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AN APPLICATION OF ELECTRON MICROPROBE AUGER SPECTROSCOPY TO THE STUDY OF SELECTIVELY OXIDIZED Cu - 0.28 WT% Al ALLOY SURFACE

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Electron microprobe Auger spectroscopy study of the surface compositional changes of a Cu - 0.28 wt% Al alloy in the initial oxidation revealed that aluminum was enriched on the surface due to its selective oxidation. The degree of its enrichment was not uniform and depended on a structure of grains and on whether places were inside grains or grain boundaries.

Auger electron spectroscopy (AES) has been proved to be a suitable technique to analyze the solid surface and its related phenomena. Although AES has high surface sensitivity, with a conventional AES apparatus it has been difficult to analyze the small area of samples due to the large incident electron probe diameter and the lack of imaging mechanism. We have newly constructed an electron microprobe Auger spectrometer (EMAS) having an spatial resolution of less than 1 μm. This new equipment has the advantages as the followings compared with the existing micro-AES equipments[1]: (i) The whole apparatus can be baked up to 150°C including the focusing system to get ultra high vacuum condition better than 10^{-9} Torr. (ii) Samples can be heated up to 1000°C within 30 seconds by passing dc current through them. (iii) The specimen chamber is large enough to be fitted up with some attachments such as a sample fracturing equipment. (iv) The out-put of a lock-in amplifier is statistically averaged with a digital averager to improve the signal to noise ratio of the spectrum. The digital averaging allows to use very low beam current density which is effective to reduce electron beam induced adsorption of oxygen and carbon. This report presents some interesting results on an oxidation of a dilute

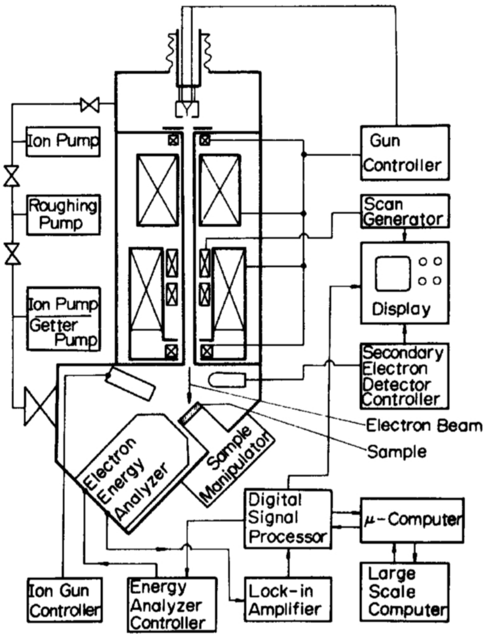

Fig. 1. Schematic diagram of EMAS.

copper alloy using this new equipment.

In Fig. 1, a schematic diagram of the equipment is shown. Electrons are accelerated in the range of 3 - 15 kV and focused onto a specimen surface with magnetic lenses and deflected with scanning coils. The primary beam current is about 1 × 10^{-7} A for the 1 μm diameter beam. The SEM (scanning electron microscope) image is observed on a cathode ray tube (CRT). The Auger electrons are detected by a large cylindrical mirror type analyzer. Besides AES point analyses, line analyses and two-dimensional analyses (Auger images) can be performed by scanning a primary electron beam along the line or in X-Y two dimensions at the fixed energy of the Auger peak.

Fig. 2. SEM image of a Cu-0.28 wt% Al alloy sample (absorbed current mode).

Heating, oxidation and reduction, and sputtering are frequently used to obtain the clean surface of solids. For multi-component systems, it is often found that the surface composition is easily changed by these treatments. But relatively little has been published on the uniformity of the change of the surface composition. The EMAS was applied to the study on the surface compositional changes of a dilute copper alloy caused by the selective oxidation. A Cu - Al alloy was used as a model sample, in which two elements had very different chemical activities for oxygen and therefore, some typical changes were expected. And also aluminum is practically used as a heat-resisting element, so its oxidation behavior is one of interesting problems. Recently the authors observed an anisotropic oxidation behavior of a dilute copper alloy, in the course of study on the exfoilation mechanism for oxidation$^{2)}$. A Cu-0.28 wt% Al alloy was studied in this paper because, in which the oxide of the alloying constituent was less soluble (probably insoluble) in the oxide of the parent metal than in Cu - 0.05 wt% Al alloy used in our previous paper$^{2)}$ and characteristic oxidation behavior were expected.

The sample was annealed more than 12 hours at 600°C in vacuo and polished electrolitically in phosphoric acid. The SEM image (absorbed current mode) of the surface obtained by the EMAS is shown in Fig. 2. The grain sizes were 50 - 100 μm. The Al Auger peak was not detected anywhere on this surface (accelerating voltage: 10 keV). The sample was heated at 500°C for 6 minutes in the presence of 5 Torr hydrogen in the apparatus (back ground pressure was about 3 × 10^{-7} Torr). This treatment changed the surface composition drastically, that is, only aluminum and oxygen Auger peaks could be detected instead of copper one all around the surface. The surface was completely covered by aluminum oxide because, even in the atmosphere of 5 Torr of hydrogen, aluminum was oxidized selectively by residual oxidative gases such as H_2O and O_2 because of its very low equilibrium dissociation oxygen pressure. Then the sample was heated at 300°C in 10 Torr of oxygen for 21 minutes. The Auger analysis showed that both aluminum and copper existed. Furthermore, the surface composition was heterogeneous, that is, each grain and grain boundary had different surface composition. Fig. 3 shows a SEM image and Auger images by Cu LMM Auger transition (920 eV) and Al KLL Auger transition (1378 eV). On these Auger images, bright regions correspond to a high concentration of the element analyzed. The recording time for one picture of these Auger images was ten minutes using a beam current of 1×10^{-7} A. The Auger images of Cu and Al show the inverse contrast each other. These heterogeneous changes of the surface composition are mainly attributed to the followings : (i) the adsorbability and reactivity of reactant gases, (ii) the diffusion rates of copper and aluminum in solid. These factors depend on (a) a structure of grains which is relating mainly to an orientation, (b) whether places are inside grains or grain boundaries. In this case, it should be noted especially that the surface compositional changes remarkably depend on a structure of grains. For example, grains A and B in Fig. 3-(a) showed very different surface composition each other, that is, the Auger peaks of copper and aluminum were observed moderately on grain A, while the Auger peak of aluminum was comparatively weak on grain B.

Fig. 4 shows a SEM image and Auger images by Cu LMM (920 eV), Al KLL (1378 eV) and O KLL (510 eV) transitions of the sample which was treated successively as described below (1) - (4).

(1) Heating at 500°C in 1 Torr of hydrogen for 20 seconds
(2) Heating at 300°C in 1 Torr of oxygen for 40 seconds
(3) Heating at 650°C in vacuo (< 9×10^{-7} Torr) for 3 minutes
(4) Heating at 300°C in 1 Torr of oxygen for 30 seconds

After the treatments of (1) and (2), both Auger peaks of copper and aluminum were detected. After the treatment of (3), striking changes were observed. First, the SEM image was changed remarkably, that is, clear contrast corresponding to grain boundaries was observed (similar to Fig. 4-(a)). Second, the characteristic difference in the surface composition appeared between intragranular regions and

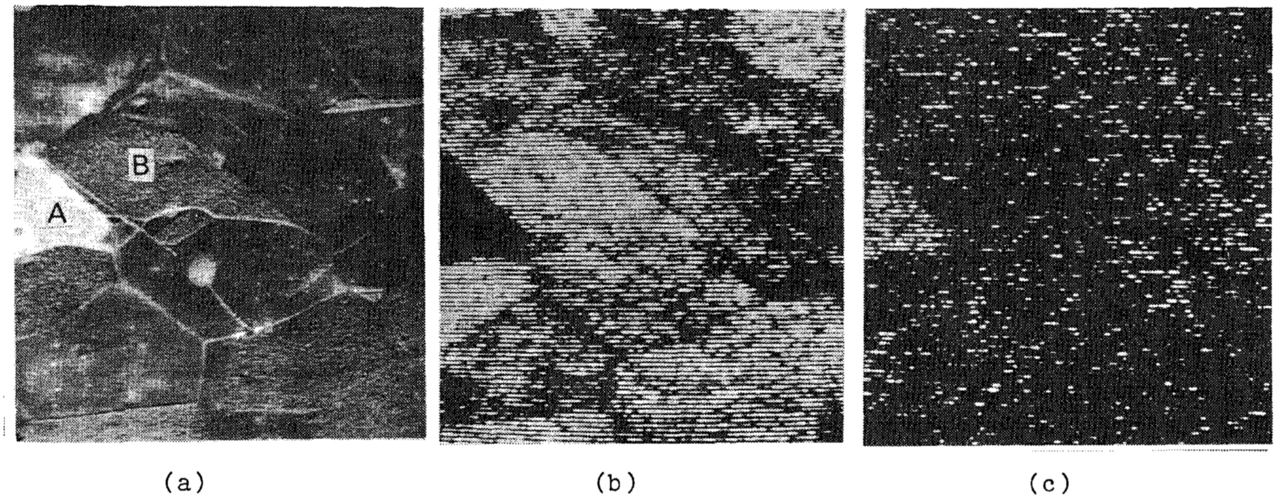

Fig. 3. (a) SEM image, (b) Auger image of Cu (LMM 920 eV), and (c) Auger image of Al (KLL 1378 eV). These images were observed on the Cu-0.28 wt% Al alloy sample after the treatments : (i) heating at 500°C in 5 Torr of hydrogen for 6 minutes, and then (ii) heating at 300°C in 10 Torr of oxygen for 21 minutes.

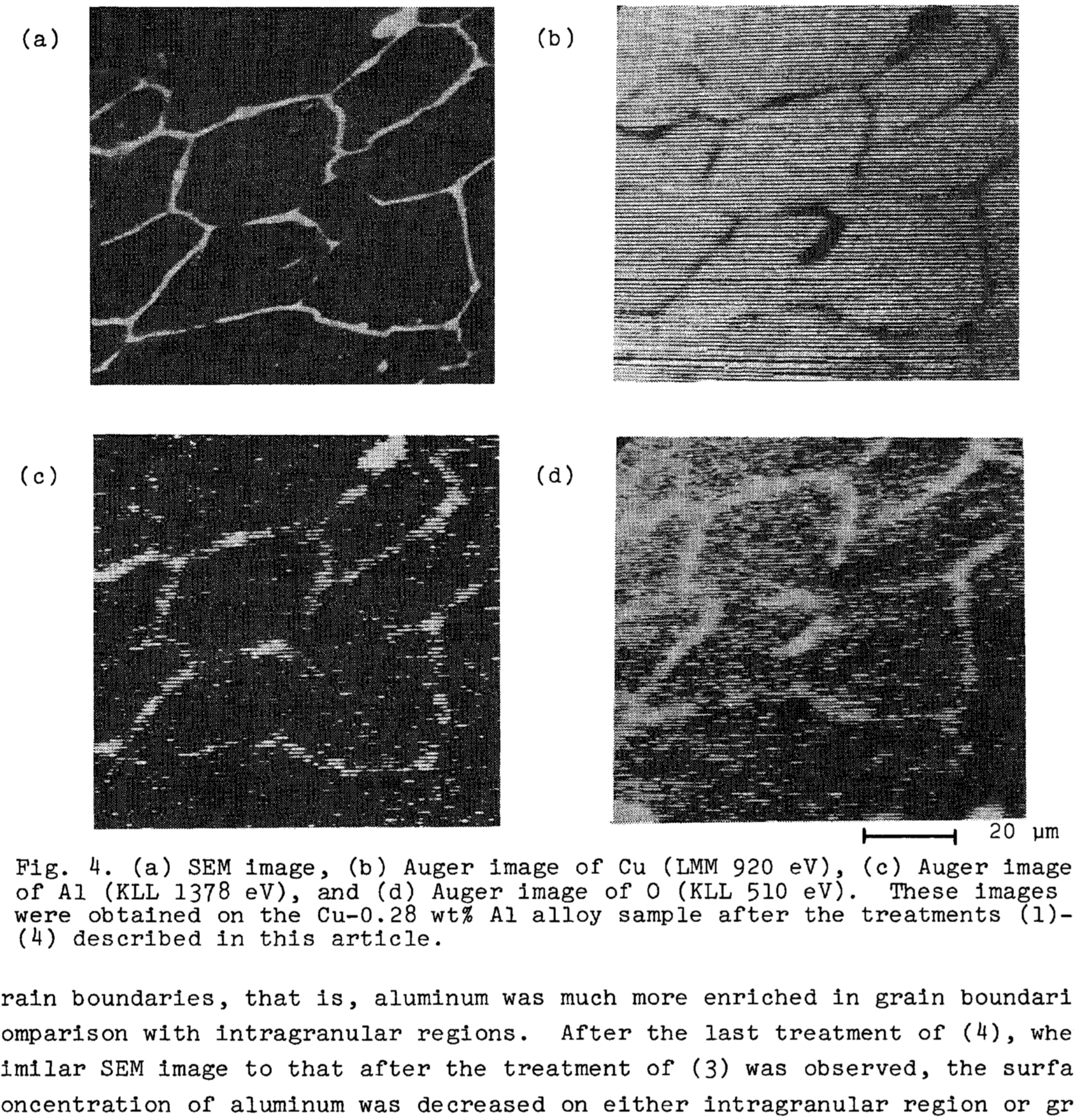

Fig. 4. (a) SEM image, (b) Auger image of Cu (LMM 920 eV), (c) Auger image of Al (KLL 1378 eV), and (d) Auger image of O (KLL 510 eV). These images were obtained on the Cu-0.28 wt% Al alloy sample after the treatments (1)-(4) described in this article.

grain boundaries, that is, aluminum was much more enriched in grain boundaries in comparison with intragranular regions. After the last treatment of (4), when the similar SEM image to that after the treatment of (3) was observed, the surface concentration of aluminum was decreased on either intragranular region or grain boundary because of copper enrichment through its oxidation and aluminum was observed only at grain boundaries. Although the mechanism of this grain boundary segregation phenomenon of aluminum has not been clear, it may be resulted from the difference in diffusion rates between grain boudaries and bulk.

The segregation of minor components and the heterogeneity of the surface composition is an interesting and important problem in various fields such as heterogeneous catalysis, corrosion phenomena, etc. In this respect, the high spatial resolution AES will become a powerful and essential tool for studying solid surfaces.

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