

Title: Oxidation of copper alloys – studied by AEM cross-sectional specimens

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## Abstract

In this work, the oxide structures of three polycrystalline copper grades, an unalloyed OF-copper and an alloyed CuAg- and DHP-copper, were studied by cross-sectional AEM samples. The oxidation treatments were carried out in air at 200°C and 350°C for different exposure times. The detailed oxide layer structures were characterized by analytical transmission electron microscopy (AEM). At 200°C, nanosized Cu<sub>2</sub>O layer formed on the all copper grades. At 350°C, nanosized Cu<sub>2</sub>O layer formed at first on the all copper grades. After longer exposure time at 350°C, a crystalline CuO layer grew on the Cu<sub>2</sub>O layer of the unalloyed OF-copper. In the case of the alloyed CuAg- and DHP-copper, crystalline and columnar shape layer, what consisting of Cu<sub>2</sub>O and CuO grains, formed on the nanocrystalline Cu<sub>2</sub>O layer. Especially at 350°C, the unalloyed copper oxidized notably slower than the alloyed coppers and its oxide structures were different compared to the alloyed coppers.

## 1. Introduction

Oxidation of copper and copper alloys is of great importance in industrial application since copper materials are widely used in different oxidizing environments and applications. These are e.g. applications requiring resistance to atmospheric or water exposure, marine applications as well as heat exchanger, condenser and electrical applications. Although, oxidation of copper has been studied extensively, for example the effect of alloying elements on the oxidation phenomenon is not still clear. In addition, most classical models of oxidation are based on measuring weight changes, and therefore they assume a uniform oxide film growth [1, 2, 3, 4, 5].

Due to the development of the experimental capabilities and equipment, it is nowadays known that the copper oxide film nucleates and grows, even at atmospheric pressure, as oxide islands not as a uniform layer. Oxidation phenomenon of copper includes a complex chemisorption period with reconstruction followed by interfacial oxide nucleation, initial growth involving islands, coalescence and finally overlayer thickening. Depending on temperature and oxygen partial pressure, oxide layers of copper consists  $\text{Cu}_2\text{O}$  only or both  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . At low temperatures ( $< 200^\circ\text{C}$ ),  $\text{Cu}_2\text{O}$  layer forms at first. When temperature increases,  $\text{Cu}_2\text{O}$  starts to react with O and  $\text{CuO}$  phase forms gradually by the following reaction [6, 7, 8, 9, 10, 11]:



The effect of the alloying elements on oxidation of copper is very complicated and still not fully known. Y. Zhu et al. have studied the influence of the impurities on the copper oxidation kinetics. They used 99.5 % (2N) and 99.9999 % (6N) pure copper specimens and oxidation was conducted at 600-1050°C in 1 atm oxygen atmosphere. Based on their studies, in the case of the high-purity copper, a thin and uniform CuO layer formed on the Cu<sub>2</sub>O layer and it was impervious to oxygen. However, if alloying elements form a porous and non-protective CuO layer, the oxidation rate increases. On the other hand, alloying elements can also slow down the initial stage of oxidation because alloying elements can impede the movement of copper atoms at the Cu<sub>2</sub>O/Cu -interface and so the growth of Cu<sub>2</sub>O nucleus becomes slower [5, 12].

M. Hirsimäki et al. have investigated oxide formation on Cu{100}, Ag/Cu{100} surface alloy and polycrystalline Cu(1wt% Ag) alloy. The experiments were carried out in pure oxygen atmosphere ( $2 \times 10^{-3}$  atm). Surface temperature was 47°C - 200°C. The surface concentration of Cu, Cu<sub>2</sub>O and CuO was determined by X-ray photoelectron spectroscopy (XPS). M. Hirsimäki et al. observed that the oxide layers on all three samples were similar even if surface geometries and initial chemical composition of the test materials differed notably from each other. Their results prove also that the adsorption of O<sub>2</sub> induces segregation of Cu to the surface at Ag-alloyed coppers. The formed Cu layer oxidized to Cu<sub>2</sub>O just like in pure Cu samples and therefore Ag did not have any influence to the oxidation behaviour of Ag containing samples. Formation of Ag oxides or CuO was not observed in these experiments. Cu<sub>2</sub>O was formed on all the three specimens and its amount was almost same on the samples treated under the same conditions [13].

L. Wang and J. C. Yang have studied the initial oxidation of Cu-50at% Au (001) single-crystal thin film and Cu (001) with *in situ* ultra-high-vacuum transmission electron microscopy. They noticed that addition of Au changed oxidation incubation time, oxide nucleation rate, oxide growth kinetics and nucleation activation energy. It was also noticed that, Au segregated to the topmost layer due to its low surface energy. For that reason it was expected that the surface is relatively inert toward oxygen adsorption. The experiments testified that  $\text{Cu}_{0.5}\text{Au}_{0.5}$  had longer incubation time during oxidation than that of Cu (001) but the oxide nucleation rate of  $\text{Cu}_{0.5}\text{Au}_{0.5}$  was much higher than that for Cu(001). In addition, the oxide saturation was reached very rapidly in  $\text{Cu}_{0.5}\text{Au}_{0.5}$  [14].

In this research project, oxidation of industrial copper and copper alloys was earlier studied with planar AEM and AFM (atomic force microscope) samples. Those studies indicated that alloying and increasing of temperature accelerated oxidation and the oxide layers consisted of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . However, the detailed structure of the oxide layer could not be revealed exactly with planar samples [15]. The aim of this work was to study the cross-sections of three different oxidized polycrystalline copper grades (Outokumpu Copper) to get more information about copper oxide layer structures. Copper oxidation treatments were carried out in air at  $200^\circ\text{C}$  and  $350^\circ\text{C}$ .

## 2. Materials and experimental

Oxidation studies were carried out for three copper grades: unalloyed OF-copper (oxygen free copper, oxygen content <5 ppm), CuAg-copper (silver bearing copper, Ag ~ 0.5 - 2 wt-%, not standard Outokumpu grade) and DHP-copper (deoxidised high-phosphor copper, P 0,013 - 0,050 wt-%). Copper materials were received in the cold rolled condition (reduction 80 - 90 %). Microstructures of the cold rolled materials were heterogenous and therefore more homogenous microstructures for oxidation treatments were produced by recrystallization treatment, resulting the average grain size of 5  $\mu\text{m}$ .

The oxidation treatments were carried out in a ceramic tube furnace in air at 200°C and 350°C. Duration of treatments at 200°C were 25 and 100 minutes and at 350°C 5, 25 and 100 minutes. Samples for the cross-sectional AEM studies of oxide layers were prepared by using methods described in Ref. [16] and [17]. The small pieces were cut from recrystallized plates with a diamond saw. The pieces were ground mechanically to size ~1.7mm x ~1mm x ~0.4mm. The grounded pieces were oxidized. Two oxidized pieces were embedded into a titanium grid so that the oxidized surfaces of the specimens were face-to-face. The samples were attached into the grid by carbon-araldite glue. The glued grid was pre-thinned by hand to thickness of ~100  $\mu\text{m}$  and then with Dimple Grinder Model 656 (Gatan Inc.) to the thickness of ~20  $\mu\text{m}$ . The final thinning was made with Precision Ion Polishing System Model 691 (Gatan Inc.). The oxidized cross-sectional samples were studied with AEM Model Jeol JEM 2010 equipped with Noran Vantage EDS-system.

### 3. Results and discussion

#### 3.1. Oxidation treatment at 200°C

The copper samples were oxidized in air at 200°C for 25 and 100 minutes. AEM images of OF-, CuAg- and DHP-copper samples after 25 minutes oxidation at 200°C are presented in Fig. 1 (a) - (c). A selected area electron diffraction (SAED) pattern taken from the oxide layer of DHP-copper is presented in Fig. 1 (d) and the selected area has been marked on Fig. 1 (c). SAED patterns of all samples were similar and they indicated a nanocrystalline copper oxide and d values corresponded closely to cubic  $\text{Cu}_2\text{O}$  ( $a \approx 0.427$  nm [18]). The oxide layer of OF-copper was non-uniform while the oxide layers of CuAg- and DHP-copper were uniform which agree with our earlier results from planar samples [15]. According to G. Zhou's and J. Yang's studies, a copper oxide layer grows via oxide islands, resulting a non-uniform layer, and finally overlayer thickening occurs [6]. The average thickness of all oxide layers was almost same.

AEM images of OF-, CuAg- and DHP-copper samples after 100 minutes oxidation at 200°C are presented in Figs. 2 (a) - (c). The SAED pattern taken from the oxide layer of OF-copper is presented in Fig. 2 (d). SAED patterns of all samples were similar and they indicated nanocrystalline  $\text{Cu}_2\text{O}$ . The oxide layers of all samples were uniform, however, the oxide layer and especially its surface of unalloyed OF-copper was much denser than that of alloyed CuAg- and DHP-copper. This finding corresponds well to

our earlier results with planar samples studies indicating that Rms surface roughness values of OF-copper were less than that of the alloyed coppers [15].

The average thicknesses of oxide layers after oxidation treatments at 200°C are presented in Fig. 3. Thickness values were measured from AEM images and each value is an average of twenty measurements. Based on these measurements, the thickness of oxide layers after 25 minutes of oxidation at 200°C was 40 nm - 50 nm. After 100 minutes oxidation the oxide layers of OF-copper were 100 nm and that of the alloyed coppers were 120 nm - 150 nm. Y. Zhu et al. have noticed that if the oxide layer becomes porous and non-protective due to the alloying elements, the oxidation rate increases [5, 12].

### **3.2. Oxidation treatment at 350°C**

The copper samples were oxidized at 350°C for 5, 25 and 100 minutes. After 5 minutes oxidation the situation was very similar to than after 100 minutes of oxidation at 200°C. The structure of oxide layer of all copper grades was nanocrystalline Cu<sub>2</sub>O and the thickness of the oxide layers was about 80 nm.

AEM images of OF-, CuAg- and DHP-copper samples after 25 minutes oxidation at 350°C are presented in Fig. 4 (a) - (c). The SADP taken from the inmost oxide layer of OF-copper is presented in Fig. 4 (d). After 25 minutes of oxidation, the structure and thickness of the oxide layer differed significantly between unalloyed copper and alloyed



coppers. All studied specimens had similar inmost 300 - 400 nm thick  $\text{Cu}_2\text{O}$  layer but the oxide layer on it was different depending on the copper grade. On pure copper, about 300 nm thick  $\text{CuO}$  layer having circular shape grains formed on the  $\text{Cu}_2\text{O}$  layer. In the case of alloyed coppers, columnar  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  grains grew on nanosized  $\text{Cu}_2\text{O}$  layer. Columnar grains consisting layers were 600 - 800 nm thick. S. Ghosh et al. have found that at low temperatures,  $\text{Cu}_2\text{O}$  layer forms at first and at higher temperatures,  $\text{Cu}_2\text{O}$  starts to react with O and  $\text{CuO}$  phase forms gradually [11]. Our results agreed well with Ghosh's et al. results because after 25 minutes oxidation at  $350^\circ\text{C}$ , also  $\text{CuO}$  was observed. In addition of oxidation temperature and exposure time, our results indicated that the alloying elements of copper grades affected formed oxide grain structure. The upper oxide layer and some tilted grains and theirs SAED patterns of OF- and DHP-copper are presented in Figs. 5 and 6.

Typical interface between  $\text{Cu}_2\text{O}$  layer and mixed oxide grains ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) containing layer is presented Fig. 7. Columnar  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  grains grew onto the randomly orientated nanosized  $\text{Cu}_2\text{O}$  layer perpendicular to the copper surface. In the Fig. 7, the interface is marked by black curve and normal axis of the copper surface is marked by arrow.

After 100 minutes oxidation at  $350^\circ\text{C}$  the structures of the oxide layers were similar to than after 25 minutes of oxidation. However, thickness of the oxide layers had grown. On the OF-copper, nanocrystalline  $\text{Cu}_2\text{O}$  layer was about 400 nm and  $\text{CuO}$  layer on the  $\text{Cu}_2\text{O}$  layer was about 560 nm. On the CuAg copper,  $\text{Cu}_2\text{O}$  layer was about 350 nm and  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  grains containing layer on the  $\text{Cu}_2\text{O}$  layer was about 1350 nm. Those

values of DHP copper were 600 nm and 1700 nm, respectively. Average thickness of the total oxide layers after oxidation treatments at 350°C are presented in Fig. 8.

#### **4. Summary**

Oxide structures of three polycrystalline copper grades were studied after air exposure at 200°C and 350°C for different exposure times. Studied copper grades were unalloyed OF-copper and alloyed CuAg-copper with silver and DHP-copper with phosphorus. All as delivered specimens were recrystallized to produce an average grain size of 5  $\mu\text{m}$ . Cross-sectional specimens for AEM studies were prepared from oxidized samples. With short exposure times at 200°C and 350°C nanosized  $\text{Cu}_2\text{O}$  layer formed on the all studied copper samples. At 350°C with 25 and 100 minutes exposure, inmost layer was also nanosized  $\text{Cu}_2\text{O}$  layer. In the case of unalloyed OF-copper crystalline  $\text{CuO}$  layer grew on the  $\text{Cu}_2\text{O}$  layer. Columnar shape  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  grains grew onto the  $\text{Cu}_2\text{O}$  layer of alloyed CuAg- and DHP-copper. The schematic drawings of the oxide structures in the unalloyed (OF) copper and alloyed (CuAg / DHP) copper after 100 minutes oxidation at 200°C and after 25 or 100 minutes oxidation at 350°C are presented in Figs. 9 (a) - (c). Alloying elements effect on the copper oxidation phenomenon but effects are not still clear. Our studies indicated that oxidation rate of alloyed coppers was generally much faster than that of unalloyed OF-copper and that the alloying elements (Ag and P) formulated thicker, larger and mixed copper oxide grain structure.

## **Acknowledgements**

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**Figure captions:**

Figure 1. AEM images of (a) OF-, (b) CuAg- and (c) DHP-copper samples after 25 minutes oxidation treatment at 200°C and (d) SAED pattern taken from the oxide layer of DHP-copper.

Figure 2. AEM images of (a) OF-, (b) CuAg- and (c) DHP-copper samples after 100 minutes oxidation treatment at 200°C and (d) SAED pattern taken from the oxide layer of OF-copper.

Figure 3. Thickness of the oxide layers ( $\text{Cu}_2\text{O}$ ) at 200°C.

Figure 4. AEM images of (a) OF-, (b) CuAg- and (c) DHP-copper samples after 25 minutes oxidation at 350°C and SAED pattern taken from the lowest oxide layer of OF-copper.

Figure 5. (a) The oxide layer of OF-copper and (b) - (d) the tilted grains of the oxide layer (marked in Fig 5 (a)) and theirs SAED patterns.

Figure 6. (a) The oxide layer of DHP-copper and (b) - (d) the tilted grains of the oxide layer (marked in Fig 6 (a)) and theirs SAED patterns.

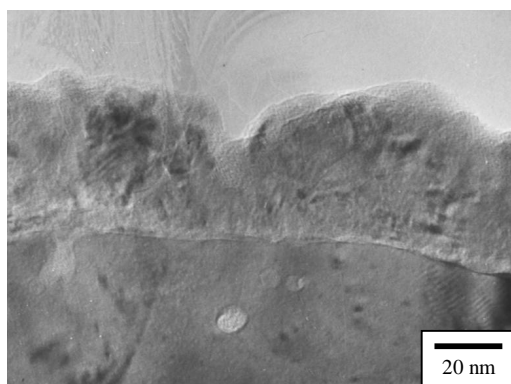
Figure 7. Typical interface between  $\text{Cu}_2\text{O}$  layer and mixed oxide grains ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) containing layer.

Figure 8. Thickness of the oxide layers at  $350^\circ\text{C}$ .

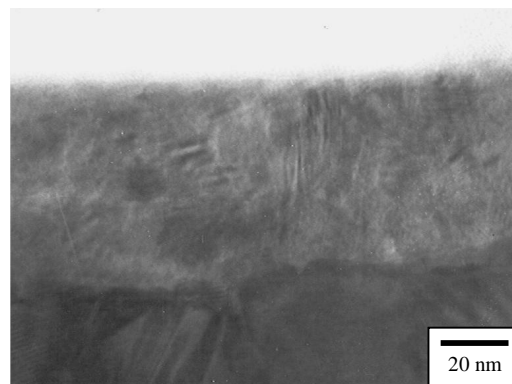
Figure 9. The schematic drawings of the oxide structures (a) after 100 minutes oxidation at  $200^\circ\text{C}$  (OF-, CuAg- and DHP-copper), (b) after 25 or 100 minutes oxidation treatment at  $350^\circ\text{C}$  in the case of OF-copper and (c) after 25 or 100 minutes oxidation treatment at  $350^\circ\text{C}$  in the case of alloyed coppers (CuAg/DHP).



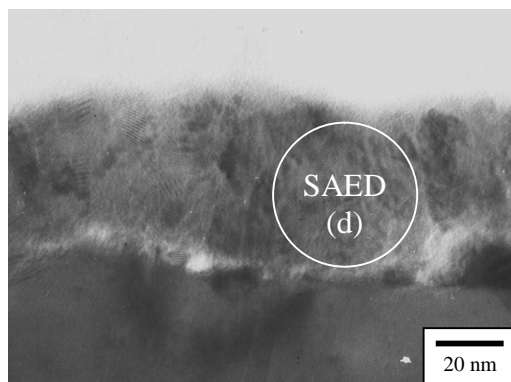
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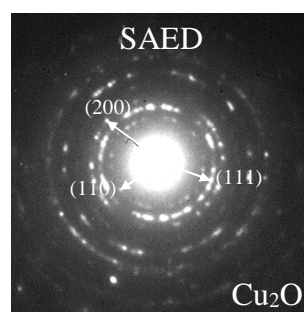
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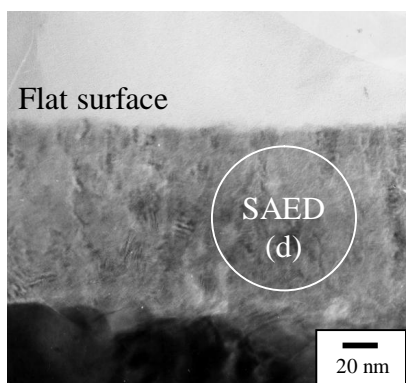


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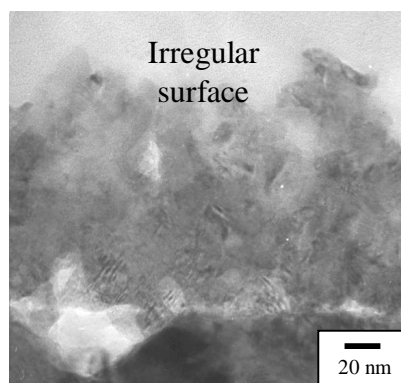


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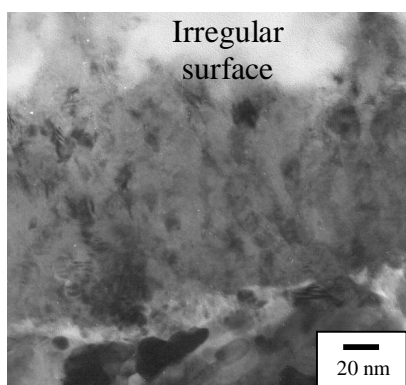
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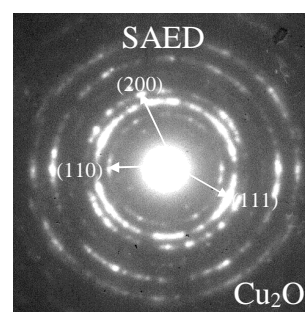
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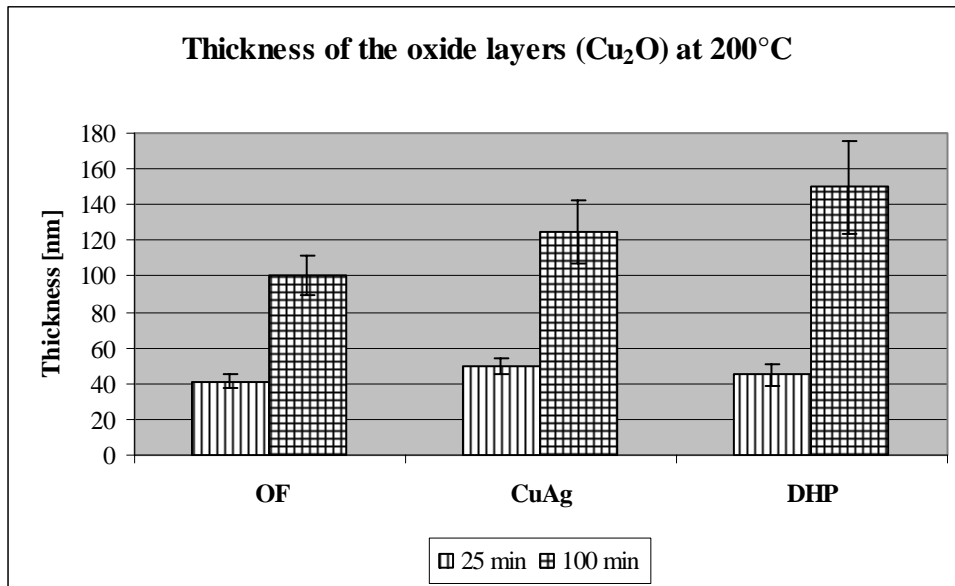


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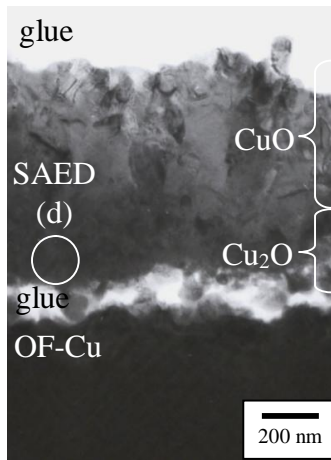


(d)

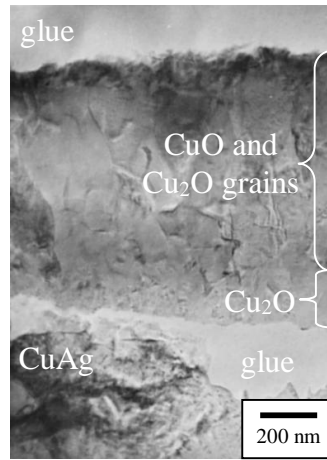
**Figure 3.**



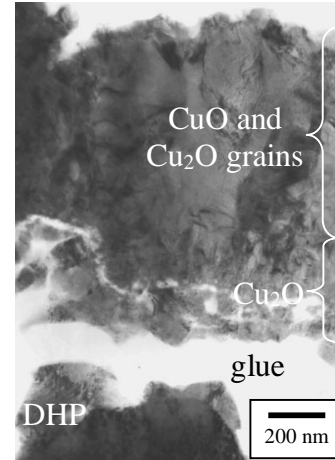
**Figure 4.**



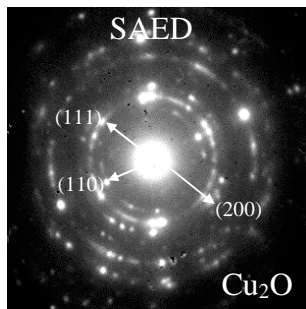
(a)



(b)



(c)



(d)

Figure 5.

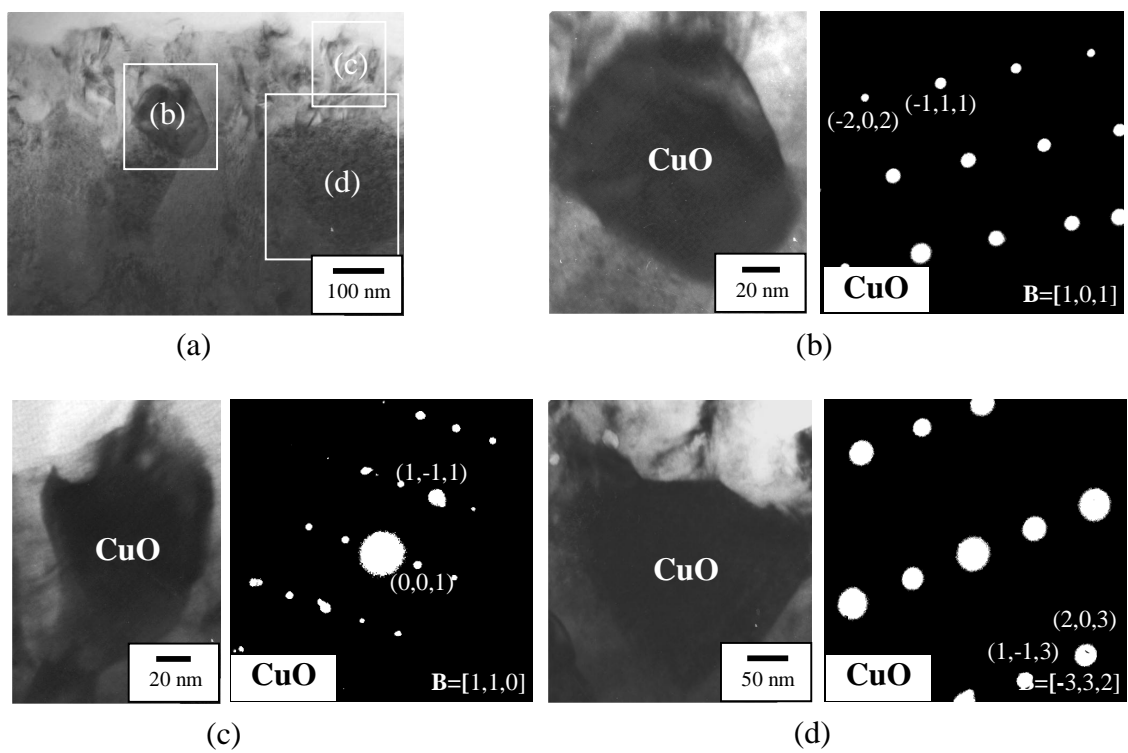
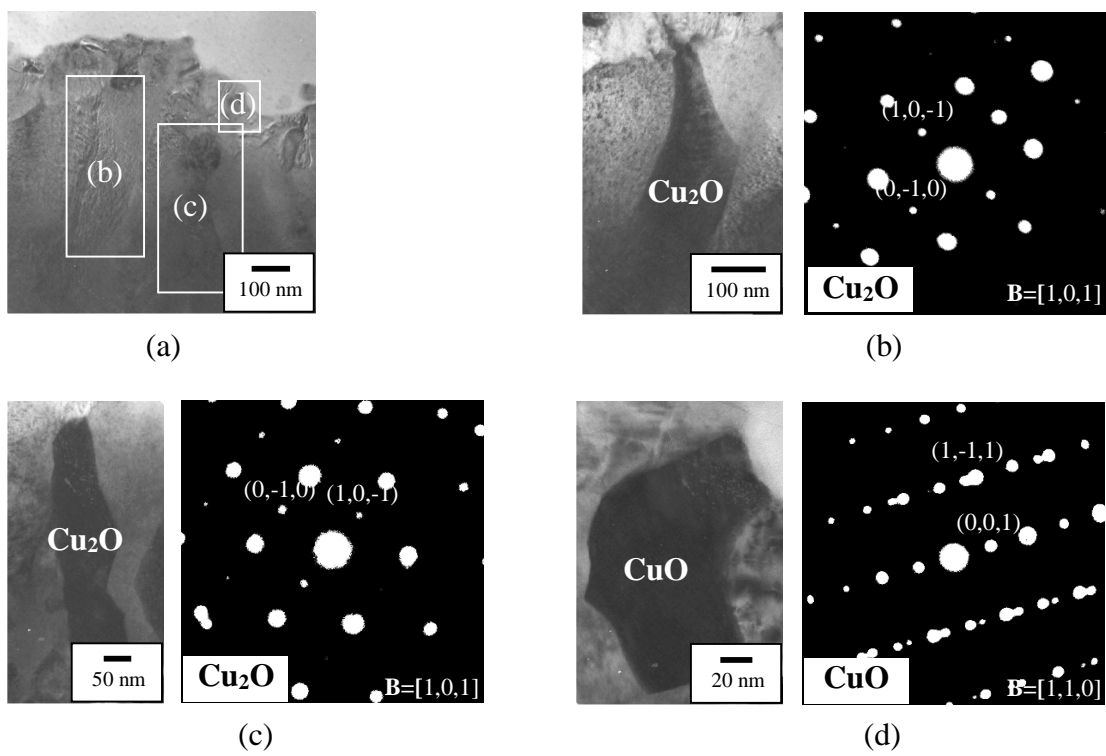
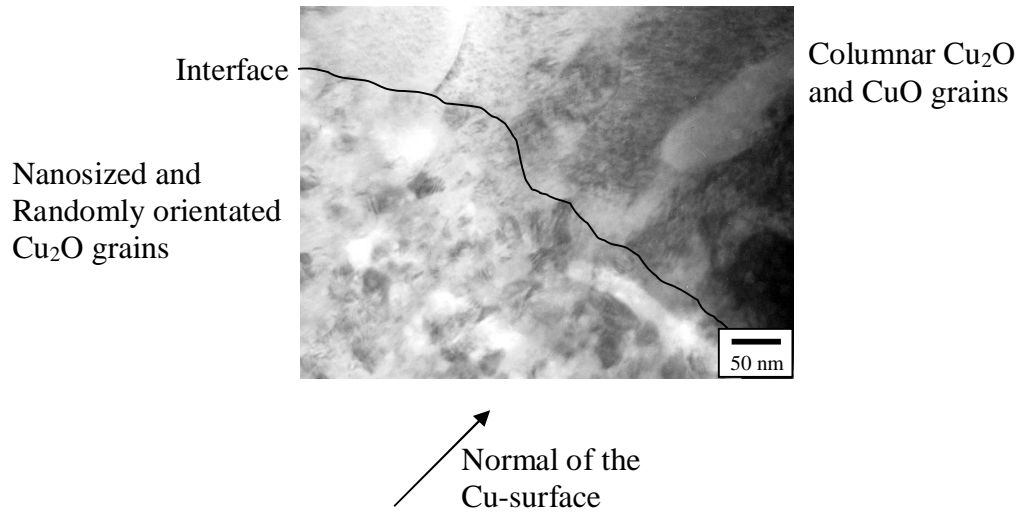


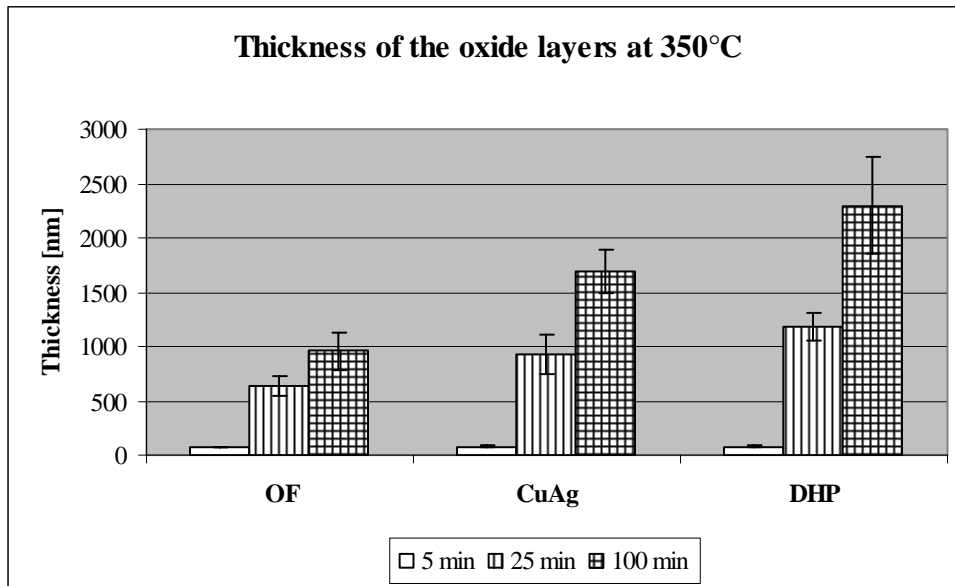
Figure 6.



**Figure 7.**



**Figure 8.**





**Figure 9.**

