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Formation of copper oxides in Cu–Au alloys and pure copper in air at 270 °C

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Abstract

Annealing studies in air at 270 °C of Cu–Au alloys and pure copper in relation to composition and structure have been performed. The progress of oxidation was monitored by the X-ray powder diffraction method, and for $Cu_{68.4}Au_{31.6}$ alloy the oxidation study was also performed on a spherical crystal. Some remarks on the formation of copper oxides in Cu–Au alloys and pure copper are made.

1. Introduction

Interaction of copper with oxygen is an important aspect of many copper-based materials possessing practical importance (used in catalysis, microelectronic and superconducting devices). It is for instance well known that various amounts of oxygen in Cu–O layers of 1-2-3-type high temperature superconductors are possible. This is crucial for these materials as it is correlated with superconducting properties (T_c, J_c). This encouraged us to undertake an X-ray study of the oxidation of pure copper and copper alloyed with noble gold, although a number of reviews covering the oxidation of metals have been published previously [1–7].

Recently we have published X-ray powder data on the oxidation of $Cu_{68.4}Au_{31.6}$, $Cu_{50}Au_{50}$ and $Cu_{25}Au_{75}$ alloys in air at 270 °C [8]. Here we present new experimental data obtained from oxidation of $Cu_{68.4}Au_{31.6}$ spherical crystals and polycrystalline copper. The oxidation was performed as in ref. 8 which allowed us to present also some summarizing results.

2. Experimental details and results

The oxidation process was performed and the progress of oxidation was examined in the way described in ref. 8.

2.1. Oxidation of $Cu_{68.4}Au_{31.6}$ crystal

The spherical crystal of a $Cu_{68.4}Au_{31.6}$ composition was prepared as in ref. 9. The photographs were taken on a Weissenberg goniometer using Cu

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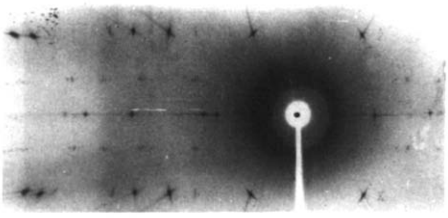
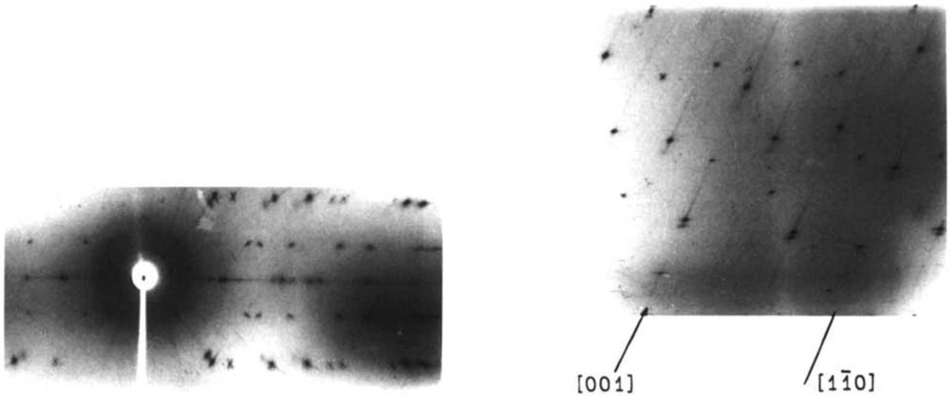


Fig. 1. The oscillation photograph of $Cu_{68.4}Au_{31.6}$ crystal (oscillation axis, [110]).



(a) (b)

Fig. 2. The photographs of $Cu_{68.4}Au_{31.6}$ crystal after annealing in air for 5 days at 270 °C: (a) oscillation photograph (oscillation axis, [110]); (b) Weissenberg zero-layer photograph.

Kα radiation. Figure 1 shows the oscillation photograph of the crystal before its oxidation. The Cu_3Au(II) long-period superstructure could be recognized. Next the crystal was annealed in air for 5 days. The oscillation and Weissenberg photographs are given in Fig. 2. From a comparison and analysis of the photographs shown in Figs. 1 and 2 it may be seen that oxidation of the crystal leads to the oriented growth of Cu_2O on it, so that the cubic axis of the mother Cu_3Au crystal and Cu_2O are parallel. However, as the lattice parameters differ substantially (3.782 Å for a subcell of $Cu_{68.4}Au_{31.6}$, 4.268 Å for the Cu_2O cell) this leads to strains and relatively smoothed reflections. However, in spite of this the same long-period superstructure of the matrix crystal could still be recognized. It was checked that after oxidation for 5 days the mother crystal does not exist any more, although the previous bulk spherical form was preserved. The photograph made by the oscillation method showed only the presence of AuCu(I) and copper oxides in a fully polycrystalline state.

2.2 *Oxidation of copper fillings*

The powder diagrams were made on a Stoe transmission diffractometer using Cu Kα_1 radiation [10]. First a diagram of a non-oxidized sample was taken. Next, the sample was heated in air for some days and examined on

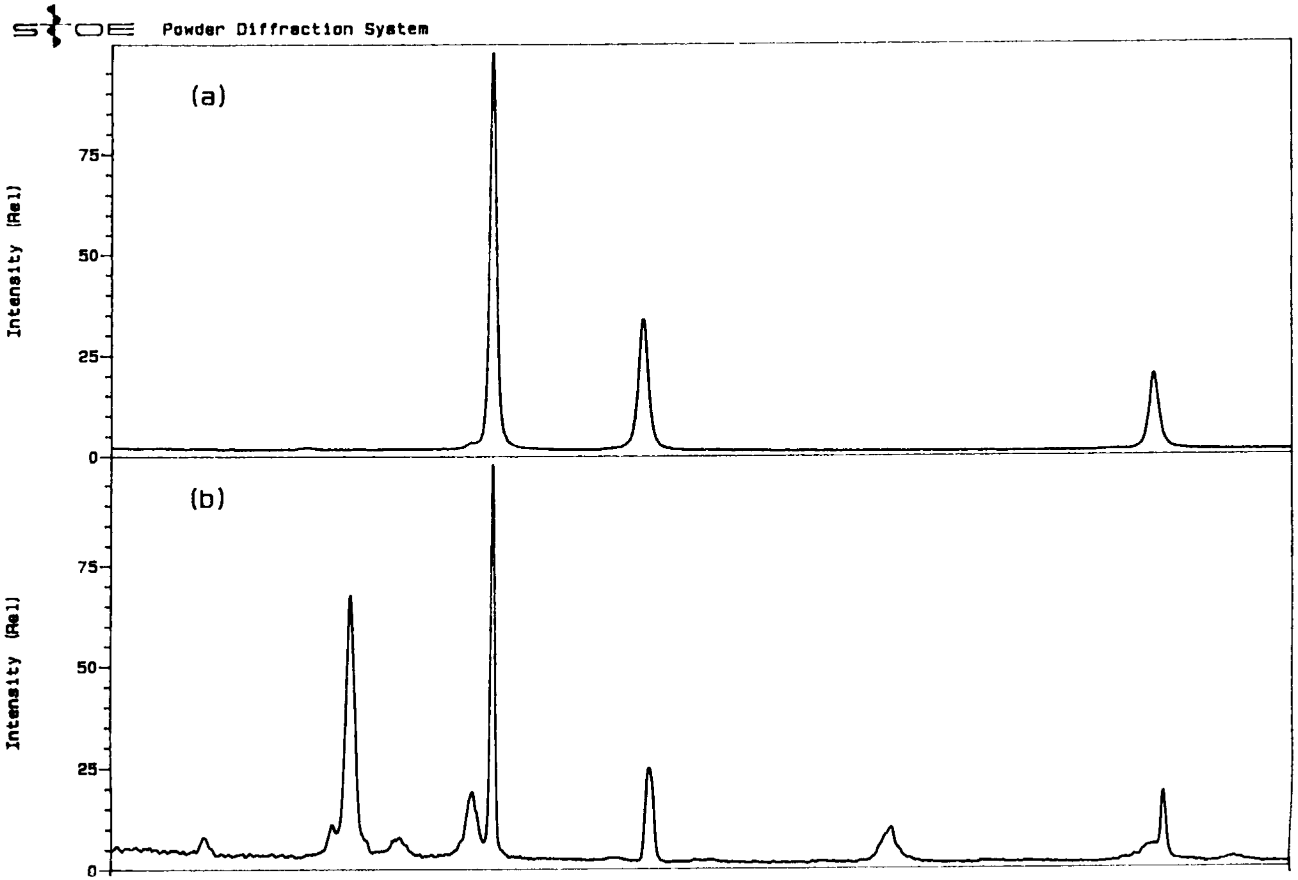


Fig. 3.

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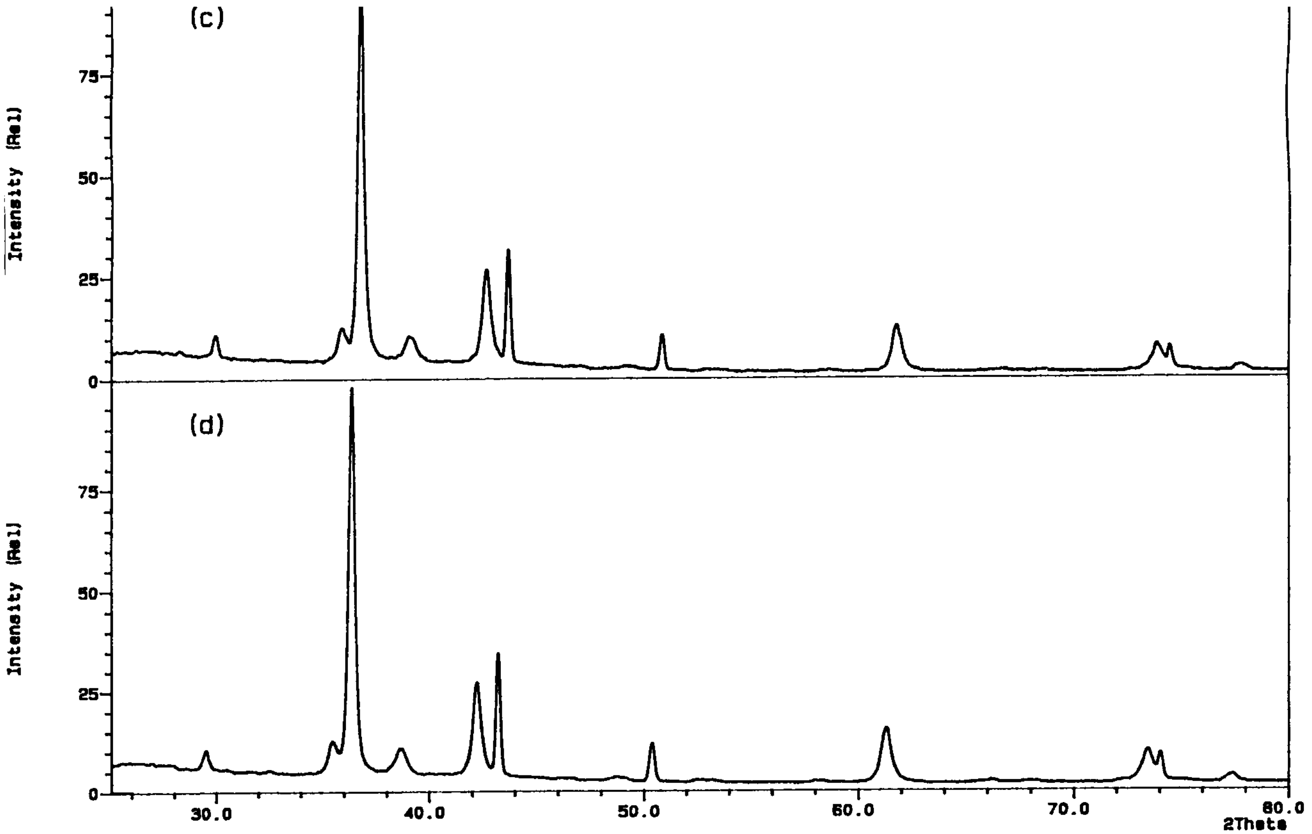


Fig. 3. X-ray powder diffraction diagrams for copper annealing at 270 °C: curve a, starting sample; curve b, after annealing for 1000 h; curve c, after annealing for 4000 h; curve d, after annealing for 5000 h.

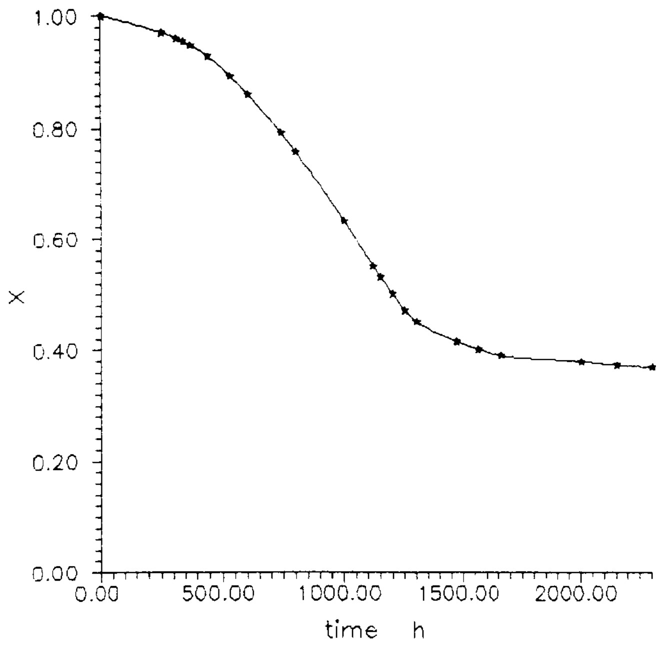


Fig. 4. The relative change of Cu/(Cu + Cu_2O) in the progress of copper oxidation.

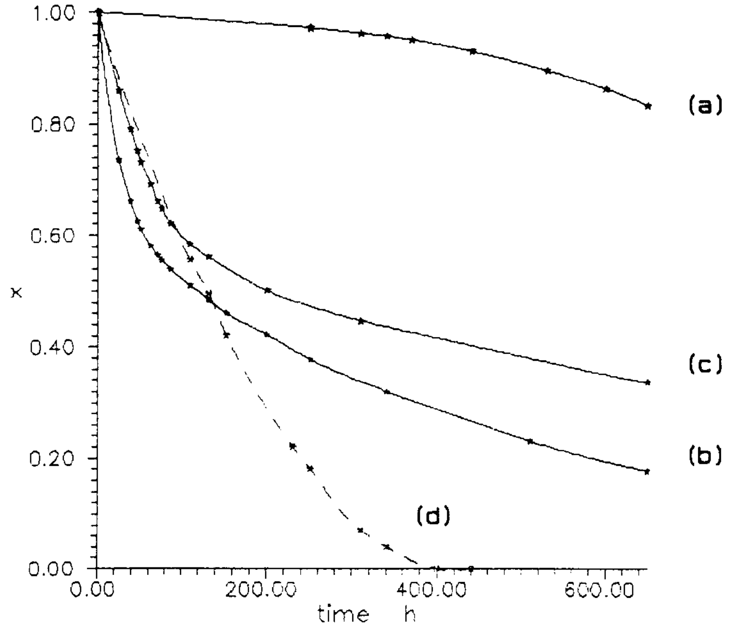


Fig. 5. The relative diminishing of copper, Cu_3Au, CuAu and $CuAu_3$ phases during the annealing process in air at 270 °C: curve a, copper; curve b, Cu_3Au; curve c, CuAu; curve d, $CuAu_3$.

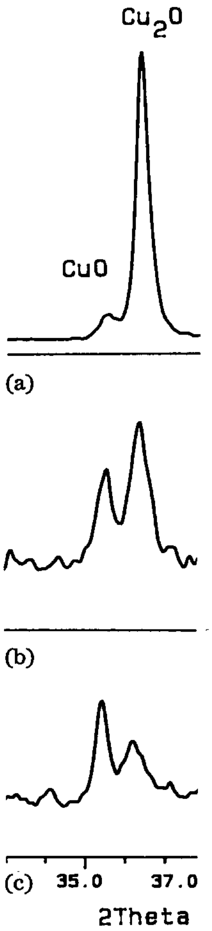
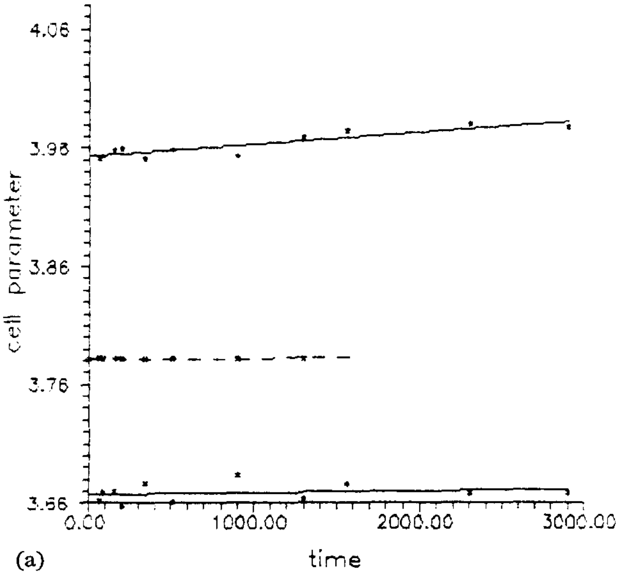


Fig. 6. The powder diffraction diagrams of the copper oxide lines ((111) line for Cu_2O, (200) and (-111) lines for CuO) after annealing of copper, $Cu_{68.4}Au_{31.6}$ and $Cu_{50}Au_{50}$ at 270 °C: curve a, for pure copper; curve b, for $Cu_{68.4}Au_{31.6}$; curve c, for $Cu_{50}Au_{50}$.

the powder diffractometer. This procedure was repeated until the intensity of the lines showed practically no more change. Selected diffraction patterns are presented in Fig. 3. Some characteristic tendencies of the oxidation of the copper fillings can be seen: (1) the oxidation became slower with time and practically stopped after 68 days, (2) the lines from Cu_2O are much more intense than the lines from CuO, (3) the sharpnesses of the diffracted lines from copper and Cu_2O are comparable.

3. Discussion

The Cu(I) oxides formed on copper spherical crystals have been previously studied in ref. 5. It was shown that the Cu_2O crystallites could possess only



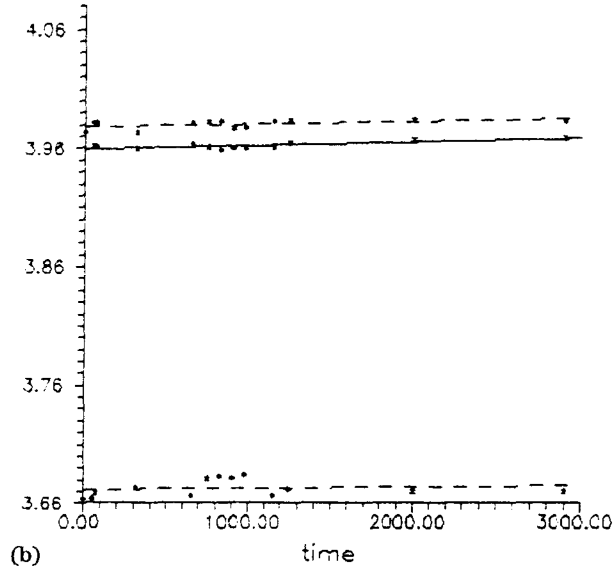


Fig. 7. (*continued*)

circular ordering about definite poles of the copper crystals. As was shown in this experiment, the cuprous oxide formed in air at 270 °C on a $Cu_{68.4}Au_{31.6}$ spherical crystal grew in a strongly oriented way, *e.g.* the cubic axes of both phases were parallel. Obviously, if the oxidation time was long enough, the decomposition of the matrix crystal led to polycrystallinity of the whole sample and loss of correlation (Fig. 4).

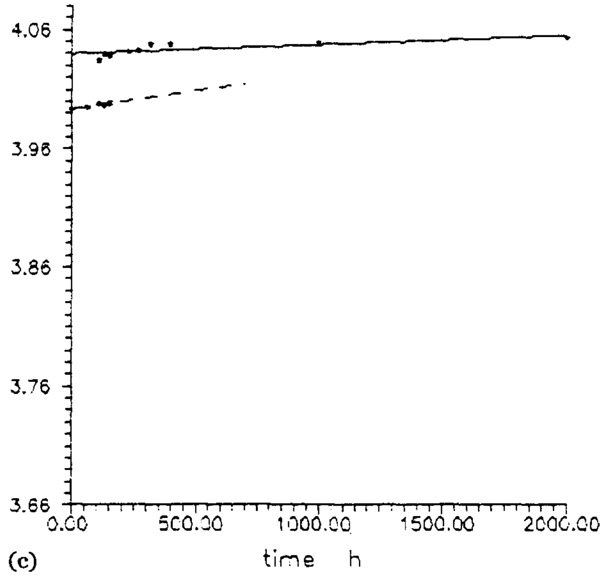


Fig. 7. Cell parameters of the diminishing mother phases and phases appearing during the annealing process in air at 270 °C (a) for $Cu_{68.4}Au_{31.6}$, (b) for $Cu_{50}Au_{50}$ and (c) for $Cu_{25}Au_{75}$: – – –, cell parameters of the starting phase; ——, cell parameters of the appearing phases.

However, another remarkable observation could be made from a comparison of the experimental results for copper, $Cu_{68.4}Au_{31.6}$, $Cu_{50}Au_{50}$ and $Cu_{25}Au_{75}$ (obtained in this work and our earlier paper [8]). The essential results are presented in Figs. 5–7. Figure 5 shows the relative diminishing of copper, Cu_3Au, CuAu and $CuAu_3$ phases at appropriate fillings by their oxidation at 270 °C in air. Figure 6 shows the powder diagrams of the copper oxide lines in a selected area observed after oxidizing of copper, $Cu_{68.4}Au_{31.6}$ and $Cu_{50}Au_{50}$ at 270 °C for 100 days. Figure 7 shows the cell parameters of the diminishing mother phase and a phase richer in gold that appears during the oxidation processes. Our observations led to the following conclusions.

(a) The oxidation of copper is slower than that of Cu–Au alloys.

(b) The oxidation of copper practically stops after a certain time interval, whereas that of Cu–Au alloys continues until complete decomposition of the alloys on gold and on copper oxides occurs (this confirms our earlier suggestion that there is a tendency of the constituent atoms in Cu–Au alloys to separate [8]; the outward diffusion of copper atoms to the alloy surface does not allow continuous and therefore protective oxide films to form).

(c) Decomposition of the mother phase does not involve a continuous concentration gradient in this phase. The sample composition changes stepwise crystallite by crystallite to the nearest gold-richer phase.

(d) The greater the gold content in a Cu–Au alloy, the greater the ratio $CuO:Cu_2O$ and the lower the crystallinity of the copper oxides.

(e) There is no direct relation between oxidation and gold content in Cu–Au alloys. The state and degree of order of the alloy should also be taken into account.

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