$$\delta\mathbf{g}\cdot\mathbf{k} \equiv \frac{\mathbf{g}_1\cdot\mathbf{k}}{g_1}\,\delta g = \frac{\mathbf{g}_1\cdot\mathbf{k}}{g_1}\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1}$$

$$= -\sin(\gamma+\theta)\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1}$$

$$= -(\gamma+\theta)\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1}$$

$$\delta s = \{2\theta-(\gamma+\theta)\}\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1} + \frac{\lambda(\delta g)^2}{2}$$

$$= (\theta-\gamma)\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1} + \frac{\lambda(\delta g)^2}{2}\,.$$

If δg is small, this reduces to

$$\delta s = (\theta-\gamma)\,\frac{\mathbf{g}_1\cdot\delta\mathbf{g}}{g_1}\,. \qquad (2)$$

The expression given by Goringe and Valdrè is obtained from Equation 2 by setting $\gamma = 0$, and is hence valid only when $\theta \gg \gamma$. This condition is often violated in practice, as for example in the studies of Jones and Williams [2] and of White [3] and the γ-dependent term can become dominant. The simple version found in [4] can, therefore, only be applied to special situations and the general form given above as Equation 1 must normally be employed.

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J. R. WHITE
Department of Materials,
Queen Mary College,
London, UK

A TEM study of precipitates in Cu_2O

The microscopic precipitate structure of cuprous oxide Cu_2O prepared either by total oxidation of copper or by growth from the melt has recently been investigated [1]. Those precipitates visible in the optical microscope are agglomerates of cupric oxide CuO formed during cooling from the elevated temperatures of crystal growth.

The work reported in this note was undertaken in order to investigate the efficiency, on a submicroscopic scale, of the annealing treatment designed to eliminate such agglomerates [1].

Single crystals were prepared from copper of two purities (99.9 and 99.999%) by total oxidation and growth by a floating zone method. Slices 0.2 mm thick were cut from annealed specimens and chemically tailored in concentrated nitric acid to form 3 mm diameter discs. These discs were polished chemically in a solution of 90% orthophosphoric acid and 10% nitric acid [2] in a double jet Tenupol apparatus until the central portion assumed a yellow colour indicating a thickness of about 1000 Å [3]. Thinning was continued either by ion bombardment (6 keV Ar ions), or chemically by immersion first in a bath of 80% orthophosphoric acid and 10% nitric acid for several minutes, and then in a solution of 80% orthophosphoric acid and 5% nitric acid until a hole was formed.

Thinned specimens were examined in a Philips EM300 electron microscope operating at 100 kV with hot stage and tilting accessories.*

At the beginning of the TEM observation, thin foils obtained by ion bombardment showed no trace of a second phase even at the limit of resolution. In chemically thinned specimens, large facetted deposits impervious to electrons were observed on the surface of the otherwise precipitate-free foils. After an observation time of typically 20 to 30 min with a low intensity electron beam, disc-shaped inclusions of 50 to 200 Å diameter developed both in foils thinned chemically and by ion bombardment (Fig. 1). Selected-area diffraction revealed the presence of

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*C.E.C.M., Vitry sur Seine.

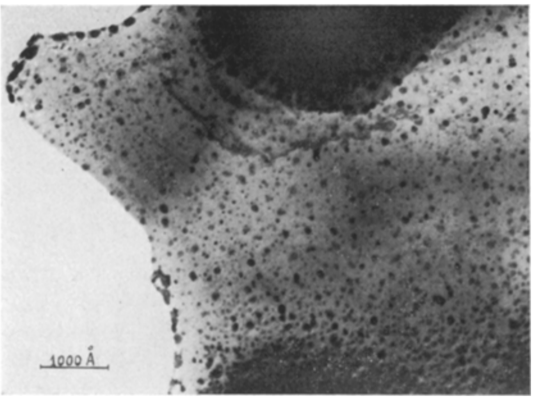


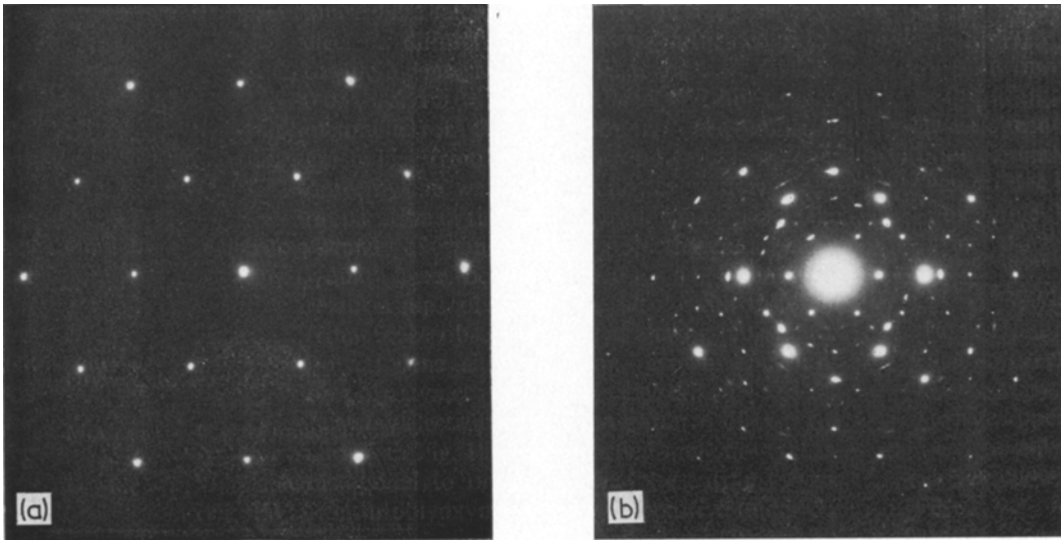
Figure 1 Precipitate structure in annealed cuprous oxide after 30 min observation at room temperature.

Cu and CuO precipitates embedded in a matrix of Cu_2O (Fig. 2). The copper precipitates had an orientation relationship

$$(100)_{Cu} \,//\, (111)_{Cu_2O}$$
$$[110]_{Cu} \,//\, [110]_{Cu_2O}\,.$$

The CuO inclusions showed no preferred orientation as they gave rise to diffuse rings. The rate of precipitate growth was accelerated by observation with a high intensity electron beam (condenser aperture withdrawn). Neither the original annealed specimen structure nor the evolution of the precipitation process were notably influenced by specimen purity.

Several chemically thinned annealed discs were heated to 360°C in the electron microscope (temperature control to within 20°C). Again, Cu and CuO precipitates were formed during TEM observation with a low-intensity beam, this time in a matter of a few seconds. The orientation relationships were identical to those encountered during room temperature observation.



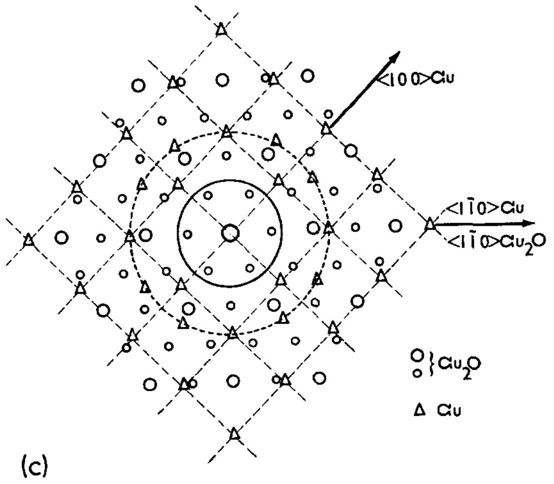


Figure 2 Selected-area diffraction patterns of (111) oriented thin foil. At the beginning of observation, only Cu_2O is observed (a). After 30 min at room temperature, a precipitate structure has been formed giving rise to a pattern of spots and rings (b) which is due to non-oriented CuO and oriented Cu distributed in the matrix of Cu_2O (c).

The effect of further heating of chemically thinned specimens after the formation of a precipitate structure either at room temperature or at 360°C was also investigated. This was done in order to check whether the observed precipitation process could be linked with the eutectoid decomposition $Cu_2O \rightarrow CuO + Cu$ which takes place below 375°C in air, as indicated by the phase diagram [4]. At 400°C a rapid and complete dissolution of the preformed Cu and CuO precipitates took place. At temperatures of 550°C and more, an equally rapid dissolution occurred, but observation was rendered difficult due to contamination of the foil surface.

It should be noted that a previous TEM observation of Cu_2O by Kužel *et al.* [5] has revealed the presence of 250 to 1500 Å diameter particles identified as unoxidized copper. This isolated presence of copper in a cuprous oxide matrix at ambient conditions of temperature and oxygen partial pressure is not readily explained either by equilibrium data [4] nor by non-equilibrium conditions existing during and after specimen preparation [1]. However, it is possible that the authors failed to detect the CuO precipitates which would be expected if the foils of Cu_2O had partially undergone a eutectoid decomposition with the formation of both Cu and CuO.

Phase transformation and precipitation during TEM observation have been reported for a number of ionic crystals such as NaCl [6], KCl [6], LiF [7], NiO [8] and topaz $Al_2SiO_4(F, OH)_2$ [9].

It is generally accepted [10], that the creation of defects by an electron beam is due either to electronic processes, to elastic collisions (momentum transfer) or to radiolysis. In the first case, an electronic state is changed or charge is moved about by the absorption of radiant energy, but no ionic or atomic defects are formed. In the second case, atoms or ions are displaced due to momentum and energy transfer by the impinging particles. In the last case, atomic or ionic defects are produced by a series of reactions beginning with an electronic excitation resulting in the creation of an electronic defect in the lattice, followed by the conversion of this electronic excitation energy into kinetic energy; the last step results in the motion and further stabilization of the ion. In the present case, only the two last mechanisms need be considered, i.e. momentum transfer and radiolysis.

The conditions for the displacement of ions by momentum transfer is that the maximum energy transferred by the incident electrons should be larger than the displacement energy of the respective ions. Assuming a working value of 30 eV for the displacement energy of ions in the Cu_2O lattice one can show that electrons of 100 keV do not transfer sufficient energy to cause displacement. Even for the specimens examined at raised temperatures (external heating plus heating by the electron beam) one cannot expect a significant reduction of the displacement energies. It may, therefore, be inferred that the observed precipitation is not imputable either to momentum transfer alone or to momentum transfer coupled with a raised sample temperature.

Let us now consider the last possibility. Radiolysis processes have previously been invoked to explain the creation of colour centres and Frenkel pairs in polar crystals [11-13]. In the light of the appearance of cupric oxide and metallic copper under the action of the electron beam at ambient temperature and the dissolution of these precipitates above 400°C, it seems certain that one is dealing with the eutectoid decomposition of cuprous oxide $Cu_2O \rightarrow CuO + Cu$. Nucleation and growth of both phases may well be triggered off by one of the above mechanisms (valence change or colour centres) followed by a charge exchange.

In conclusion, it can be stated that the annealing and cooling cycle which eliminates optically visible cupric oxide precipitates [1] also results in precipitate-free specimens on the scale of the electron microscope. The previously reported [5] submicroscopic particles in annealed Cu_2O were probably formed in the electron microscope.

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M. MARTINEZ-CLEMENTE*
R. D. SCHMIDT-WHITLEY†
Laboratoire de Physique des Matériaux,
Centre National de la Recherche Scientifique,
92190 Meudon, France

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*Present address: Laboratorio de Microscopia Electronica, Facultad de Ciencias, Universidad Complutense de Madrid, Madrid, Spain.

†Present address: IRSID, Station d'Essais, 57210 Maizières-lès-Metz, France.