Characteristic Depth Profiles of Surface Layers Formed in Cu-based Alloys by Annealing in Low Partial Pressure of Oxygen*

Shigeru Suzuki¹, Tarou Kimura², Masatoshi Eto², Masazumi Mori² and Yoshio Waseda¹

¹ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
² Technology Development Center, Nippon Mining & Metals Co. Ltd., Hitachi 317-0056, Japan

Secondary ion mass spectrometry (SIMS) has been used for characterizing the depth distribution of alloying elements in three different copper-based dilute alloys, i.e. copper-chromium, copper-iron and copper-nickel-silicon alloys, which were annealed at high temperatures under low oxygen partial pressure. SIMS depth profiles showed that oxygen penetrated into the copper-based alloys, and chromium and silicon were enriched to the surface side so as to form oxides during annealing. Chromium and silicon were depleted beneath the enriched layer. On the other hand, depth profiles of iron and nickel were similar to that of copper. These phenomena were likely to be associated with the reactivity of alloying elements with oxygen. The formation kinetics of the depleted zones of chromium and silicon was discussed coupled with the selective oxidation of these alloying elements.

(Received November 7, 2003; Accepted January 16, 2004)

Keywords: copper-based alloy, selective oxidation, secondary ion mass spectrometry, x-ray photoelectron spectroscopy

1. Introduction

Copper-based alloys are often used as electrical parts and structural elements, and their electrical conductivity and strength are improved by controlling the process conditions. These copper-based alloys contain various kinds of alloying elements, of which the chemical characters are different from those of copper. Therefore, some alloying elements are likely to be reacted with gas species during annealing; for instance, the selective oxidation of titanium has been shown to occur in a surface layer of copper-titanium alloys by annealing under a low partial pressure of oxygen.¹ As copper-based alloys are processed and served under various conditions, the surface properties of copper-based alloys are required to be controlled.²⁻⁴ In order to control the surface properties, such as reaction with solder and plating, thin surface layers as well as thick oxide layers formed in copper-based alloys should be characterized.

Figure 1 shows Ellingham diagram for copper and related alloying elements such as nickel, iron, chromium and silicon, which are sometimes added to copper-based alloys. Different annealing conditions, which are specified by temperature and oxygen partial pressure, are denoted as (a) to (d) in Fig. 1. Conditions of oxidation at room temperature, that is native oxidation, and high temperature oxidation under atmospheric air correspond to zones (a) and (b) in Fig. 1, respectively. If copper-based alloys are annealed under low oxygen partial pressure, as exemplified in zone (c) of Fig. 1, a surface layer formed in the copper-based alloys is considered to be different from that for the alloys annealed in high oxygen partial pressure. Alloying elements, such as chromium and silicon, may be selectively reacted with oxygen in a surface layer, because copper itself is not oxidized. Furthermore, if copper-based alloys are annealed at high temperature under ultra-high vacuum, which corresponds to an extremely low oxygen partial pressure, as denoted in zone (d) of Fig. 1, a surface-active element is segregated on the surface so as to reduce the surface free energy.⁵ Thus, formation processes of surface layers in copper-based alloys are classified into different cases, depending on temperature and oxygen partial pressure in an atmosphere.

The objective of this work is to characterize thin surface layers formed in different copper-based alloys by annealing under low oxygen partial pressure. Secondary ion mass spectrometry (SIMS) was mainly applied for analyzing depth profiles of surface layers formed in the alloys by annealing. SIMS depth profiles provide the microscopic compositional distribution of elements in the surface layers, in spite of difficulty of compositional quantification. Characteristic features of the depth profiles of alloying elements and the formation kinetics of the surface layers were discussed.

*This Paper was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Sapporo, on October 13, 2003
coupled with the reactivity of the alloying elements in copper-based alloys with oxygen.

2. Experimental

Sample sheets of 0.1mm in thickness of copper-0.23 mass% chromium (Cu-Cr), copper-1.2 mass% iron (Cu-Fe) and copper-2.5 mass%nickel-0.45 mass% silicon (Cu-Ni-Si) were prepared by rolling and annealing. The grain size of these samples was about 30 μm. They were cut to about 10 mm square, and mechanically polished to obtain the flat surface. They wereannealed in the temperature range between 773 and 873 K in low oxygen partial pressure, which was in argon-10% hydrogen gas containing water vapor. The oxygen partial pressure in this annealing atmosphere was estimated to be about 10⁻¹⁷ Pa at those temperatures. Under these annealing conditions, chromium and siliconwere likely to be oxidized, while copper, nickel and iron were not oxidized, as shown in zone (c) of Fig. 1. When the annealed samples were transferred to an ultra-high vacuum chamber for SIMS analysis, the sample surface was exposed to air.

SIMS measurements were carried out using PHI-6600 with quadrupole-type mass spectrometer. A beam of Cs⁺ ions of 5 keV was irradiated in the incident angle of 45° to the sample surface. The sputtered area was about 500 μm square on the sample surface, and the beam current was set to about 300 nA. As secondary CsM⁺ ions are known to be less dependent of the matrix species, secondary ¹⁹⁶(CsCu)⁺, ¹⁸¹(CsCr)⁺, ¹⁹⁸(CsFe), ¹⁹¹(CsNi)⁺, ¹⁶²(CsSi)⁺ and ¹⁸⁰(Cr)⁺ ions from the sample surface were counted. The sputtering rate in SIMS depth profiling was estimated from measurement of the sputtered crater depth by a surface profilometer. The selection of Cs⁺ ions was due to their high ionization efficiency in SIMS measurements. An XPS apparatus (PHI-5600) was also used for analyzing the surface composition of samples, which was evaluated from XPS spectra taken by incident Mg-Kα.

3. Results and Discussion

3.1 Depth profiles of surface layer in copper-based alloys

Figures 2 show SIMS depth profiles of positive secondary ions from the surface of Cu-Cr, Cr-Fe and Cu-Ni-Si, respectively. These alloys were annealed at 873 K under low oxygen partial pressure. Monotonic decreases in secondary ion counts of oxygen are clearly found with increasing depth. This indicates that oxygen penetrated into the matrix of these copper-based alloys, and the oxygen potential gradually decreases on the matrix side. On the other hand, the SIMS depth profiles of ions relevant to alloying elements provide characteristic features of the distribution of elements in the surface layer. The amount of chromium in Cu-Cr decreases with increasing depth, as shown in Fig. 2(a). This chromium profile corresponds to the gradient of the oxygen potential in the surface layer, suggesting the formation of chromium oxides on the surface side. A chromium-depleted zone is found to form beneath the surface layer. This is attributed to outward diffusion of metallic chromium to form oxides on the surface side. Beneath the chromium-depleted zone, the chromium composition increases with increasing depth, approaching to the bulk concentration. Similar enrichment of silicon on the surface side and formation of depleted zone are observed in Cu-Ni-Si, as shown in Fig. 2(c). This is also likely to be caused by the selective oxidation of silicon in the surface layer. On the other hand, SIMS depth profiles of iron and nickel relevant ions are similar to that for copper in Cu-Fe and Cu-Ni-Si annealed under low oxygen partial pressure of at 873 K, as shown in Figs. 2(b) and (c). These results indicate that iron and nickel are less sensitive to the oxidation under the present annealing condition.

XPS spectra were measured for the surface of samples annealed under low oxygen partial pressure, in order to confirm the enrichment of reactive elements on the sample surface. The XPS spectra for Cu-Fe and Cu-Cr annealed under low oxygen partial pressure are shown in Figs. 3(a) and (b), respectively. Small carbon peaks are allocated to contamination originating from air. Oxygen peaks come from not only an oxide formed during annealing, but also a native oxide formed by exposure to air at room temperature. Nevertheless, clear surface enrichment of chromium was observed in Cu-Cr, indicating the formation of chromium oxides on the surface. On the other hand, iron was not significantly detected on the surface of Cu-Fe. These results are consistent with the depth profiles shown in Fig. 2.

3.2 Kinetics of formation of surface layers

The selective oxidation of chromium and silicon observed in this work is considered as internal oxidation of a reactive alloying element in copper-based alloys, although the surface layer is very thin. The general kinetics of the internal...
oxidation was described using several parameters,\textsuperscript{7)} which are not easily estimated. However, a formation process of a depleted zone of reactive elements in the copper-based alloys may be described by a simple model, since reactive alloying elements such as metallic chromium and silicon diffuse outward so as to form oxides on the surface side. Figure 4 illustrates a schematics diagram for a surface layer formed by the selective oxidation of chromium in Cu-Cr. Then, as the effective concentration in metallic chromium is null at the surface, this case is quite similar to a diffusion process under specific boundary conditions.\textsuperscript{8)} Then, the depth profile of chromium \(c_{Cr}\) at depth \(d\) at time \(t\) is approximated to be as follows;

\[
c_{Cr} = A \text{erf}(d/2\sqrt{Dt}),
\]

where \(A\) and \(D\) are a constant and diffusion coefficient. It is noted in the present analysis that the oxide layer thickness is assumed to be very thin.

In order to compare curves calculated from eq. (1) with the experimental depth profiles, the depth profiles of normalized chromium relevant ions in Cu-Cr and normalized silicon relevant ions in Cu-Ni-Si are shown in Figs. 5(a) and (b), respectively. The sputtered depth was estimated from depth measurements. Calculated lines are fitted to the experimental depth profiles, which are plotted as marks. The calculation is, in the authors’ view, rather good, because the calculated curve fairly reproduces the experimental depth profile in the depleted zone. Thus, effective diffusion coefficients of alloying elements can be obtained from eq. (1). Temperature dependences of effective diffusion coefficients of chromium and silicon in copper, which were estimated from the present experiments, are plotted as shown in Fig. 6. Temperature dependences of diffusion coefficients of chromium and silicon in copper are also available in a data book,\textsuperscript{9)} which are given as lines in Fig. 6. Agreements of the present data with data given in the literature are satisfactory, and therefore it is not too much to say that a control process in the formation of the surface layer by selective oxidation in the copper-reactive elements alloys is outward diffusion of the elements in copper.

However, if oxygen penetrates into an alloy deeply, the surface containing oxides is likely to extend into the bulk. Then, the effective position of the sample surface, which is assumed as the initial condition in the calculation of a compositional profile, may shift to the matrix side. In addition, an attention should be paid to atomistic processes in a surface layer during ion sputtering of SIMS measurements. Typically, the surface composition of alloys is known to be influence by ion sputtering,\textsuperscript{10,11)} and this effect may affect depth profiles. However, it is likely to be short-range
compared to changes in the composition of a surface layer by annealing, since the surface layer with a depleted zone is enhanced by the selective oxidation of reactive elements in copper-based alloys. Thus, microstructural changes in selective oxidation and atomistic processes in sputtering may, more or less, may cause a deviation from simple theoretical estimation.

4. Concluding Remarks

Secondary ion mass spectrometry (SIMS) has been used for analyzing surface layers formed in copper-chromium, chromium-iron and copper-nickel-silicon alloys, which were annealed under oxygen low partial pressure. The main results obtained are as follows:

1) SIMS profiles showed that oxygen penetrated into the copper alloys by annealing. Chromium in the copper-chromium alloy and silicon in the copper-nickel-silicon alloy were enriched to a surface side so as to form oxides by annealing at high temperatures. Depleted zones of chromium in the copper-chromium alloy and silicon in the copper-nickel-silicon alloy were found below the chromium and silicon enriched layer, respectively.

2) The shapes of depth profiles of iron in copper-iron and nickel in the copper-nickel-silicon alloy were similar to that for copper. These phenomena are likely to be associated with the reactivity of the alloying elements with oxygen in the copper-based alloys.

3) The depth profiles of reactive elements formed during annealing indicate that the formation kinetics of the depleted zones is controlled by outward diffusion of the reactive elements in the surface layers.

Acknowledgements

The present authors would like to express sincere thanks to Mr. T. Sato and Mr. M. Ito for their help and maintenance of SIMS apparatus.

REFERENCES


Fig. 6 Arrhenius plot of effective diffusion coefficients of chromium in Cu-Cr and silicon in Cu-Ni-Si, which were estimated in this work and denoted as marks. Data from the literature are denoted as lines.