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Preparation of dispersion-hardened copper by internal oxidation

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Internal oxidation experiments in CO_2/CO atmospheres on Cu–Al alloys for preparation of dispersion-hardened Cu are described. The oxygen pressures of the atmospheres used in the experiments were controlled with a solid electrolyte oxygen cell based on ZrO_2 (CaO). The particle size distributions of the Al_2O_3 phase obtained in the oxidation experiments show that good reproducibility can be obtained with this method, both for specimens oxidized in the same run and for specimens oxidized in different runs under nominally identical conditions. The experiments also indicate that particle size increases with decreasing oxygen pressure of the atmosphere.

1. Introduction

Internal oxidation of Cu–Al alloys is an important method for the preparation of dispersion-hardened Cu. As described by Meijering and Druyvesteyn [1, 2], this process primarily requires that the oxygen pressure of the atmosphere used for the oxidation does not exceed the equilibrium pressure of oxygen for the Cu/Cu_2O system. Secondly, it is important that the oxygen pressure can be closely controlled during the oxidation, and in the method proposed by Rhines *et al.* [2, 3] this is obtained by heat-treating the specimens in a Cu/Cu_2O powder mixture. From an experimental point of view, this method has the disadvantage that the oxygen pressure and the specimen temperature cannot be varied independently, but this disadvantage is overcome in the method proposed by Kupcis and Ramaswami [4], in which the specimen and the Cu/Cu_2O mixture are separated into two interconnected furnaces, whose temperatures can be adjusted independently. Another way to overcome this disadvantage is to perform the oxidation in a flowing atmosphere with adjustable oxygen pressures, and the purpose of the present work is to investigate the reproducibility of this method. In order to obtain reproducible oxidation conditions with this method, however, the oxygen pressure of the atmospheres used must be closely controlled. Because of the low oxygen pressures required, this control cannot be achieved by conventional gas analytical methods (e.g. gas chromatography) and in the work under discussion a solid electrolyte oxygen cell was developed for this purpose.

2. Experimental

2.1. Atmospheres for oxidation experiments

In the present study the flowing atmospheres with controlled oxygen pressures were prepared by mixing CO_2 and CO. The oxygen pressures of the atmospheres selected for the oxidation experiments were calculated as follows:
For the equilibrium

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2 \tag{1}$$

the equilibrium constant, K_p, can be expressed as

$$K_p = [CO] \times p_{O_2}^{1/2}/[CO_2] = 1/R_M \times p_{O_2}^{1/2} = \exp(\Delta G_T^\circ/RT) \tag{2}$$

where R_M is the initial mixing ratio of CO_2 and CO, R the gas constant, ΔG_T° the standard free energy change of the reaction and T the absolute temperature. According to [5], ΔG_T° can be expressed empirically as

$$\Delta G_T^\circ = -68\,290 - 0.42T\log_{10}T - 0.97 \times 10^{-3}T^2 + 0.865 \times 10^5\,1/T + 23.15T\,\text{cal mol}^{-1} \tag{3}$$

By combining Equations 2 and 3 the oxygen

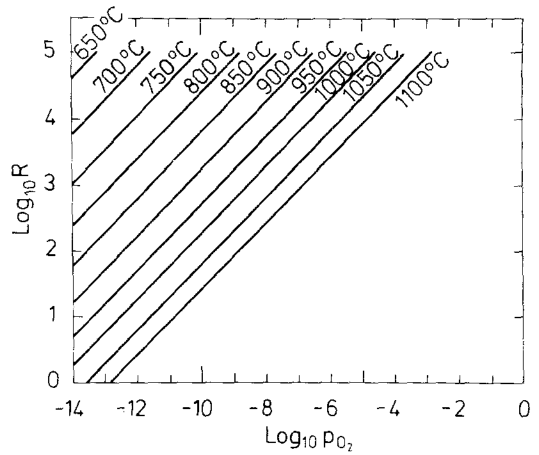

Figure 1 CO_2/CO ratio as a function of oxygen pressure.

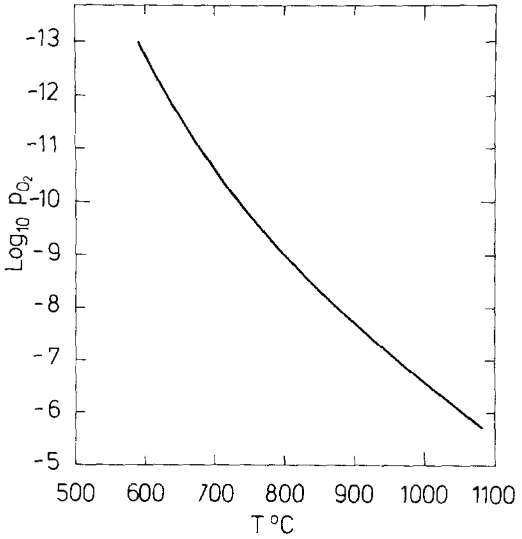

Figure 2 Equilibrium oxygen pressure for $Cu–Cu_2O$.

pressure for a given CO_2/CO ratio ($= R$) can easily be calculated at a given temperature. This is shown in Fig. 1, where $\log_{10}R$ is shown as a function of $\log_{10}p_{O_2}$ and with T as a parameter (° C).

The equilibrium pressure of oxygen for the $Cu–Cu_2O$ system at the oxidation temperature selected for this investigation was calculated from the following equation:
For the equilibrium

$$2Cu + \tfrac{1}{2}O_2 \rightleftharpoons Cu_2O \qquad (4)$$

we find

$$K_p = \frac{[Cu_2O]}{[Cu] \times p_{O_2}^{1/2}} \simeq \frac{1}{p_{O_2}^{1/2}} = (\Delta G_T^0/RT) \qquad (5)$$

and according to [5] we have

$$\Delta G_T^0 = -40\,550 - 1.15T\log_{10}T - 1.1 \times 10^{-3}T^2 - 0.1 \times 10^{-5}\,1/T + 21.92\,\text{cal mol}^{-1} \qquad (6)$$

Thus the equilibrium oxygen pressures at a given temperature can easily be calculated by combining Equations 5 and 6. In Fig. 2, $\log p_{O_2}$ is shown as a function of temperature.

2.2. Principle of the solid electrolyte cell

The principle of the solid electrolyte oxygen cell developed for atmosphere control is shown schematically in Fig. 3. The solid electrolyte used in this cell was a Ca-stabilized ZrO_2 tube (13.8 mol % of CaO) closed at one end. Porous platinum electrodes were applied inside and outside at the closed end of the tube and on an outside track along the tube by painting with platinum paste and firing in air at about 1000° C. Contact to the internal electrode is obtained with a platinum wire welded to a thin platinum disc that is pressed against the electrode with an alumina support tube. A four-bore thermocouple protection tube placed inside this tube contains the contact wire as well as a Pt/Pt, Rh (10%) thermocouple. With flanges fastened gas-tight to the ZrO_2 tube and to the support tube, the system is arranged so that a reference gas can be supplied to the internal electrode through the support tube.

The e.m.f. for a reversible cell of the type

$$p'_{O_2}/Pt\,|\,ZrO_2(CaO)\,|\,Pt/p''_{O_2}$$

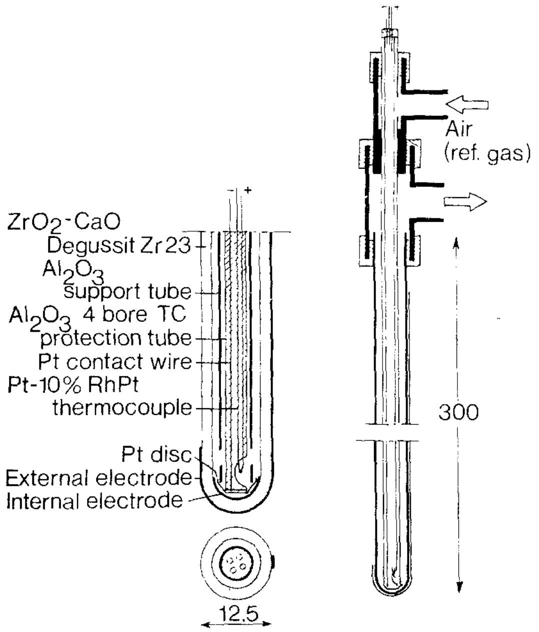

Figure 3 Principle of ZrO_2 (CaO) cell.

is given by [6]

$$E = \frac{1}{4F}\int_{\mu'_{O_2}}^{\mu''_{O_2}} t_{\mathrm{ion}}\,\mathrm{d}\mu_{O_2} \qquad (7)$$

where F is the Faraday equivalent, μ'_{O_2} and μ''_{O_2} the chemical potentials of oxygen on the two sides of the electrolyte, and t_{ion} the ionic transport number. According to the definition of chemical potential

$$\mu_{O_2} = \mu^0_{O_2} + RT\ln p_{O_2} \qquad (8)$$

Combining Equations 8 and 9 for $t_{\mathrm{ion}} = 1$, the following expression can be obtained for E:

$$E = RT/4F\ln\frac{p''_{O_2}}{p'_{O_2}}. \qquad (9)$$

At constant temperature, a linear relationship thus exists between E and $\log_{10}(p''_{O_2}/p'_{O_2})$ and if, for instance, p''_{O_2} is kept constant by a continuous supply of a reference gas to this side of the electrolyte, the partial pressure of oxygen on the other side can be determined from the e.m.f. of the cell. If air is used as a reference gas, the following equation for E applies:

$$E = -0.03369 \times T - 0.0496 \times T \times \log_{10}p'_{O_2}. \qquad (10)$$

The cell was calibrated with CO_2/CO mixtures in which the composition was checked by gas-chromatographic measurements. From the calibration curve obtained, which is shown in Fig. 4, it will be noted that for $p_{O_2} > 10^{-18}$ atm. the measured e.m.f. closely corresponds to the theoretical values calculated from Equation 11, indicating that the basic requirement for measurements of a high ionic conductivity ($t_{\mathrm{ion}} = 1$) is fulfilled in this pressure range.

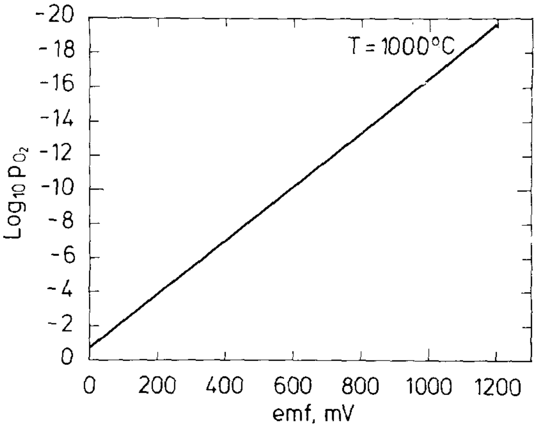

Figure 4 Theoretical calibration curve for the ZrO_2 (CaO) cell.

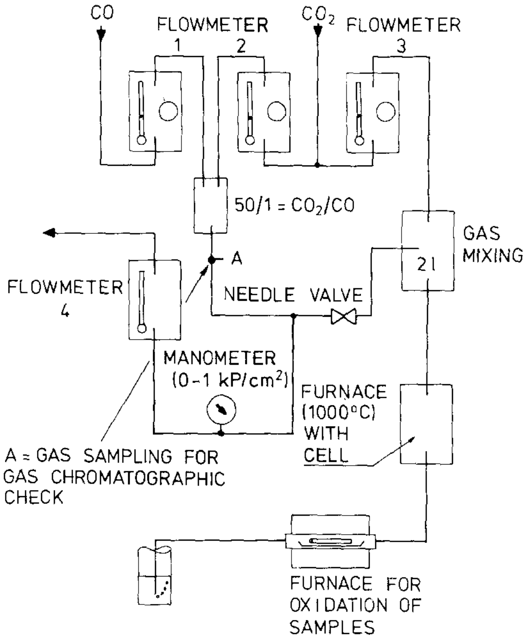

Figure 5 Principle of equipment used in internal oxidation experiments.

2.3. Equipment

As indicated in Figs. 1 and 2, the equilibrium pressures of oxygen for the Cu/Cu_2O system require extreme mixing ratios of CO_2 and CO, and in order to obtain these, the gas-mixing system shown schematically in Fig. 5 was developed.

The extreme mixing ratios required cannot be obtained in a single step, and in this system CO_2 and CO are therefore first premixed in a ratio of 50: 1. Then part of this mixture is added to pure CO_2 through a needle valve in such a proportion that the desired ratio is obtained, as measured by the e.m.f. of the cell. In order to obtain a steady flow through the needle valve the pressure in the premixing container is kept slightly higher than the pressure in the final mixing container.

2.4. Materials and oxidation conditions

The oxidation experiments were carried out on single crystal bars of Cu–0.19% Al, under the following conditions

TABLE I Oxidation conditions

Temperature (° C)	Pressure ratio (p_{O_2}/p'_{O_2})	Time (h)	e.m.f. (mV, 1000° C)
1030	1	20	387
1030	1/2	37	407
1030	1/5	92	433

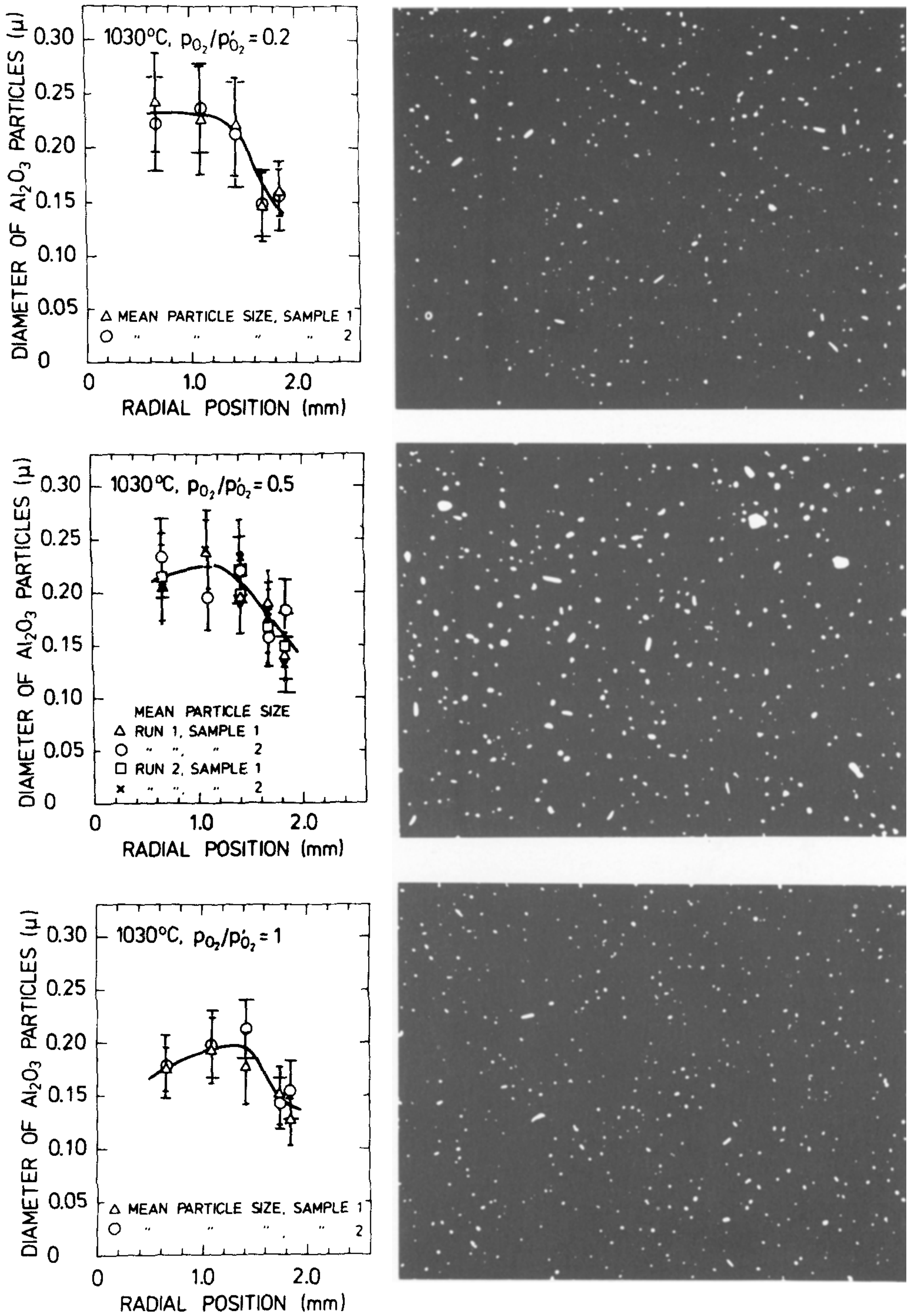

Figure 6 Particle size distribution in internally oxidized specimens. A typical SEM micrograph (2930 X) is shown beside each diagram.

where p'_{O_2} is the equilibrium pressure of oxygen for the Cu/Cu_2O system. Two specimens were oxidized in each run and in order to check the reproducibility of the method, two runs were carried out with $p_{O_2}/p'_{O_2} = 1/2$.

2.5. Measurement of particle size

The particle sizes were determined on SEM micrographs by measuring the area of the particle cross-sections by means of an automatic image analyser (Zeiss: TAS). In order to obtain the true mean particle sizes, a correction factor was applied which corrected for the fact that particles observed by SEM appear larger than they really are. This factor was determined by measuring particles on SEM and TEM micrographs taken on the same section of a specimen. These comparisons showed that the particle size measured on SEM micrographs was 15% higher than the real particle size, and independent of the shape and the size of the particles.

3. Results and discussion

The mean particles size and standard deviation of the Al_2O_3 particles measured at different radial positions on the oxidized specimens are shown in Fig. 6. Each diagram shows the specimens oxidized under the same conditions. A typical SEM micrograph is shown beside each diagram.

By comparing the particle size distributions across the specimens obtained in the different runs shown in the figure, it is evident that the reproducibility with this method is good, both within the two specimens treated simultaneously in a given run and within specimens treated in different runs but under the same oxygen pressures.

This indicates that oxidation in atmospheres of closely controlled oxygen pressures provides uniform conditions in the furnace and that it is possible to reproduce the oxygen pressures in the atmospheres from run to run with the solid electrolyte $ZrO_2(CaO)$ cell.

Comparing the particle sizes obtained under the different oxygen pressures used in this work it will also be noted that to a certain extent the particle size is controlled by the oxygen pressure of the atmosphere, because decreasing oxygen pressures give increasing particle sizes. The reason for this effect is probably that the longer oxidation times necessary for complete oxidation at lower oxygen pressure give a greater possibility for diffusion of the dissolved Al towards the initially formed Al_2O_3 particles. A more detailed examination of this effect, as well as of the influence of the oxidation temperature on the mean particle size and its distribution throughout the specimens, has been started and the results obtained will be described in a later publication.

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