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# MICROGRAVIMETRY ON THE HIGH TEMPERATURE OXIDATION OF SHORT RANGE ORDERED CRYSTALS OF NEAR $Au_2Cu_3$ COMPOSITION*

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## ABSTRACT

For gold + copper alloys of composition near 60 atom per cent copper the process of oxidation of copper to copper(I) oxide has been studied by microgravimetry in ultrahigh vacuum over the 775–885 K temperature range and the 5 μTorr to 2 mTorr oxygen pressure range for (100) surfaces. For an approximately constant oxide coverage a linear rate equitation applies and near linear pressure dependence was found.

## INTRODUCTION

For many years the copper + gold alloy has been a favourite system for studies on long range-short range order phenomena; in the present case short range order implies ordered regions in a random matrix arrangement of Au and Cu atoms having the fcc structure. This paper presents studies of the surfaces of short range ordered single crystals and the kinetics of the oxidation process $2\ Cu + \frac{1}{2}O_2 \rightleftarrows Cu_2O$ on these surfaces on such conditions that the $Cu_2O$ is selectively formed (Ref. 1). We shall discuss recent results for near $Au_2Cu_3$ composition while demonstrating the technique of making comparative measurements on the basis of experiments where the total weight of the sample after each experiment is approximately constant. While UHV Auger analysis of the Au-Cu-O system has been reported (Ref. 2) the present paper elucidates the oxidation kinetics of single crystal surfaces of the alloy primarily based on microgravimetric UHV analysis.

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## EXPERIMENTAL

For the microgravimetric measurements a CAHN RG electrobalance was used. This was located on top of a water-cooled platinum ribbon furnace placed in a stainless steel system under a bell jar, all mounted upon a rigid heavy steel construction bolted to a heavy concrete wall. Mechanical performance was improved by using very thin, 0.03 mm diameter, carefully annealed platinum wires, which were firmly attached to the balance beam. For the experimental pressure range 5 μTorr to 2 mTorr oxygen a load to precision ratio of about $3 \times 10^7$ was obtained. The zero-point stability was better than $10^{-6}$ $gd^{-1}$. As counterweight carefully outgassed platinum sheets were used. Pressures were controlled to within 0.5 per cent by APC (Series 220, Granville-Phillips Co., U.S.A.) and read by an ionization gauge (MilliTorr, Varian Associates, U.S.A.). The gas supply was 99.998 per cent pure oxygen (Alfax AB, Sweden). A continuous record was kept of the gas composition through quadrupole residual gas analysis (250 B, EAI - Varian Associates, U.S.A.) and of the temperatures as measured by Pt/Pt/Rh and chromel-alumel thermocouples. The sample temperatures were taken as those measured by a thermocouple suspended into the furnace 5 mm from and to the same level as the center of the sample. Shields secured very low temperature gradients near the sample. Temperature stability was ± 0.1 K for constant pressure, and ± 1 K for the complete isotherm.

The system was evacuated by cryo pumps, ion pumps and a titanium sublimation pump to a base pressure of about 10 nTorr after a moderate bakeout of the balance compartment to 115 °C and of the rest of the system to 200 °C. The residual pressures as measured by RGA showed base oxygen pressures below 0.1 nTorr.

During oxidation experiments, differential pumping was applied so that the balance beam, lamp, etc. were held at about 5 μTorr.

The samples were prepared by high vacuum Bridgman crystal growth. The material, 99.999 atom per cent (a/o) Cu and 99.95 a/o Au, was melted in a graphite mould at about 0.5 μTorr, and 15-18 mm diameter crystals were then grown during 8 hours followed by 15 hours annealing at temperatures ca. 50 °C below the melting point of the alloy. The temperature of the crystal was then gradually lowered during two hours to 450 °C and then quenched to room temperature during a few minutes in order to preserve the short-range order crystal structure.

Disks were then produced from the crystal ingots by spark erosion cutting, and levelling to within approximately 0.5° of the (100) plane through control by Laue back reflection X-ray techniques with a spread of less than 1°. The disks were finished by 1/4 µm diamond and electrical polishing (Ref. 3) until bright smoothness was observed by optical microscopy in × 200 magnification.

The composition and homogeneity of the samples was checked by X-ray, electron microprope and atomic absorption spectrophotometric analysis. No inhomogeneity was observed. For powder analysis a carefully cleaned diamond file was used.

A comparison of the results from the three methods of analysis gave the following results: a) Debye-Scherrer and Guinier X-ray: 59.73 a/o Cu, b) electron microprope: 59.21 a/o Cu and c) atomic absorption spectrophotometry: 59.22 a/o Cu.

We see that the crystal composition is near $Au_2Cu_3$. a) was obtained via a lattice constant determination of 3.833(2) Å (CuKα radiation with and without Si reference) and a 4th order polynomial fit interpolation on the lattice constant data selected by Pearson (Ref. 4) for alloys quenched from temperatures just above the order transition temperature. b) was obtained through use of the Mα line for Au and the Kα line for Cu with a correction factor of 1.224 for Au and 0.865 for Cu. c) was obtained after comparison with a prepared standard solution of nearly same composition as known from chemical analysis. We note an excellent agreement of methods b) and c).

After an initial UHV bakeout procedure at which the temperature of the sample itself was kept below approximately 80 °C - the microbalance furnace temperature was raised within a few minutes to temperatures sufficiently high to avoid ordering followed by twinning strain distortion.

## RESULTS

For the low index single crystal surface planes the oxidation behaviour of the gold + copper system resembles, as to kinetics and to surface structures, that of pure copper.

This paper presents recent results on isothermal oxidation of (100) surfaces of samples of short-range ordered crystals of composition very near $Au_2Cu_3$. The oxygen pressure range was from 5 µTorr to 2 mTorr and the temperature range from 775 K to 885 K.

After an initial oxidation period, which consists of an induction period of non-measureable weight increase followed by a gradual transition to near linear rate law kinetics, a series of measurements were carried out at constant temperature but at different oxygen pressures (Fig. 1) for a period of time at such a length that when comparing experiments within the above temperature range, the total mass uptake per unit area was approximately the same, i.e. approximately constant coverage was established. The uptake was close to 5 μg $cm^{-2}$ corresponding to an oxide amount of 45 μg $cm^{-2}$. For all pressures and temperatures investigated the mass uptake varied linearly with time.

After completion of each experiment the samples were observed by optical and scanning electron (JSM 25, JEOL, Japan) microscopy (SEM) (Fig. 2). A near uniform distribution of even-sized oriented nuclei was found in most cases and was taken as a prerequisite for use of the data for theoretical treatment.

## DISCUSSION

The rate constant k for each segment of the isotherm was plotted against the oxygen pressure $p(O_2)$ and a linear dependence was found (Fig. 3). As previously discussed (Ref. 5) for gold + copper alloys with low copper content the straight line of Fig. 3 will cut the axis of zero weight change, $\Delta w = 0$, for $p(O_2) = P_d(O_2)$, the dissociation equilibrium pressure for the process discussed. For the high copper content of this investigation it is difficult within the present experimental accuracy to determine $P_d$, which is very low as seen in Fig. 3.

For a constant oxygen pressure an apparent activation energy $E_a$ was calculated. Fig. 4 shows an Arrhenius plot which gives $E_a \simeq 77.6$ kJ $mol^{-1}$ for this oxidation process (with a correlation coefficient of -0.925).

In these experiments we may disregard the dissolution of oxygen into the bulk as compared to the oxygen incorporated in oxide. Also, the effect of surface enrichment on these alloys is very small. (Ref. 8)

Based on the observed linear kinetic behaviour of the oxidation process at these high temperatures and on the pressure proportionality it is now suggested that initially a prenucleation thin oriented oxide film is formed already at very low oxygen exposure. The process of the following nucleation is then rate determined as a surface-controlled reaction, at least as long as the distances between the surface nuclei are large compared to the size of the nuclei. Furthermore, for the present conditions of alloy composition, temperatures and pressures, we can assume the decomposition rate to be small compared to the reaction rate. It is proposed that a molecular species

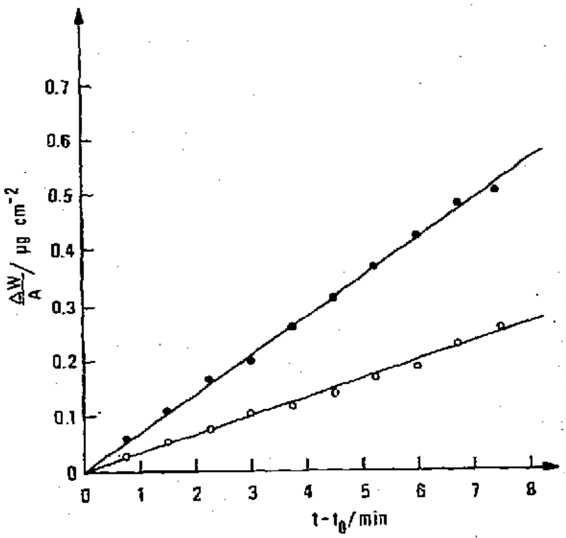

Fig.1. Mass change per unit area vs. time at 798 K, o, 0.36 mTorr; ●, 0.72 mTorr.

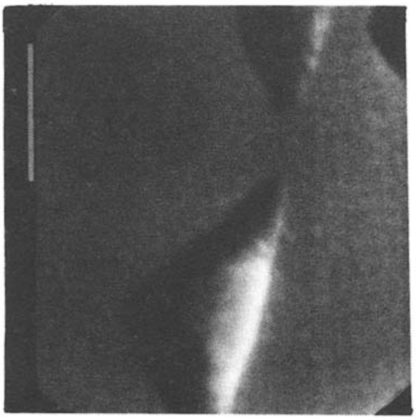

Fig.2. Oxide nuclei formed at 798 K, SEM × 30.000, 15 kV, surface 30° tilted, length of marker 1 µm.

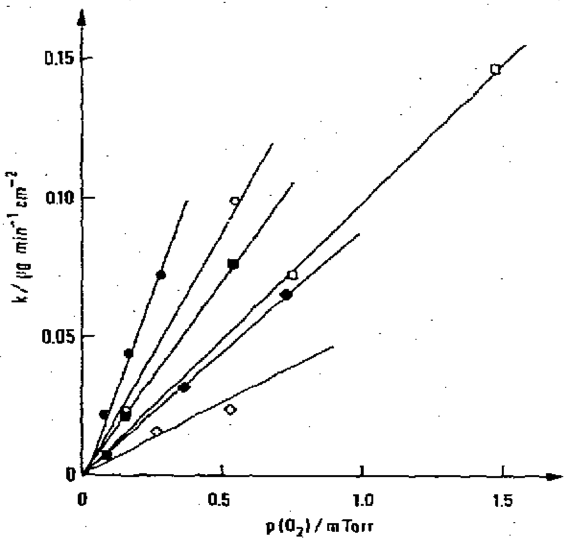

Fig.3. Rate constant vs. oxygen pressure. ◇, 783 K; ◆, 798 K; □, 812 K; ■, 823 K; ○, 844 K; ○, 885 K.

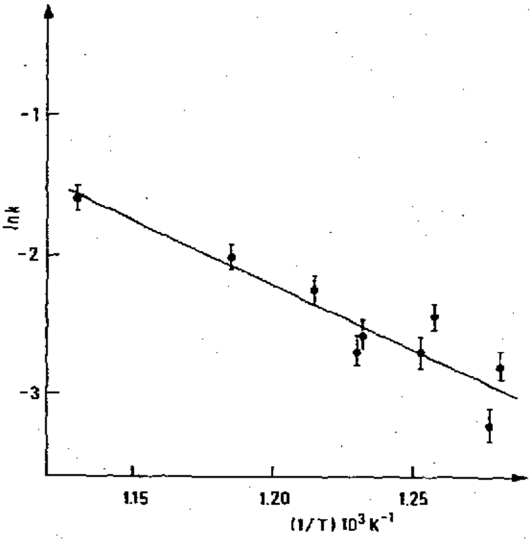

Fig.4. Arrhenius plot, p($O_2$) = 0.75 mTorr.

is involved, e.g. dissociation, ionization or adsorption, and possible oxygen ions at surface can be taken as have approached a steady-state value. It should be remembered that electron diffraction experiments have given evidence (Ref. 6,7) for formation of a thin layer of $Cu_2O$ (111) followed by a hexagonal structure on surfaces of gold + copper alloys of various compositions.

The even distribution of even-sized nuclei, as observed by optical and scanning electron microscopy, seems to reveal evenly spaced ordered regions throughout the surface structure.

Experiments are in progress which may further elucidate the kinetics and surfaces thermodynamics of these alloys.

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