Characterization of Thin Surface Layers Formed in Copper-Based Alloys

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ABSTRACT

An attempt has been made to describe recent systematic results on characterization of thin surface layers formed in copper-based alloys, which were exposed to mild atmospheres, such as ultra-high vacuum and low partial pressures of oxygen at a high temperature. Surface analytical techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) were used for studying the thin surface layers formed in copper-based alloys. The results show that a surface-active element is segregated on the surface of copper-based alloys by annealing at high temperatures in ultra high vacuum. The selective oxidation of reactive elements was found to take place in a surface layer formed in copper-based alloys by heating under a low partial pressure of oxygen, in which matrix copper is not oxidized. In addition, the formation of a native oxide layer on the surface of copper-based alloys, which occurs by exposure to air at room temperature, is also discussed. The formation of these surface layers is interpreted on the basis of the thermodynamic character of elements in copper-based alloys.

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

1. INTRODUCTION

Copper and copper-based alloys are extensively utilized as materials for a variety of components or parts for machines, electric products and so on, because they have a number of excellent properties such as strength, ductility and conductivity. As copper-based alloys are processed and served under various conditions, control of the surface properties of copper-based alloys is also important. Typically, corrosion products such as passivation films formed on the surface of copper-based alloys in atmosphere containing water are still of great interest from a viewpoint of control of corrosion resistance /1-3/.

On the other hand, as control of surface reactions in copper-based alloys in a gas at high temperature is also required, the high-temperature oxidation of several copper-based alloys has been studied /4-6/. Oxidation experiments in these studies have been carried out for annealing at relatively high temperatures in air, in which the partial pressure of oxygen is high. These oxidation conditions are denoted as zone (a) in Fig. 1, indicating an Ellingham diagram for several elements. Since free energies of the oxide formation for copper and many alloying elements in copper-based alloys are lower than about –200 kJmol^{-1}, these elements are oxidized under

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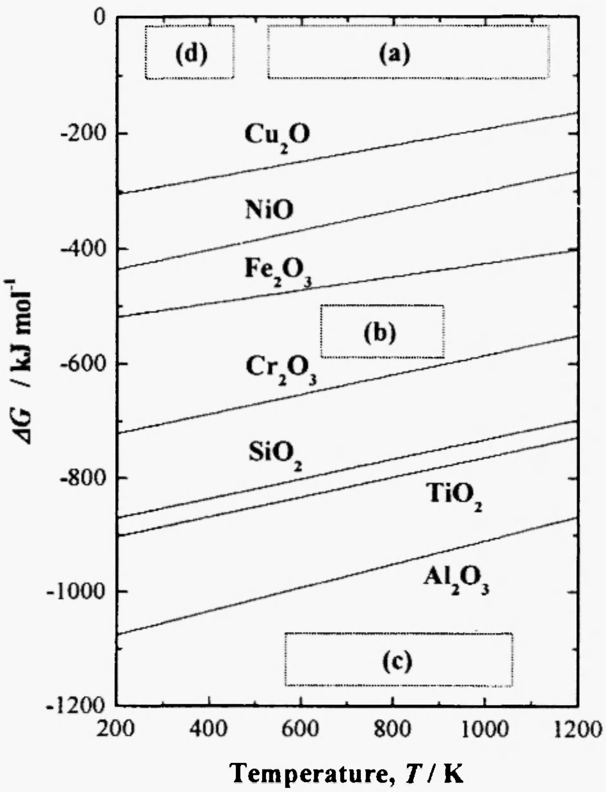

Fig. 1: Ellingham diagram for some oxides in the high temperature oxidation.

these conditions. Then a relatively thick oxide layer of mainly copper oxides is formed, depending on annealing temperature and time. Reactive elements to oxygen, which are alloying elements in copper-based alloys, are likely to be distributed in the copper oxide layer in a characteristic manner.

If copper-based alloys are annealed under a low partial pressure of oxygen, as exemplified in zone (b) of Fig. 1, a surface layer formed in the copper-based alloys may be different from that for the alloys annealed in a high pressure of oxygen. This is because reactive alloying elements such as titanium and silicon are selectively oxidized in the surface layer, while copper itself is not oxidized under the low partial pressure of oxygen. Then, the formation of a characteristic surface layer containing some oxides of the reactive elements is expected. Furthermore, if copper-based alloys are annealed at high temperature under ultra-high vacuum, which corresponds to an extremely low partial pressure of oxygen, as denoted in zone (c) of Fig. 1, a surface-active element is likely to be segregated on the surface so as to reduce the surface free energy. This is because the alloy surface is not influenced by oxygen in such an annealing condition, and alloying elements in copper-based alloys are mobile at high temperature. The segregated layer formed in copper-based alloys is considered to be very thin. In addition, a surface oxide layer is formed in copper-based alloys by exposure to air at about room temperature, which is referred to as a native oxide layer. The surface layer is very thin, since its oxidation rate is very low because of oxidation at room temperature. Such oxidation conditions are shown in zone (d) of Fig. 1.

Thus, the formation processes of surface layers in copper-based alloys may be classified into different cases, which depend on temperature and partial pressure of oxygen in an atmosphere. A large number of copper-based alloys have been developed by addition of various alloying elements and modification of processes for improving their mechanical processes so far. However, in order to control the surface properties such as feasibilities of soldering and plating, surface layers formed in copper-based alloys should be well characterized.

The objective of this paper is to describe characterization of surface layers formed in a few copper-based alloys under different conditions, in which the reactivity and surface-activity of alloying elements are taken into account. Surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and secondary electron mass spectrometry (SIMS), have been used for analyzing surface layers under ultra-high vacuum and different partial pressures of oxygen, and these recent experimental results are discussed in conjunction with the previous data.

2. EXPERIMENTAL

2.1. Samples

Buttons of high-purity copper-chromium alloys and copper titanium alloys were prepared from 6N copper, 4N chromium and 6N titanium by plasma arc melting /7,8/. Alloys used in this work were a copper-0.41mass% chromium alloy (Cu-0.4Cr) and copper-0.50 mass% (Cu-0.5Ti), 1.0mass% (Cu-1.0Ti), 1.5mass%

(Cu-1.5Ti), 2.0mass% (Cu-2.0Ti) and 3.4mass% (Cu-3.4Ti) titanium alloys. Surface segregation and native oxide formation were mainly studied in Cu-0.4% Cr. Surface layers formed by selective oxidation of a reactive element were investigated in Cu-Ti alloys. A surface layer formed in a commercial copper-2.6mass% nickel-0.6% silicon alloy (Cu-Ni-Si) by annealing was also studied for comparison. The buttons were cold rolled to 0.5 mm thick sheets, and the sheets were cut to about 10 mm square. The detailed procedures for sample preparation are described in previous works /9,10/.

2.2. Measurements

XPS measurements were carried out in the same manner as in the previous works, in which the incident X-ray was Al *K*α or Mg *K*α radiation /11, 12/. XPS spectra of main elements were recorded, and their relative sensitivity factors given in the spectrometer were used for quantification. The take-off angle, which is defined as the angle between the direction of an analyzer and the sample plane, was changed from 15 degrees (0.0262 rad) to 75 degrees (1.31 rad) in angle resolved X-ray photoelectron spectroscopy (AR-XPS). Angle resolved X-ray excited Auger electron spectra (AR-DAES) were also measured for studying the chemical state of copper /12/. Ordinary XPS spectra were obtained in the take-off angle of 45 degrees.

In surface segregation experiments, the surface of a sample annealed under ultra-high vacuum was analyzed by AR-XPS without exposure to air. A native oxide layer formed on the sample surface by exposing it to air was characterized by AR-XPS and AR-XAES /11, 12/. In analysis of a surface layer formed by selective oxidation, XPS spectra were measured after the sample surface was slightly sputtered by argon ions, since a very thin contaminated layer adsorbs to the sample surface during exposure to air after annealing.

SIMS depth profiles were obtained using an apparatus with quadrupole-type mass spectrophotometer, in which primary Cs^+ ions of 5 keV were irradiated to samples. Secondary ions, mainly $^{196}(CsCu)^+$, $^{181}(CsTi)^+$ and $^{16}O^+$ ions, from the sample surface were counted, in order to evaluate changes in the amount of constituent elements in the depth profiles. The sputtering rate in SIMS depth profiling was estimated from measurement of the sputtered crater depth.

3. SURFACE SEGREGATION

Surface segregation of non-transition elements was studied in copper-tin /13/ and copper-antimony /14/ systems. In these experiments, Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunnel microscopy (STM) were used for analyzing the surface composition and structure of single crystal alloys. The results showed that tin and antimony are easily segregated on the alloy surfaces to form a specific surface structure. However, information on surface segregation of transition elements is limited so far, because these elements are not very surface-active and surface segregation of surface-active impurity elements, such as sulfur, prevents us from observing the surface segregation of transition elements. Recently, the surface segregation of chromium has been successfully investigated by preparing high-purity Cu-0.4Cr /10/.

Figure 2(a) shows a wide XPS spectrum from the surface of Cu-0.4Cr, which was sputter-cleaned by argon ion bombardment. Cr 2p XPS peaks are little observed in this spectrum, because the bulk concentration of chromium is low. However, chromium segregation was found on the sample surface by annealing in the temperatures over 600 K in which chromium dissolved in the alloy is mobile. Figure 2(b) shows an XPS spectrum from the surface of Cu-0.4Cr annealed at 973 K for 600 s. Heights of the Cr 2p XPS peaks and Cr LMM XAES peaks become large by annealing, indicating that chromium segregation is taking place. Furthermore, an XPS spectrum from the sample surface with chromium segregation, which was subsequently exposed to air at room temperature for 600 s, is shown in Fig. 2(c). This spectrum indicates that a native oxide layer is formed on the sample surface with chromium segregation, of which characterization will be described in the following section.

AR-XPS has been applied for analyzing the chromium segregated layer in Cu-0.4Cr non-destructively, since the segregated layer is very thin. Figure 3 shows the concentration of copper and

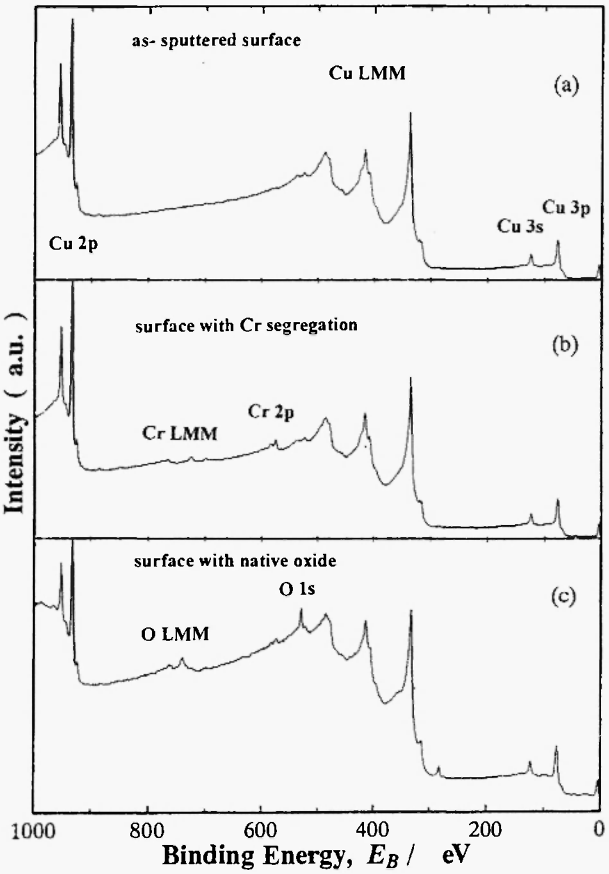

Fig. 2: XPS wide spectra from the surface (a) sputter cleaned, (b) annealed at 973 K, and (c) subsequently exposed to air in Cu-0.4%Cr alloy.

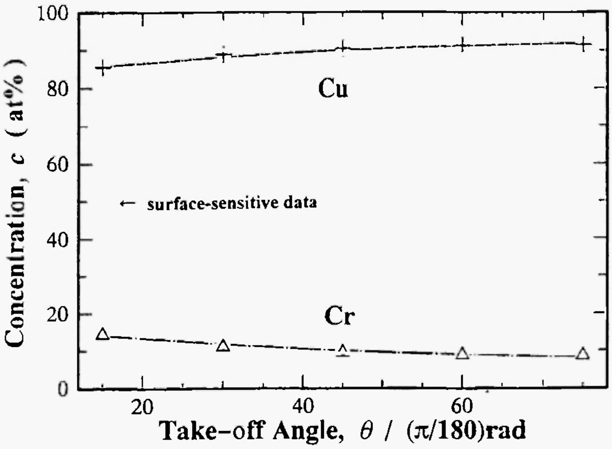

Fig. 3: The concentration of copper and chromium versus the take-off angle in Cu-0.4%Cr alloy, which was annealed at 973 K under ultra high vacuum. Experimental data and calculated results are denoted by marks and lines, respectively.

chromium obtained from XPS peak intensities as a function of take-off angle in Cu-0.4Cr, which was annealed at 973 K for 600 s under ultra-high vacuum. Experimental results are plotted as marks, while calculated results on the basis of a layered structure model /11/ are denoted as lines. By fitting the calculated curves to the experimental data, the thickness of the chromium segregated layer and the average concentration of chromium in the layer are estimated to be about 0.8 nm and 15 at%, respectively. As the bulk composition of chromium is 0.41mass% (0.53at%), the enrichment ratio of chromium at the surface is nearly thirty. This enrichment ratio is higher than that for chromium segregated in iron-based alloys /11/. Thus, chromium is found to be a surface-active element in high-purity copper-based alloys. The average chromium concentration, 15 at%, in the segregated layer suggests a possibility that chromium may be precipitated as a second phase, as inferred from the binary alloy phase diagram /15/. However, the fact that the segregated layer is limited in a few atomic layers indicates that the surface segregation of chromium occurs by annealing in ultra-high vacuum.

4. NATIVE OXIDE LAYER

Systematic information has been obtained with respect to the growth of a native oxide layer formed on the surface of ultra high-purity copper by means of AR-XPS non-destructively /12,16/. The results suggest that the thickness of native oxide layers formed on the copper surface at room temperature is a nanometer in magnitude, and the thickness of the oxide layers gradually increases with increasing exposure time even at room temperature, as shown in Fig. 4. A contaminated layer consisting of mainly hydrocarbon, which covers the sample surface, is also shown to become thick with increasing time. For comparison, an increase in the thickness of a native oxide layer formed on the surface of ultra high-purity iron by exposure is also shown in Fig. 4, which indicates that the growth of the native oxide layer of iron almost stops at room temperature. Thus, it is noted that the growth of native oxide layers in iron is different from that for copper, and this may be attributed to a difference in the mobility of

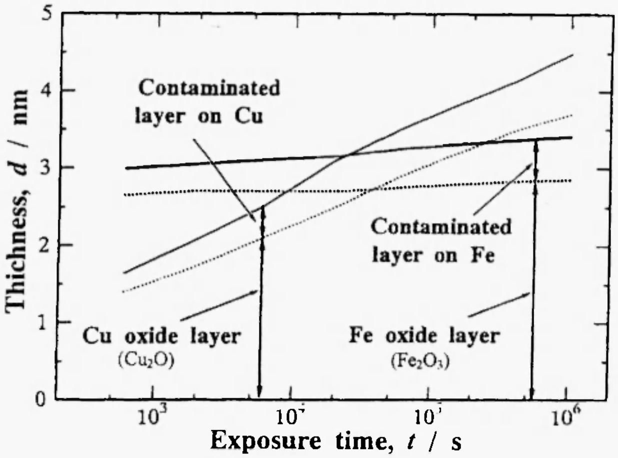

Fig. 4: Thickness of oxide layers and contaminated layer formed on the surface of ultra high-purity copper and iron as a function of air exposure time.

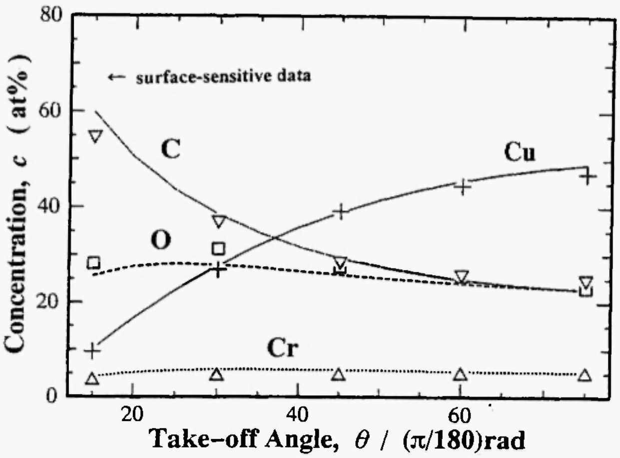

Fig. 5: The concentration of copper, chromium, oxygen and carbon versus the take-off angle in Cu-0.4%Cr alloy, which was exposed to air for 4.1 × 10^5 s after segregation. Experimental and calculated results are denoted by mark and line, respectively.

ions in oxides at room temperature.

Chromium segregated on the iron surface is known to reduce the growth of native oxide layers in iron-based alloys /11,16/, which is considered to arise from a protective character of chromium to oxidation. Therefore, it is of great interest whether the chromium segregation in copper-based alloys influences the growth of a native oxide layer or not. The wide XPS spectrum from a native oxide layer formed on the Cu-0.4Cr surface with chromium segregation is shown in Fig. 2(c). The surface layer of this sample was characterized by AR-XPS and AR-XAES in detail. Figure 5 shows the concentration of copper, chromium, oxygen and carbon as a function of take-off angle in Cu-0.4Cr with chromium segregation, which was exposed to air for 4.2 × 10^5 s at room temperature. The effective thickness of native oxide layers was evaluated in the same model previously reported /16/, in which a Cu_2O layer is assumed to cover the surface of copper. From comparison between experimental and calculated results, the thickness of the oxide layer was estimated to be about 3 nm. The thickness of this oxide layer is comparable to that of a native oxide layer formed on the high-purity copper, which is shown in Fig. 4. This implies that the chromium segregation does not appear to suppress the growth of the oxide layer so much. However, small changes in the Cu 2p AR-XPS spectra by chromium segregation were also observed in this sample, which implies that the chromium segregation suppresses the formation of CuO on the copper surface /10/.

Cu LMM XAES spectra were measured in order to analyze the chemical state in an oxide layer formed on the surface of Cu-0.4Cr with the surface segregation of chromium. Figure 6 shows Cu $L_3M_{45}M_{45}$ AR-XAES spectra obtained in the take-off angle of 15, 30, 45, 60 and 75 degrees for Cu-0.4Cr with the chromium segregation, which was exposed to air for 4.2 × 10^5 s. A spectrum of the Cu $L_3M_{45}M_{45}$ XAES from metallic copper is given in Fig. 5(f), for comparison. The spectra of Cu $L_3M_{45}M_{45}$ AR-XAES for this sample can be assigned to the signals from copper oxide (Cu^+ : 916.2 eV) and metallic copper (Cu^0 : 918.6 eV) /17,18/. It may safely be said that an oxide layer with Cu^+ covers the metallic copper, as a peak due to Cu^0 increases with increasing take-off angle in this sample. This is consistent with the compositional results of the take-off dependence of the measured concentration, as shown in Fig. 5.

Moreover, AR-XPS was used for analyzing changes in the chemical state of surface segregated chromium by air exposure. Figure 7 shows Cr 2p AR-XPS spectra obtained in the take-off angle of 15, 30, 45, 60 and 75

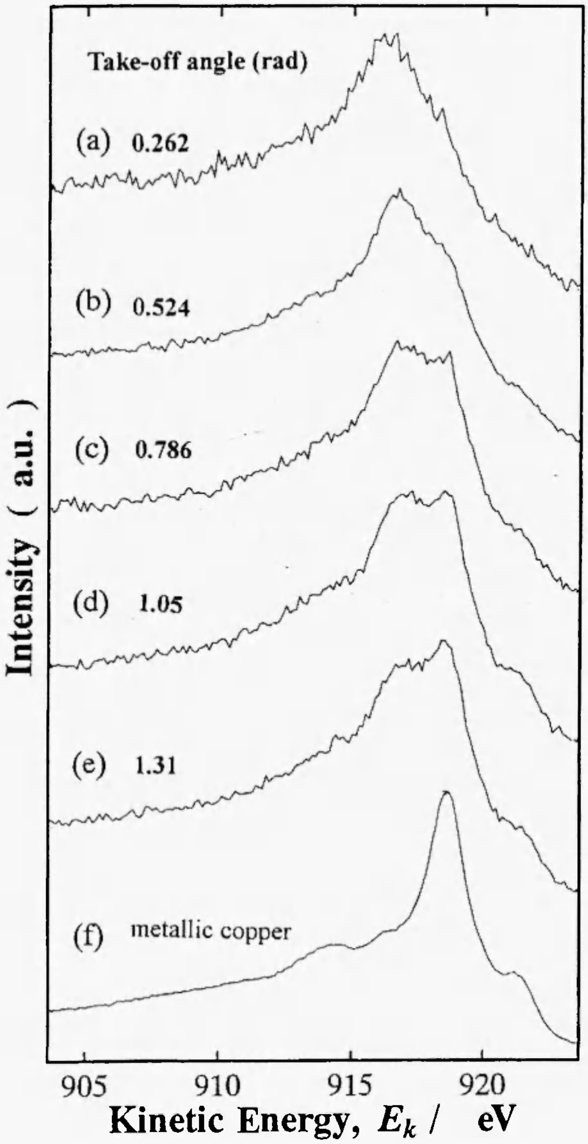

Fig. 6: Cu $L_3M_{45}M_{45}$ AR-XAES spectra obtained in the take-off angle of (a) 0.262 rad, (b) 0.524 rad, (c) 0.786 rad, (d) 1.05 rad and (e) 1.31 rad for Cu-0.4%Cr exposed to air for 4.2×10^5 s, and (f) Cu $L_3M_{45}M_{45}$ XAES spectrum for metallic copper.

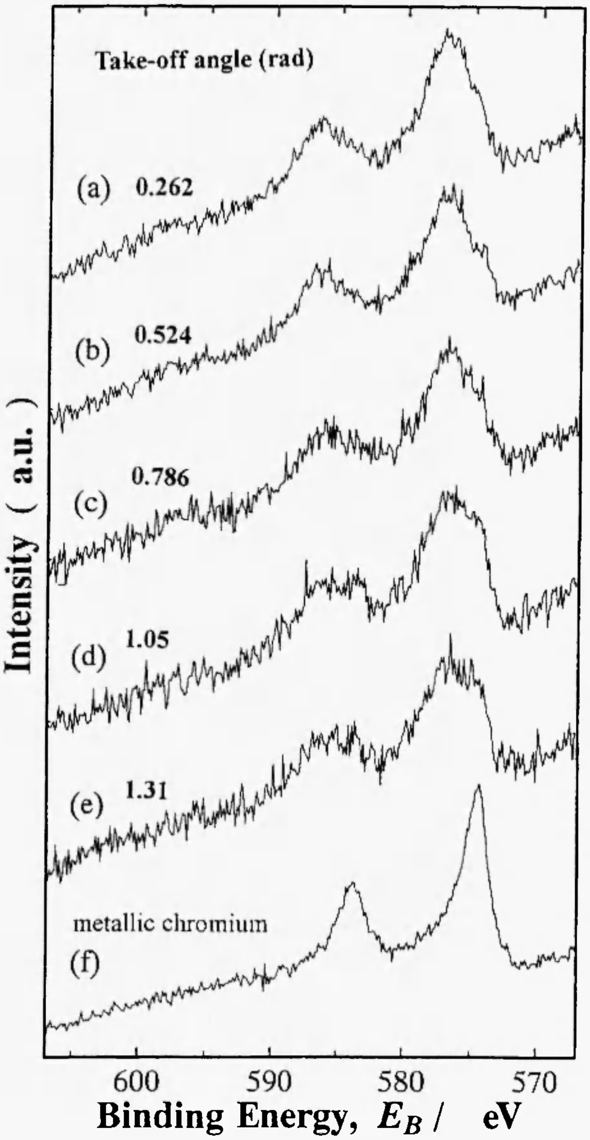

Fig. 7: Cr 2p AR-XPS spectra obtained in the take-off angle of (a) 0.262 rad, (b) 0.524 rad, (c) 0.786 rad, (d) 1.05 rad and (e) 1.31 rad for Cu-0.4%Cr exposed to air for 4.2×10^5 s, and (f) Cr 2p XPS spectrum for metallic chromium segregated on the surface.

degree for Cu-0.4Cr with chromium segregation exposed to air for 4.2×10^5 s. A spectrum of the Cr-2p XPS from metallic chromium, which is segregated on the sample surface, is shown in Fig. 7(f), for comparison. Since the Cr $2p_{3/2}$ peak positions of Cr^0 and Cr^{3+} are 574.4 and 576.9 eV, respectively /18/, the results indicate that most of the chromium segregated on the sample surface is oxidized. However, a slight Cr^0 peak is likely to be observed in the Cr $2p_{3/2}$ XPS spectra measured at high take-off angle in the oxidized sample. From these results, the present author maintains the view that chromium segregated on the sample surface does not fully cover the copper surface with an ideal layered structure, but is heterogeneously present on the surface. This is considered to be one of the reasons why the surface segregation of chromium does not sufficiently reduce the growth of the native oxide layer.

5. SELECTIVE OXIDATION

Copper-based alloys are used for electrical parts such as lead frame and connector because of their high electrical conductivity and high strength, which are improved by the addition of alloying elements and modification of processes. Typically, titanium is sometimes added to copper-based alloys for improving the hardness and conductivity /19,20/, but the chemical properties of titanium are quite different from those of copper, as exemplified in Fig. 1. From the viewpoint of control of surface properties, the growth kinetics of internal oxidation of copper-titanium alloys was also studied by observing surface layers formed at high temperatures /21/. However, microscopic elemental distribution formed in the surface layer of copper-titanium alloys is not yet sufficiently clear. Surface analytical techniques have been applied in order to clarify characteristic features of surface layers formed in high-purity copper-titanium alloys prepared in a low partial pressure of oxygen. The results are summarized as follows.

The high-purity copper-titanium alloys were annealed at 873 K in argon-9.8% hydrogen gas containing water vapor, which passed water at 290 K /9/. The oxygen partial pressure in this annealing atmosphere is estimated to be about 5.2×10^{-18} Pa, of which the annealing condition is in zone (b) of Fig. 1. Under this condition, pure titanium is oxidized, while pure copper is not oxidized, although the degree of oxidation of an alloying element in a copper-based alloy should be strictly discussed using the activity of the alloying element. X-ray photoelectron spectroscopy (XPS) and secondary mass ion spectrometry (SIMS) can provide important information on the microscopic distribution of these elements and oxygen in the surface layers.

5.1. Surface analysis by XPS

Figure 8 shows the surface concentration measured by XPS as a function of the bulk titanium concentration in the high-purity copper-titanium alloys, which were oxidized under the low partial pressure of oxygen /9/. Oxygen detected at the surface of these samples originates from two kinds of oxides: a titanium oxide formed by annealing at 873 K, in zone (b) of Fig. 1, and a native oxide formed by exposure to air at room temperature after annealing, in zone (d) of Fig. 1. Oxygen detected on the surface of pure copper is attributed to the native oxide, of which the composition is nearly Cu_2O. The titanium concentration of the alloy surface presently determined is much higher than the bulk titanium concentration, indicating that titanium is enriched to the alloy surface to form titanium oxides during annealing in the low partial pressure of oxygen. As the bulk titanium concentration in the alloys increases, the surface concentration of oxygen and titanium increases, while the surface concentration of copper decreases. A titanium oxide which is inferred to form on the alloy surface is nearly TiO_2, since the contribution of a native oxide formed on the surface of metallic copper to the total oxygen concentration on the alloy surface is small.

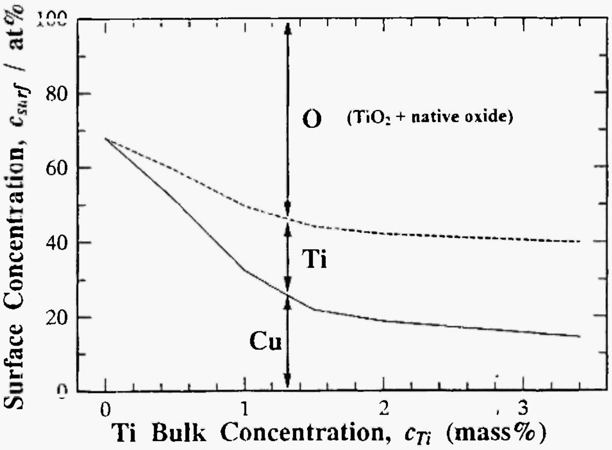

Fig. 8: Surface concentration obtained by XPS versus titanium bulk concentration in Cu-Ti alloys annealed at 873 K.

In order to analyze the elemental distribution in-depth of the surface layer, XPS sputter depth profiles of copper, titanium and oxygen were measured for Cu-3.4Ti annealed in the low partial pressure of oxygen, as shown in Fig. 9. The depth profiles show the monotonic

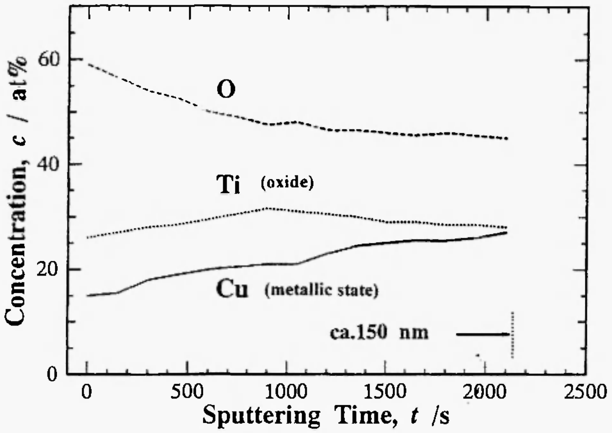

Fig. 9: XPS depth profiles of O, Ti and Cu for Cu-3.4Ti.

variation in the concentration of oxygen and copper with increasing sputtering time. This indicates that oxygen penetrates into the bulk by annealing. On the other hand, the titanium alloys concentration appears to show a peak at the depth of about 70 nm by sputtering for about 1000 s. Such a peak in the depth profile of titanium is also observed in SIMS profiles, as shown later.

Ti XPS spectra and Cu LMM XAES spectra were measured as a function of argon ion sputtering time, in order to characterize the chemical state of titanium and copper in the surface layer. Figure 10 shows Ti 2p XPS spectra from the surface of Cu-3.4Ti, which were sputtered for 0s, 30s, 150s, 300s and 450s, respectively. Peaks in Ti $2p_{3/2}$ XPS spectra are located between about 459 and 455 eV in binding energy, which shows that titanium is present as not metallic but Ti^{4+} and/or Ti^{2+} oxides /9/. Some influence of ion sputtering on the chemical state should be taken into account in sputter depth profiles, since oxygen is often preferentially sputtered from the oxide surface. Nevertheless, titanium is considered to form oxide as TiO_x in the surface layer of this alloy, as predicted from the annealing condition.

On the other hand, Cu LMM XAES spectra, which are sensitive to the chemical state of copper /16,17/, were also measured for characterizing the chemical state in the surface layer, and the results are described in Fig. 11, indicating Cu $L_3M_{45}M_{45}$ XAES spectra from the surface of Cu-3.4Ti sputtered for 0s, 30s, 150s, 300s and 450s. The peak position in the XAES spectra obtained from the alloy surface exposed to air at room temperature after annealing is at about 916.2 eV, which is the same as the peak position for a native oxide as shown in Fig. 6. This implies that a thin native oxide layer is formed by air exposure under a condition in zone (d) of Fig. 1. On the other hand, the peak position in the XAES spectra obtained from the sputtered alloy surface is at about 918.6 eV, indicating that copper in the surface layer is metallic in spite of titanium oxidation. These spectral data are consistent with thermodynamic prediction for copper-titanium alloys annealed in the low partial pressure of oxygen, as shown in Fig. 1.

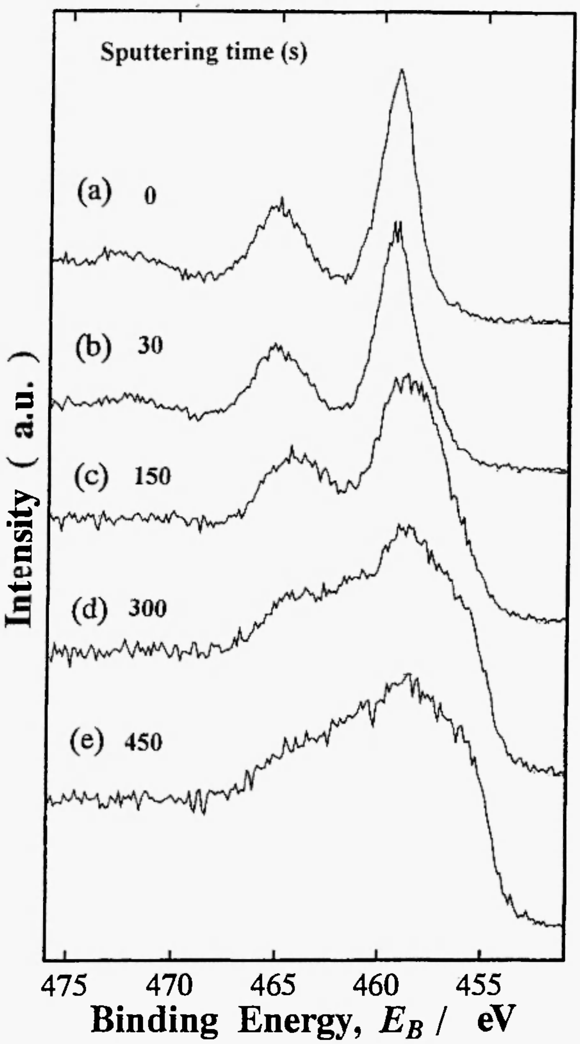

Fig. 10: Ti 2p XPS spectra from the surface of Cu-3.4Ti, which were sputtered for (a) 0s, (b) 30s, (c) 150s, (d) 300s and (e) 450s.

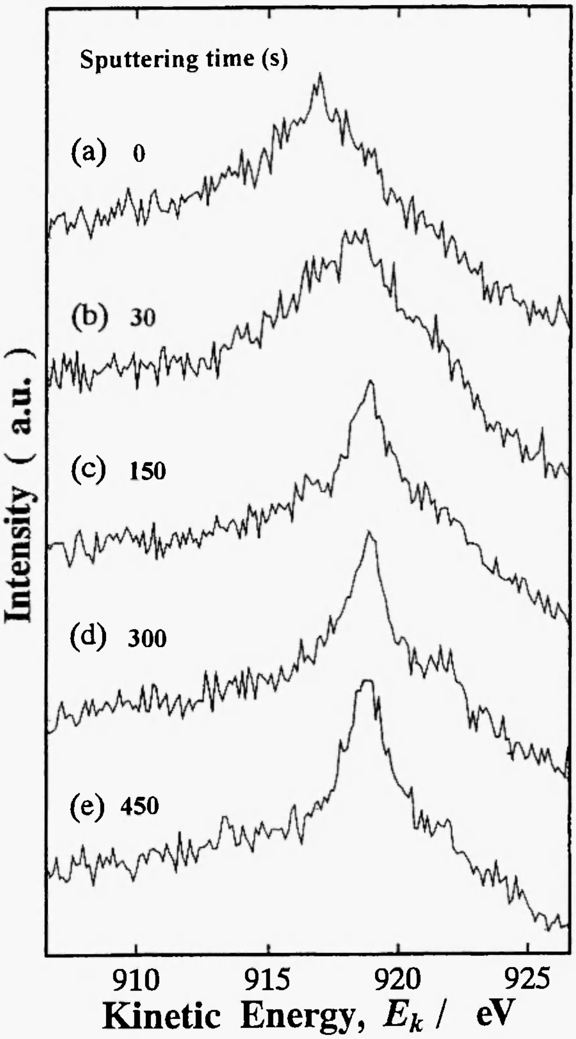

Fig. 11: Cu LMM XAES spectra of Cu-3.4Ti, which were sputtered for (a) 0s, (b) 30s, (c) 150s, (d) 300s and (e) 450s.

5.2. Depth Profiles by SIMS

SIMS depth profiling, whose signals are generally high-sensitive and whose sputtering rate is high, is very useful for analyzing the distribution of elements in relatively deep layers. It should, however, be noted that quantification of the elemental content in the surface layer is not simple. Figure 12 shows SIMS depth profiles of O^+, $CsTi^+$ and $CsCu^+$ from the surface of Cu-3.4Ti, which was annealed in the same condition as above. The depth sputtered for 1800 s was about 5 µm. These SIMS depth profiles demonstrate characteristic features of the distribution of elements in the surface layer. A monotonic decrease in secondary ion counts of oxygen is found with increasing depth. This indicates that oxygen penetrates into the matrix of Cu-3.4Ti, and the oxygen potential in the surface layer is gradually reduced on the matrix side. On the surface side, the amount of titanium decreases with increasing depth up to about 1 µm. This titanium profile corresponds to the gradient of the oxygen potential in the surface layer. This suggests that titanium moved to the surface side so as to form titanium oxides. On the other hand, a titanium-depleted zone is formed in the location of depth of about 1 µm, which is likely to be formed by titanium movement due to formation of titanium oxides on the surface side. Beneath the depth about 1 µm of the surface layer, the titanium concentration increases with increasing depth and approaches to the bulk concentration. The $CsCu^+$ ion counts in the depth profile appear to increase with increasing depth, but it is considered to arise from the matrix effect on occurrence of secondary ions of $CsCu^+$, which depend on the bulk concentration of oxygen and titanium. Thus, an elemental profile in the surface layer, which is formed under an annealing condition, may be controlled by partial pressure of oxygen in annealing atmosphere, annealing temperature, an oxygen potential gradient formed in the surface layer, and so on. This feature is consistent with elemental process in internal oxidation which occurs in an alloy containing a reactive element with oxygen /22/.

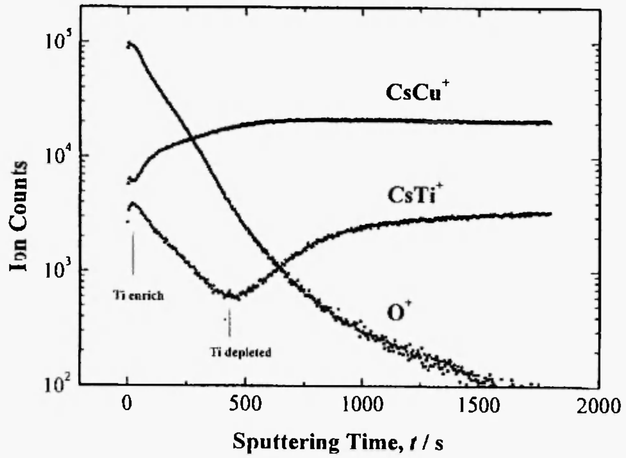

Fig. 12: SIMS depth profiles of O^+, $CsTi^+$ and $CsCu^+$ for Cu-3.4Ti.

6. ELEMENTAL DISTRIBUTION IN SURFACE LAYER

Formation processes of the characteristics elemental distribution in surface layers of copper-based alloys, which is formed by exposure to various atmospheres, should be discussed on the basis of the above results, in order to understand factors controlling the surface properties. Surface segregation of an alloying element in copper-based alloys occurs by annealing in ultra high vacuum without influence of atmospheric gas, as denoted in zone (c) of Fig. 1. The driving force for the surface segregation is the difference between a surface free energy and a bulk free energy in the alloys, which is reduced by segregation of a surface-active element on the surface. The amount of the segregated element on the alloy surface approaches to a level by annealing, so as to be in equilibrium with the bulk amount. The thickness of the surface layer formed in this way, that is, a surface segregated layer, is a few atomic layers. Such a thin surface layer may influence a subsequent reaction within a thin surface layer, like the native oxide formation, as was clearly observed in iron-chromium alloys with chromium surface segregation /11, 16/. However, the effect of the chromium segregation on the native oxide is not so strong in the copper-based alloy, and it may result from the small amount of chromium segregated on the surface and the relatively rapid growth of the native oxide layer in copper. Furthermore, the surface layer with chromium segregation is considered to be too thin to modify a reaction with gas at high temperatures, because gas species may feasibly penetrate into the bulk through the thin layer.

Next, let us consider characteristic depth profiles of the surface layer formed in copper-based alloys containing a reactive element, like titanium, by annealing in the low partial pressure of oxygen. The formation process of this surface layer is likely to be accompanied by microscopic phenomena, such as formation of fine oxide particles of the reactive element in metallic copper. A schematic diagram for the microscopic elemental distribution formed in the surface layer is given in Fig. 13, on the basis of the results of Fig. 12. If a copper-based alloy contains an alloying element reactive with oxygen, other than titanium, a similar depth profile will be expected. In fact, a depth profile measured in Cu-Ni-Si, which was annealed at 873 K in a low partial pressure, revealed the depleted zone of silicon in the surface layer, as shown in Fig. 14, in which depth profiles of O^+, $CsNi^+$, $CsSi^+$ and $CsCu^+$ are given. It is interesting to note that the depth profiles of oxygen and silicon are analogous to those for oxygen and titanium in Cu-Ti alloys. This is because silicon is also a reactive element with oxygen, as shown in Fig. 1. Such selective oxidation of silicon has also been observed in surface layers of iron-silicon alloys annealed under a low partial pressure of oxygen, although oxygen distribution in the surface layers is complicated in the iron alloys /23,24/. On the other hand, as shown in Fig. 14, the nickel depth profile is likely to be similar to the copper cases. This is attributed

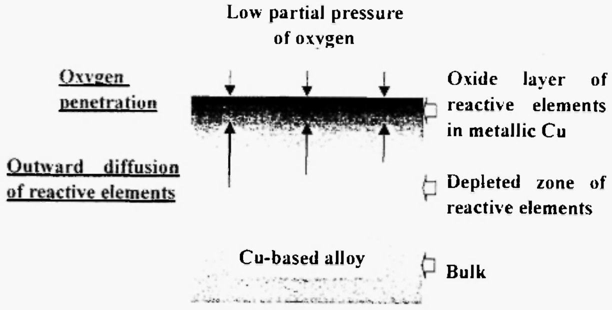

Fig. 13: Schematic diagram for the concentration profile in the surface layer formed by selective oxidation of reactive elements.

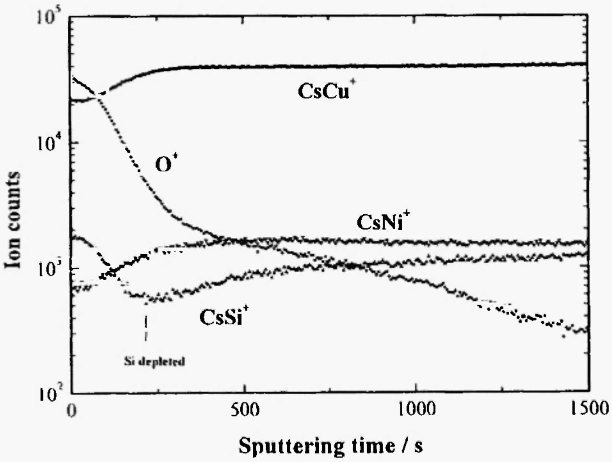

Fig. 14: SIMS depth profiles of O^+, $CsNi^+$, $CsSi^+$ and $CsCu^+$ for Cu-Ni-Si.

to the relatively lower reactivity of nickel with oxygen, as easily seen in Fig. 1, suggesting that nickel is not oxidized in the surface layer under the annealing condition.

Finally, let us discuss the growth kinetics of the surface layer formed by selective oxidation of a reactive element in copper-based alloys. An elemental profile in the surface layer is influenced by the partial pressure of oxygen in annealing atmosphere, annealing temperature, oxygen potential gradient in the surface layer, and so on. The oxidation of the reactive element takes place by meeting of oxygen from the surface and the reactive element from the bulk. Since the diffusivity of a reactive element, that is, a reactive element in copper, is much lower than that of oxygen /21, 25/, the growth of the surface layer is likely to be controlled by outward diffusion of the reactive element. For example, the depth profile of titanium beneath the depleted zone in the surface layer could be fairly described by a diffusion profile of titanium in a Cu-Ti alloy, which was annealed in a low partial pressure of oxygen /9/. More precisely, the accurate size and shape of oxide particles of the reactive element and microscopic diffusion paths of oxygen and titanium should be considered, in order to describe realistic formation processes of the surface layer. Nevertheless, it is satisfactory to say that the growth process of the surface layer by selective oxidation of a reactive element in copper-based alloys is dominated by mainly diffusion of the reactive element in copper.

6. SUMMARY

The present paper describes the results for a few kinds of surface layer formed on copper-based alloys under different conditions. AR-XPS was used for studying surface segregation of chromium in a copper-chromium alloy, and then the effect of chromium segregation on the formation of native oxide was also investigated in this alloy. XPS and SIMS were applied for analyzing surface layers formed by selective oxidation of a reactive element in copper-titanium alloys. The main conclusions obtained in these experiments are as follows:

1. Chromium is segregated on the surface of a high-purity copper chromium alloy by annealing at high temperatures under ultra high vacuum, indicating that chromium is one of the surface-active elements in copper. According to a simple layered model, the effective thickness of the segregated layer is estimated to be a few atomic layers.
2. The results of the alloy surface with chromium segregation, which was exposed to air after annealing, show that the segregated chromium does not significantly inhibit the growth of a native oxide of copper. The small effect of chromium segregation on the native oxide is considered to result from the relatively high oxidation rate of copper and the microscopic heterogeneity of segregated chromium.
3. In the surface layer formed in copper alloys containing a reactive element, like titanium, by annealing in a low partial pressure of oxygen, the reactive element is enriched to the surface side to form its oxides, while copper is kept metallic.
4. The depth profiles show that the amount of oxides of a reactive element formed in the surface layer decreases with increasing depth, which is likely to correspond to the oxygen potential gradient in the surface layer. A depleted zone of the reactive element is found to form beneath the surface layer.
5. Formation processes of surface layers formed in copper-based alloys under different conditions could be interpreted by the thermodynamic character of copper and alloying elements.

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