X-Ray Elemental Imaging in Depth by Combination of FE-SEM-EDS and Glow Discharge Sputtering

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SEM-EDS is a powerful tool for fast, nondestructive x-ray elemental analysis of a localized region. Elemental mapping is also possible by scanning the electron beam. Since the penetration depth of the electron beam is about a few μm , SEM-EDS is useful for determining elemental composition near the surface of the sample. To obtain information regarding the depth of the sample, the surface layer must be removed. For this purpose, we attempted to use glow discharge sputtering. A commercially available rf glow discharge sputtering device (Horiba, Tensec) enables fast sputtering in an area 4 mm in diameter. The combination of SEM-EDS and glow discharge sputtering would be useful for observation of the distribution of inclusions buried in metal samples. Al_2O_3 particles were mixed with Cu powders, and then pressed into a disk, which was measured. The same area of the sample was analyzed by FE-SEM-EDS and sputtered. The result indicated the possibility of 3D distribution analysis of inclusions in the sample.

KEY WORDS: FE-SEM; SEM-EDS; glow discharge; sputtering; elemental imaging; 3D-elemental mapping.

1. Introduction

Inclusions in the steel sample influence its physical and chemical properties. Therefore, it is very important to know the 3D distribution of those inclusions. Usually, we can apply various types of surface analytical techniques to know the distribution of inclusions that appear on the surface of the sample. However, we must consider how to dig out the inclusions buried in the metal sample. An Ar ion gun is a common tool for sputtering a localized region, and it is applied with other surface analytical methods such as XPS and AES. However, the area sputtered by the Ar ion gun is not large enough for observing the distribution of inclusions. Glow discharge sputtering is also a candidate technique for this purpose.^{1,2)} Glow discharge plasma can be well controlled and applied as an optical emission source and ion source for mass spectrometry. Many types of glow discharge tubes have been studied. A Grimm-type glow discharge tube forms a stable plasma.^{1,2)} The typical inner diameter of a Grimm-type glow discharge tube is 4 mm. That means, an area 4 mm in diameter is sputtered. This large area is very suitable for our purpose of knowing the distribution of inclusions in a large area. In addition, another advantage of glow discharge is its large sputtering rate. As mentioned below, a sputtering rate of 50 nm/s was obtained for Cu. For x-ray elemental analysis, SEM-EDS is one of common fast techniques.^{3,4)} Therefore, we considered that the combination of glow discharge sputtering and SEM-EDS analysis would be useful for in-depth elemental mapping, leading to 3D distribution of inclusions. This concept is illustrated in

Fig. 1. The analyzing depth of SEM-EDS is about 1 μm . Thus, we attempted to reveal the buried layer inside the sample by using glow discharge device for SEM-EDS analysis. In this paper, we demonstrate the depth elemental imaging for artificial sample, that is, Al_2O_3 particles in Cu matrix. The aim of this paper is to demonstrate the possibility to rapidly and simply show the elemental distribution of particles in a large region (1 940 $\mu\text{m} \times 1 330 \mu\text{m}$ in lateral, about 60 μm in depth). There are no previous papers where the feasibility of elemental images in a large area is discussed and experimental results of distributions of particles in depth as well as lateral distribution are shown. As far as the authors know, this is the first paper showing x-ray elemental imaging in depth by combination of FE-SEM-EDS and glow discharge sputtering.

2. Experiment

2.1. Sample

2 mass% of Al_2O_3 particles (diameter: 120 mesh) and Cu powder were mixed well. This mixed sample was then

Fig. 1. Experimental concept of combination of SEM-EDS and glow discharge sputtering.

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pressed at a pressure of 300 kN in an Al ring (inner diameter: 15 mm, outer diameter: 18 mm, height: 5 mm). The pressed total mass was about 2.5 g.

2.2. FE-SEM-EDS

FE-SEM (JEOL, JSM-6500F) was applied for observing the surface morphology of the sample. The FE-SEM was operated with an accelerating voltage of 15 kV and an electron current of 0.1 nA. A Si(Li) EDS detector was installed into a FE-SEM. The energy resolution of the Si(Li) was 144 eV at Mn $K\alpha$. This EDS detector has a thin polymer window; therefore, low-Z elements like Al could be easily analyzed. The SEM-EDS images were taken with a dwell time of 0.1 ms and 30 sweep times at 512×384 pixels.

2.3. Glow Discharge Device and Experimental Procedure

A commercial glow discharge device (Horiba, Tensec) was used. The device was operated with an Ar gas (purity: 99.9999%) pressure of 1 000 Pa with a typical applied power of 20 W. The sputtered area corresponded to the inner diameter of discharge tube, which was about 4 mm. After the glow discharge sputtering, the sample was quickly moved to the FE-SEM on a different floor in the same building. After SEM-EDS analysis, the sample was moved to the glow discharge device. To sputter the same position, a special Al ring to guide the sample was prepared. The surface morphology of the sputtered crater was measured by a surface profiler (Kosaka Seiki, SE300). This measurement enabled estimation of the sputtering rate.

3. Results and Discussion

3.1. Sputtering Rate

The sputtered depth was estimated for pure Al, Cu, and Zn plates by using the surface profiler after 20 s, 40 s, and 60 s discharges. The results are shown in Fig. 2. From these

results, the sputtering rates for Al, Cu, and Zn were determined to be 0.015, 0.05, and $0.13 \mu\text{m/s}$, respectively. In this paper, we measured Cu samples including Al_2O_3 particles. The sputtered depth was roughly estimated by using the sputtering rate obtained for Cu. For more precise quantitative discussion, we have to consider the variation of sputtering rate during the progress of sputtering. In addition, we could not prepare the Al_2O_3 material for evaluation of its sputtering rate. The sputtering rate of Cu might be changed by existence of Al_2O_3 particles. However, as described in 2.1 section, Al_2O_3 particles were mixed with a concentration of 2 mass% in Cu. In our rough estimation of sputtering rate of Cu, we ignored the influence of Al_2O_3 particles in this paper.

3.2. SEM Images of Al_2O_3 Inclusions in Cu

Figure 3(a) is a typical SEM image of an Al_2O_3 particle in the Cu matrix. The top of the particle had a different contrast. Thus, the point indicated with 1 in Fig. 3(a) was analyzed by SEM-EDS. The obtained x-ray spectrum is shown

Fig. 2. Sputtered depth as a function of sputtering time for Al, Cu, and Zn.

Fig. 3. SEM image (a) and x-ray spectra obtained at 1(b) and 2(c) indicated in Fig. 3(a), after the sample was sputtered for 1 200 s.

Fig. 4. SEM images of sample sputtered by glow discharge for 20 s (a), 300 s (b), 700 s (c), 1200 s (d).

in Fig. 3(b), where Al and O were measured, indicating an Al_2O_3 particle. Similarly, the x-ray spectrum obtained at point 2 in Fig. 3(a) is shown in Fig. 3(c), where only characteristic Cu x-rays were measured. From the SEM image, it seems that the Al_2O_3 particle remained although the Cu, which surrounded the Al_2O_3 particle, was sputtered. This is probably due to the difference in sputtering rates of Cu and Al. As shown in Fig. 2, the sputtering rate of Al is lower than that of Cu. The result shown in Fig. 3 suggests that glow discharge sputtering does not proceed homogeneously, but depends critically on the elements or chemical compounds involved.

Figures 4(a)–4(d) shows SEM images obtained at the same area of the sample at different sputtering times of 300 s, 500 s, 700 s, and 1200 s. These sputtering times correspond to the sputtered depth of roughly $1\mu\text{m}$, $15\mu\text{m}$, $35\mu\text{m}$, and $60\mu\text{m}$, respectively. It is clearly shown that some particles disappeared and other particles appeared in the progress of glow discharge sputtering. The sputtering rate of Al_2O_3 particles was smaller than that of the Cu; however, Al_2O_3 particles were steadily sputtered. This sputtering process leads to know the shapes and the depth distributions of Al_2O_3 particles in the Cu.

3.3. Al $K\alpha$ Images in Depth

The same area of the Al_2O_3 particles in the Cu sample was sequentially measured by SEM-EDS after glow discharge sputtering with different sputtering times. The glow discharge was operated at 20 W and an Ar pressure of 1000 Pa, leading to a Cu sputtering rate of $0.05\mu\text{m/s}$. Figures 5(a)–5(p) shows Al $K\alpha$ images obtained from the same sample after different sputtering times of 20 s (a), 40 s (b), 60 s (c), 80 s (d), 100 s (e), 120 s (f), 140 s (g), 160 s (h), 180 s (i), 200 s (j), 240 s (k), 300 s (l), 500 s (m), 700 s (n), 900 s (o), and 1200 s (p), respectively. The depth roughly estimated from the Cu sputtering rate is also shown in each figure. The Al $K\alpha$ images in Fig. 5 indicate the distributions of Al_2O_3 particles in depth. These series of Al $K\alpha$ images clearly show that some Al_2O_3 particles were sputtered and disappeared while other particles, which were buried in the Cu matrix, appeared during the glow discharge sputtering process. Therefore, we can know where Al_2O_3 particles existed in the Cu and which shapes they had. The

Fig. 5. Al $K\alpha$ images obtained at the same area of the sample sputtered by glow discharge for 20 s (a), 40 s (b), 60 s (c), 80 s (d), 100 s (e), 120 s (f), 140 s (g), 160 s (h), 180 s (i), 200 s (j), 240 s (k), 300 s (l), 500 s (m), 700 s (n), 900 s (o), 1200 s (p). The depth roughly estimated from the Cu sputtering rate is also shown in each figure.

surfaces of both Al_2O_3 particles and Cu matrix might be influenced by sputtering, leading to rough surface morphology. However, this influence would not be observed by EDS analysis due to poor lateral resolution in SEM-EDS analysis. This technique would be useful not for obtaining precise surface morphology of each particle but for rough and fast estimation of lateral and depth distribution of particles.

4. Conclusions

SEM-EDS and glow discharge sputtering is a very simple combination of procedures. Both techniques can be performed in a short time. By using this combined technique, it was possible to know the distribution of Al_2O_3 particles in a large area (about $1\,940\,\mu\text{m} \times 1\,330\,\mu\text{m}$) in depth up to $60\,\mu\text{m}$, leading to 3D distribution images of the particles. It is expected that this simple and fast technique would be applied to the 3D analysis of actual inclusions in steel samples. Although we did not show, it will be possible to construct a 3D image of Al_2O_3 particles in the analyzed volume.

Since the glow discharge sputtering does not proceed homogeneously, we have to carefully analyze the obtained results. In this paper, we measured a simple artificial sam-

ple. However, actual samples include various inclusions with different compositions. Depending on the difference of sputtering rates of each inclusion, there is a possibility that we may obtain the elemental images in depth that are different from the real distributions. In this case, it will be required to correct the difference of sputtering rates of inclusions.

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