was relatively easily broken during cooling after annealing at high temperature. Such surface characteristics of an aluminum oxide thin film formed on rough surface should be considered in discussing the physical property of the samples.

E. Resistivity of aluminum oxide thin films

Finally, the electrical resistivity of the FeCo-V alloys with aluminum oxide films was measured to compare the surface analytical results with the property. The electrical resistivity of the FeCo-V alloys with different surface roughness is plotted as a function of aluminum content, as shown in Figure 12. These alloys were annealed under a low partial pressure of oxygen. The resistivity of the alloys with the smooth surfaces was higher than that of the alloys with rough surfaces, which is likely a result of the inhomogeneity in thickness and crystallinity of aluminum oxide thin films on the alloys with rough surfaces. A difference of area of the aluminum oxide film between XPS analysis and resistivity measurement should be also taken into account, when the relationship between the resistivity and aluminum content is strictly discussed. This is because XPS is surface-sensitive analytical method, while the electrical resistivity in the present measurement condition is likely to be affected by the roughness of the sample surface. Nevertheless, the results obtained by the present investigation indicate that the smoothness of surfaces and aluminum content are important

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**Figure 10:** (a) Ellingham diagram of Co, Fe, V and Al. (b) Schematics of layered structure of samples annealed under different annealing conditions.

**Figure 11:** Wide XPS spectra from Sample B with the smooth surface (a) and the rough surface (b).
factors for controlling the resistivity by the coverage of alu-
minum oxide thin films in present alloys.

IV. CONCLUSIONS

X-ray photoelectron spectroscopy, ellipsometry, and CL were utilized for characterizing oxide films formed on sur-
faces of FeCo-V alloys added with small amounts of alumi-
num by annealing under a low partial pressure of oxygen. The results showed that thin films of aluminum oxide formed via the preferential oxidation of aluminum during annealing. The thickness of the oxide films obtained by non-destructive ellipsometry was less than 100 nm, which increased with the aluminum content. Additionally, it was shown that aluminum oxide thin films formed homoge-
nously on smooth surfaces, whereas metallic elements of the alloys were detected on rough surfaces. The electrical resis-
tivity increased significantly with the aluminum content on
the smooth surface, which corresponds to the present results
obtained by surface analytical methods. Although more sys-
tematic characterization may be required to well control of the surface properties, these results indicate that the rough-
ness of alloy surfaces and aluminum content are important factors for preparing aluminum oxide thin films with high
resistivity by annealing under a low partial pressure of oxy-
gen.

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