Surface analysis of thin stainless steel films and thick-coated steel by simultaneous application of conversion electron and X-ray Mössbauer spectroscopy

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Abstract

A dual He/Ar gas counter for simultaneous measurements of conversion electron and X-ray Mössbauer spectra (CEMS and XMS) has been developed and applied to characterization of thin stainless steel films and thick-coated steel. For thin stainless steel films, three depth-selective CEMS spectra were simultaneously obtained by detecting the electrons with three different energy ranges (1 to 3 keV, 3 to 6.5 keV, and 6.5 to 12 keV). The iron oxide layer (4 nm in thickness) on stainless steel was clearly observed by detecting high-energy electrons (>6.5 keV). Ferromagnetic phase was produced by a magnetron Ar sputtering of austenitic stainless steel, and the average hyperfine magnetic field increased from 25 to 28 T by thermal treatment. The magnetic phase was partially converted into austenite (γ-phase) at 500 °C.

In the case of thick-coated steel, where the coating was produced by electrochemical sulfurization, CEMS and XMS spectra were simultaneously obtained by detecting all the resonant electrons above 3 keV as well as X-rays between 3 and 6.5 keV. The area ratios of the subspectra assigned to the austenite and ferrite phases were different in the CEMS and the XMS spectra. This suggests that austenite and ferrite at the surface had selective reactivity with the sulfurizing agent.

It was shown that the phase analysis of the surface, interface, and substrate was simply and effectively realized by using a dual He/Ar gas flow counter.

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1. Introduction

Mössbauer spectroscopy provides numerous information on electron density or chemical states, electron configurations, and magnetic states around resonant nuclei. Conversion electron Mössbauer spectroscopy (CEMS) is useful for characterization of surface states of iron steel [1]. Following the Mössbauer effect of $^{57}\text{Fe}$ (recoilless nuclear absorption of a 14.4 keV γ-quantum), 7.3 keV K-electrons (the emission probability: 80%), 13.6 keV L-electrons (8%), and 5.5 keV Auger electrons (63%) are emitted together with secondary electrons of reemitted 6.4 keV Kα X-rays (23%) and 14.4 keV γ-rays (10%). The percentage values refer to the γ-absorption as 100%. It was estimated that 65% of all the conversion electrons formed in Fe metal are emitted from within 60 nm, and 90 % of them from within 300-nm depth of the surface [2]. The structure of the interface region on steel substrate beneath phosphate coating can be investigated using the relative intensities of sextet peaks of the iron substrate observed in CEMS spectra. It was found, nondestructively, that the smooth surface became rough when the iron specimen was kept in the phosphating bath for a long time [3].

On the other hand, oxidized stainless steel becomes a good pH sensor with a quick response [4]. Stainless steel with a gentle oxidizing pretreatment is used for vacuum vessels because the thin oxide film absorbs less gases than the pure metallic surface [5]. The oxide surfaces of austenitic stainless steels such as AISI (or SUS) 316 and AISI (or...
SUS 304 [6] have been characterized by integral CEMS (ICEMS). However, ICEMS is not so sensitive to the uppermost surface layer because of the contribution of secondary electrons of resonant X-rays and γ-rays. The possibility of depth-selective analysis of samples using a gas flow proportional counter has been demonstrated [7], and a semiquantitative analysis was reported [8]. A He gas counter has high efficiency to detect all conversion electrons and insensitivity to incident γ- and X-rays. The possibility of depth-selective analysis of samples using a gas flow proportional counter has been demonstrated [7], and a semiquantitative analysis was reported [8]. A He gas counter has high efficiency to detect all conversion electrons and insensitivity to incident γ- and X-rays. For better practical applications, we improved our CEMS measurement system so as to obtain three Mössbauer spectra simultaneously by detecting the electrons discriminated into three energy regions such as low (1 to 3 keV), middle (3 to 6.5 keV), and high energy (6.5 to 12 keV). Electrons emitted from a large depth of the solid have a significant energy loss. The detected electrons, which have lower energy, deliver chemical information from deeper regions. The high-energy range contains the components of 7.3 keV K conversion electrons and 7.3 + 5.5 keV pile-up peaks. Liljequist et al. [9] theoretically estimated that the maximum depth range for 6.6 keV energy lost electrons of 7.3 keV conversion electrons in Fe/Stainless steel is about 100 nm. The middle energy range contains 5.5 keV Auger electrons, secondary electrons of 6.4 keV X-rays, and energy loss electrons of 7.3 keV conversion electrons. The detectable low-energy electrons contain many energy loss electrons through scattering in the deep layers. Thus, depth-selective CEMS or differential CEMS (DCEMS) can provide a simple layer-by-layer analysis within several 100 nm although the precise depth analysis is difficult. The state of the thin interface region between the oxide layer and Fe–Cr ferritic stainless steel substrate can be characterized by the analysis of hyperfine field distributions of DCEMS spectra recorded with a He gas counter [10]. Surface layers of carbonitridized stainless steels have been studied by CEMS and XMS [11]. CEMS spectra of electrodeposited and ion beam mixed Fe–Ni–Cr alloys show a broad magnetic sextet [12]. The principle of CEMS is simple, but there are not so many DCEMS and XMS data published for practical analysis.

In this paper, the simultaneous measurement of three DCEMS spectra using a He gas counter was applied to the analysis of thin stainless steel films deposited by an RF magnetron Ar sputtering method. Simultaneous measurement of CEMS and XMS spectra was applied to the analysis of thick surface coatings prepared by sulfurizing high-tension steel. Simple and practical layer-by-layer analysis was effectively carried out using a dual He/Ar gas counter.

2. Experimental setup

Stainless steel films with thickness of ca. 200 nm were deposited on Si wafer by an RF magnetron Ar gas sputtering...
method using SUS304 austenite plate as a target. Some deposited films were further oxidized in air by heating at 400 and 500 °C for 2 h. Steel specimens thickly coated by electrochemical sulfurization were obtained as commercial products. A dual gas flow counter was designed and built in our laboratory (Fig. 1). Two gas chambers were separated with Al-deposited Mylar film, and one chamber was fed with He+CH₄ gas flow for CEMS and the other one with Ar+CH₄ gas flow for XMS measurements. The direction of the incident γ-rays was perpendicular to a sample plane. Three DCEMS spectra were simultaneously recorded using ⁵⁷Co(Cr) radiation source of 1.85 GBq activity, He+5% CH₄ gas at 15 cm³/min flow rate, and applying high voltage at 950 V. XMS spectra were obtained with the help of flowing Ar+5% CH₄ gas and applying high voltage at 1300 V. The spectrum analyses including calculation of hyperfine field distributions were carried out with the Moss-winn program [13]. Glow discharge optical emission spectroscopy (GDOES; Jobin Yvon RF5000, Holiba) was used for the depth profile analysis of the elementary composition under the conditions of 13.56 MHz frequency, 40 W power, and 6.8 kPa Ar pressure. The sampling time was 0.01 s, and the area of 4-mm diameter was sputtered with Ar⁺ ions of low energy (50 eV) at a current density of the order of 100 mA mm⁻². Transmission electron microscopy (TEM) and scanning atomic force microscopy (AFM) were complementarily used for the estimation of the oxide layer thickness as well as the surface roughness on the oxide layers.

3. Results

3.1. DCEMS of as-deposited stainless steel films

No other peaks were observed else a broad sextet in DCEMS of the as-deposited film by Ar sputtering. The stainless steel deposited films were heated in air at 400 and 500 °C for 2 h. DCEMS and GDOES spectra are shown in Figs. 2 and 3. It was estimated from GDOES that the total thickness of the oxide layers produced was about 10 nm. Fe atoms were concentrated in the uppermost layers within 5 nm, and Cr atoms were located in the intermediate layers between 4 and 10 nm, and Ni concentration decreased within the overall surface oxide layers. Three CEMS spectra were simultaneously obtained.

Fig. 2. DCEMS (left) and GDOES (right) spectra of as-deposited films, oxidized in air at 400 °C for 2 h. Sputtering time of 1.0 s corresponds to 24 nm in thickness. Electrons in CEMS detected are: top, high energy (>6.5 keV); center, middle energy (3–6.5 keV); and bottom, low energy (1–3 keV).
by discriminating three different energy regions of emitted electrons, and fit by two sextets, one with Lorenzian line shape and another one with magnetic hyperfine field distribution.

The magnetic sextet with hyperfine field, $H_{mf} = 51$ T, quadrupole shift, $\Delta = -0.33$ mm/s and isomer shifts, $\delta = 0.33$ mm/s, was observed in DCEMS. It is clearly assigned to hematite ($\alpha$-Fe$_2$O$_3$). The hyperfine field of 51 T was a little smaller than that of hematite powder (52 T). The iron oxides may be mixed with a small amount of Cr to form $\alpha$-(Fe, Cr)$_2$O$_3$. A large amount of hematite was located at the top layer because its sextet in the CEMS spectra was most intense for the high-energy range of the electrons detected (>6.5 keV). The intensity of this sextet decreased with the decrease of the electron energy. This shows that the layer-by-layer analysis by a He gas counter can be simply realized. CEMS spectra obtained by detecting low-energy electrons had a low peak-to-background ratio because the low-energy region contains many nonresonant secondary electrons due to photoelectric and Compton effects.

The angular dependence of the relative peak areas of a magnetic sextet appearing in $^{57}$Fe Mössbauer spectra (representing the $I=3/2$ to $1/2$ nuclear spin transition) is generally given by the following expressions:

$$A_1(\theta) = A_6(\theta) = \frac{3}{16} (1 + \cos^2\theta),$$
$$A_2(\theta) = A_5(\theta) = \frac{4}{16} \sin^2\theta,$$
$$A_3(\theta) = A_4(\theta) = \frac{1}{6} (1 + \cos^2\theta),$$

where $\theta$ is the angle between the respective directions of the $\gamma$-ray and the effective magnetic field ($\mathbf{H}$); the area subscripts refer to the peak numbers of the sextet. Because the direction of magnetic moments in the thin surface layer of the iron foil is parallel to the plane of the surface, the area intensity ratio between the sextet peaks becomes $A_1=A_6=3$: $A_2=A_5=4$: $A_3=A_4=1$ for $\gamma$-rays of perpendicular incidence.

The CEMS spectra of as-deposited stainless steel films by Ar sputtering of austenitic stainless steel consisted of a broad magnetic sextet, which was similar to ferritic stainless steel. The hyperfine field distributions were calculated by using the ratio, based on the Hesse–Rübertsch method [14].

Fig. 3. DCEMS (left) and GDOES (right) spectra of as-deposited films, oxidized in air at 500 °C for 2 h. Sputtering time of 1.0 s corresponds to 24 nm in thickness. Electrons in DCEMS detected are: top, high energy (>6.5 keV); center, middle energy (3–6.5 keV); and bottom, low energy (1–3 keV).
The Mössbauer spectrum with hyperfine field distribution can be written as

\[ y(v) = \sum_{i=1}^{N} P(H_i) \cdot L_\alpha(H_i, v) \]  

(2)

where \( L_\alpha(H_i, v) \) denotes the sextets characterized by an effective magnetic field, \( H_i \). \( P(H_i) \) is the hyperfine field distribution function. The range of the hyperfine-fields of interest is divided into \( N \) equal intervals (\( \Delta H \)) with \( H_{\text{max}} = H_{\text{min}}^i + (N - 1) \times \Delta H \) and \( H_{\text{min}}^i + (i - 1) \times \Delta H \).

The calculated distributions are shown in Fig. 4. The average hyperfine field, \( H_{\text{av}} \), of the as-deposited films was 25 T. By heating at 400 and 500 °C, the magnetic field increased by about 3 T. It suggests that the ferromagnetic exchange interaction became stronger because of decreased average distance between Fe atoms. From a measurement by thin film XRD, it was confirmed that the lattice constants of bcc structure were \( a_{\text{av}} = 0.2864 \) nm for as-deposited samples and \( a_{\text{av}} = 0.2858 \) nm after heating.

A paramagnetic singlet with \( \delta = -0.09 \) mm/s was observed in CEMS spectra of the samples heated at 500 °C as shown in Fig. 3. It shows that the austenitic \( \gamma \)-phase was partially formed.

The relative intensity (11%) of the sextet representing iron oxides formed on the surface by heating at 500 °C was smaller than that (18%) for the sample heated at 400 °C. This shows that the concentration of Fe atoms decreased in the surface oxide layer by diffusion of Cr atoms into the surface. These were supported by depth profiles obtained by GDOES. Fe concentration dropped to one half of the bulk value within 4-nm depth. The total thickness of the oxide layer increased to about 14 nm by heating at 500 °C, and the interface region between the Fe oxides and the substrate (4–14 nm in depth) was enriched in Cr.

### 3.2. CEMS and XMS of coating steel by sulfurizing

Fig. 5 shows DCEMS and XMS spectra of steel treated by electrochemical sulfurization. DCEMS spectra were not always different by detecting emitted electrons of different energies. When the paramagnetic part of the spectra was decomposed into two doublets, the parameters \( \delta = 0.40 \) mm/s, \( \Delta = 0.77 \) mm/s, Area int. = 68% for Doublet 1 and \( \delta = 0.14 \) mm/s, \( \Delta = 0.75 \) mm/s, and 16% for Doublet 2 were obtained. Doublet 1 showed Mössbauer parameters close to those of pyrite, FeS\(_2\) (\( \delta = 0.307 \) mm/s, \( \Delta = 0.610 \) mm/s [15]). The original steel used consists of retained austenite (singlet; \( \delta = -0.09 \) mm/s) and ferrite phases (sextet: \( \delta = 0 \) mm/s, \( H_{\text{av}} = 33 \) T). The austenite-to-ferrite ratio was 0.15 for XMS but 0.93 for CEMS of sulfurized steel. When the paramagnetic peaks were fit as one doublet only, the
parameters were $\delta = 0.35$ mm/s, $\Delta = 0.76$ mm/s, and Area int. = 84% for the total paramagnetic contribution. The ratio of austenite-to-ferrite was 0.21 for XMS and 1.2 for CEMS. Thus, there remained some ambiguous products, but the relative ratio of austenite-to-ferrite was obviously different as observed by CEMS and XMS probing different depths of the surface layer, ca. 100 nm and 10 $\mu$m (for Fe metal), respectively. The coating of uniform thickness was about 3 $\mu$m although the coating did not always have high density because some small cracks were observed in scanning microscope images. These suggest that selective dissolution of ferrite occurred at the surface of the substrate steel when the steel was electrochemically sulfurized.

4. Conclusions

DCEMS and XMS spectra using a dual He/Ar gas counter have been applied to characterization of thin stainless steel films and thick-coated steels. Thin stainless steel films prepared by sputtering austenitic SUS304 steel with Ar gas were characterized effectively by DCEMS and GDOES. The as-deposited films consisted of magnetic phase. The observed hyperfine field in the films increased upon thermal treatment. The magnetic phase was converted partially into austenite inside the films by heating at 500 $^\circ$C. Surface oxide layers produced by heating in air are basically composed of Fe$_2$O$_3$ and Cr$_2$O$_3$. Simultaneous measurements of CEMS and XMS were applied to the analysis of thick sulfurized coating on steel. It was found that the austenite-to-ferrite ratio was different in the CEMS and XMS spectra of the same specimen. This suggests that primarily ferrite took part in the electrochemical sulfurization reaction of steel. DCEMS using a gas counter is simple and useful for the analysis of layered thin films with several 10 nm in thickness, whereas the simultaneous application of CEMS and XMS is effective for thick coatings with 10 $\mu$m in thickness.

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