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A thermogravimetric study of the oxidation of $CuFeO_2$

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The oxidation kinetics of $CuFeO_2$ have been studied between 500 and 1000° C under various oxygen partial pressures using thermogravimetric analysis (TGA). The oxidation rate was found to increase as the oxygen partial pressure was increased, and for a given partial pressure of oxygen it was found to be maximum at ~700° C. The enthalpy and activation energy for the oxidation of $CuFeO_2$ were calculated to be ~26.6 ± 2 and ~18 ± 2 kcal mol^{-1} respectively. The oxidation of $CuFeO_2$ resulted in the formation of $CuFe_2O_4$ and CuO, and the rate of reaction followed an S-type curve as found in the pearlitic transformation in steels.

1. Introduction

The properties of copper ferrite are rather controversial because there are several possible stable phases [1–4] in this phase region, for example $CuFe_2O_4$, $CuFe_5O_8$ and $CuFeO_2$. The phases present in the Cu–Fe–O system depend critically upon various factors like the Cu/Fe ratio, and the temperature and atmosphere during sintering. Yamaguchi and Shiraishi [5] studied the stability of spinel phase near $CuFe_5O_8$ and found that under non-oxidizing conditions it undergoes a eutectoidal transformation to $CuFeO_2$ and Fe_2O_3, or to $CuFe_2O_4$ and Fe_2O_4, depending upon whether the Cu/Fe ratio is greater or less than 1/5.

Besides these phase transformations, it is also interesting to study the valence state of the Cu and Fe ions in these compounds. The valence states of these ions have not yet been established presumably due to the ease with which Cu and Fe ions can change their valence. But various oxidation reactions are possible, some of which are given below:

$$4CuFeO_2 + O_2 = 2CuFe_2O_4 + 2CuO \quad (1)$$

$$4CuFe_5O_8 + O_2 = 4CuFe_2O_4 + 6Fe_2O_3 \quad (2)$$

The purpose of the present work was to study the oxidation of $CuFeO_2$ to $CuFe_2O_4$ and the resulting precipitation of cupric oxide. The kinetics of the oxidation were studied using a thermobalance [6] and the nature of the precipitation was followed by using optical metallography.

2. Experimental procedure

2.1. Preparation and TGA

Copper delafossite ($CuFeO_2$) containing Cu/Fe in the ratio 1 : 1 was prepared in the following manner: reagent grade CuO and Fe_2O_3 were mixed in a jar mill and the resultant mixture was prefired at 800° C for 10h in air. X-ray examination of this prefired powder revealed that $CuFe_2O_4$ and CuO were the constituent phases. In order to prepare $CuFeO_2$ (delafossite), the prefired powder was placed in a thermobalance and heated to 950° C in nitrogen with a heating rate of 100° C h^{-1}. The weight loss agreed with the calculated weight loss for the reduction reaction.

$$2CuFe_2O_4 + 2CuO = 4CuFeO_2 + O_2\uparrow \quad (3)$$

Thus $CuFeO_2$ (delafossite) was obtained. This was further checked by X-ray analysis of the sample quenched from 950° C.

In order to study the oxidation of $CuFeO_2$, the sample ($CuFeO_2$) was cooled from 950° C in nitrogen to various temperatures. Such cooling under nitrogen caused no increase in the weight of the sample, indicating that $CuFeO_2$ was not oxidized. On cooling to the temperature of interest, oxygen was added to the flowing nitrogen to the desired extent. The gain in the weight of the sample was monitored isothermally till the weight remained constant. The oxidized sample was subjected to X-ray analysis and the presence of $CuFe_2O_4$, CuO and $CuFeO_2$ was detected.

2.2. Metallographic examination

In order to study the precipitation of CuO on the oxidation of $CuFeO_2$ via Equation 1, tablets were pressed out of the prefired material, sintered at 1100° C for 4 h in nitrogen and cooled in nitrogen. The only phase detected by the X-rays in such a sample was $CuFeO_2$. The $CuFeO_2$ sample was prepared for metallographic examination by grinding away 1 mm from the surface, and by subsequently polishing with various grades of emery papers and finally with 1 μm diamond paste. The sample was then etched with a solution of 47.5 wt% HCl + 47.5 wt% H_2O + 5 wt% $FeCl_3$. To study the precipitation, the polished and etched sample of $CuFeO_2$ was heated at 900° C in nitrogen and oxidized at 900° C by introducing oxygen. The sample was then slightly polished and etched with the etching solution mentioned above, for 5 to 10 sec to reveal the CuO precipitates.

3. Results and discussion

3.1. X-rays

Table I summarizes the various phases detected in the composition under study, i.e. CuO $(Fe_2O_3)_{0.5}$ when the heat treatments given were different. The sample prefired at 800° C in air showed the presence of $CuFe_2O_4$ and CuO phases, whereas the sample heated in nitrogen above 900° C showed presence of $CuFeO_2$ phase only.

TABLE I X-ray analysis

Phases Present	Temperature (°C)		
	800 (Air)	950 (Nitrogen)	900 (Oxygen)
CuO	VS	–	VS
Fe_2O_3	–	–	–
$CuFe_2O_4$	VS	–	VS
$CuFeO_2$	–	VS	W

Key: VS = Very strong, W = Weak.

3.2. Thermogravimetric analysis

The oxidation of $CuFeO_2$ under isothermal conditions at various temperatures and in atmospheres containing various percentages of oxygen in nitrogen was studied. As the sample oxidized, it gained weight and the maximum weight gains in $CuFeO_2$ at various temperatures of oxidation in various atmospheres is given in Fig. 1. It can be seen that there was a change in slope of the curve at a characteristic temperature and that this characteristic temperature decreased with the oxygen content of the atmosphere. This can be explained in terms of the oxidation reaction of Equation 1. When oxygen was $\leqslant 0.05\%$ in the ambient atmosphere, the oxidation was not observed even at room temperature, and this may be due to slow kinetics of oxidation of $CuFeO_2$ at low temperature as described below. The equilibrium constant K_0 and enthalpy ΔH of the reaction are related by the following equations:

$$K_0 = (p_{O_2}^{eq})^{-1} \tag{4}$$

and,

$$\log p_{O_2}^{eq} = \Delta H/RT - \Delta S/R. \tag{5}$$

where $p_{O_2}^{eq}$ = equilibrium partial pressure of oxygen, R = gas constant, T = absolute temperature and ΔS = change in entropy.

When the partial pressure of oxygen in the oxidizing atmosphere becomes greater than the equilibrium partial pressure as given by Equation 5, the oxidation of $CuFeO_2$ starts accounting for the change in the slope of the curve in Fig. 1. Fig. 2 shows the plot of the logarithm of the oxygen con-

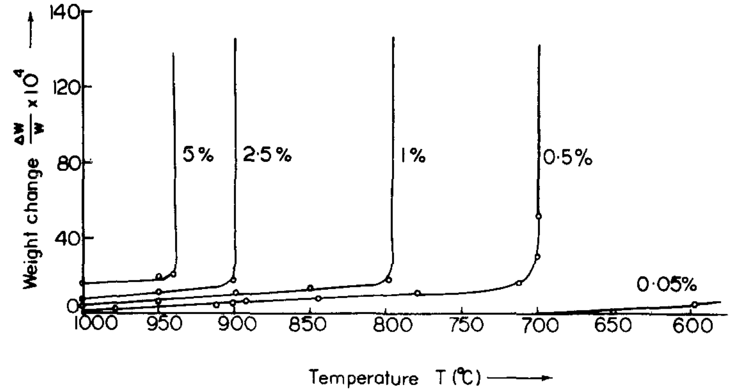

Figure 1 Equilibrium weight changes versus temperature at constant atmospheric oxygen.

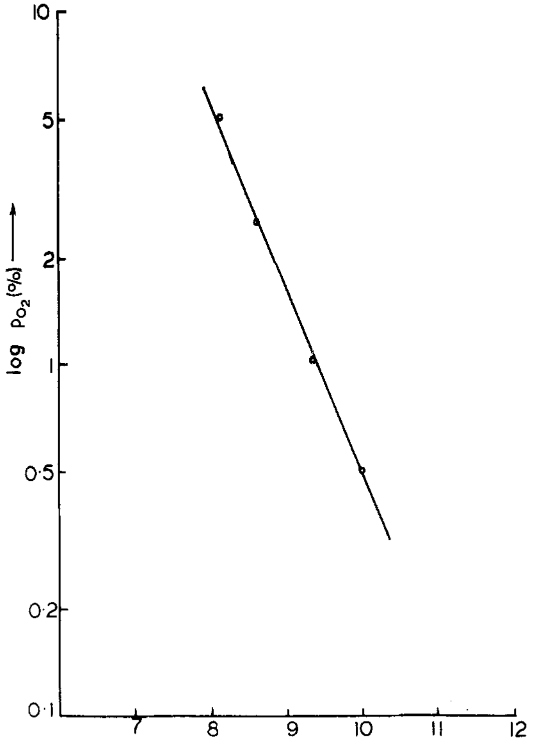

Figure 2 Log p_{O_2} versus reciprocal absolute temperature *T*.

tent versus the reciprocal of the absolute temperature where the oxidation starts. It is a straight line whose slope gives the enthalpy of the reaction of Equation 1 as ~26.6 ± 2 kcal mol^{-1}. This enthalpy may be compared with the enthalpy for oxidation of Cu_2O to CuO, which is 34 kcal mol^{-1} [7]. The difference is due to the fact that during oxidation of $CuFeO_2$, not only do the Cu^+ ions oxidize to Cu^{++} ions, but there is also a simultaneous precipitation of CuO.

Below the characteristic temperature, the oxidation took place at various rates. Fig. 3 gives a typical example when the atmosphere of oxidation contained 2.5% oxygen. The rate of oxidation increased as the temperature was lowered from 900° C, reached a maximum at ~700° C, and again decreased at lower temperatures. Fig. 4 shows the time – temperature diagram of such an oxidation giving contours of constant percentages of oxidation. Fig. 4 is quite similar to the time–temperature diagram for the decomposition of austentie in steels [8]. The behaviour can be explained from the fact that the oxidation taking place in the solid state depends upon the diffusivity of various ions and hence at lower temperatures the rate of oxidation is slower.

If Avrami's equation [9]

$$1-f = \exp(-kt^n), \qquad (6)$$

where f is the mass fraction oxidized, is assumed to be valid in this case, the exponent n can be determined from the appropriate plot (Fig. 5). The vlaue of n varied between 1 and 1.9, the higher values being found when oxidation took place at higher oxygen partial pressures (Fig. 6).

The Arrhenius plot of rate constant k of Equation 6 shows two slopes (see Fig. 7), i.e. a positive slope at high temperature and a negative

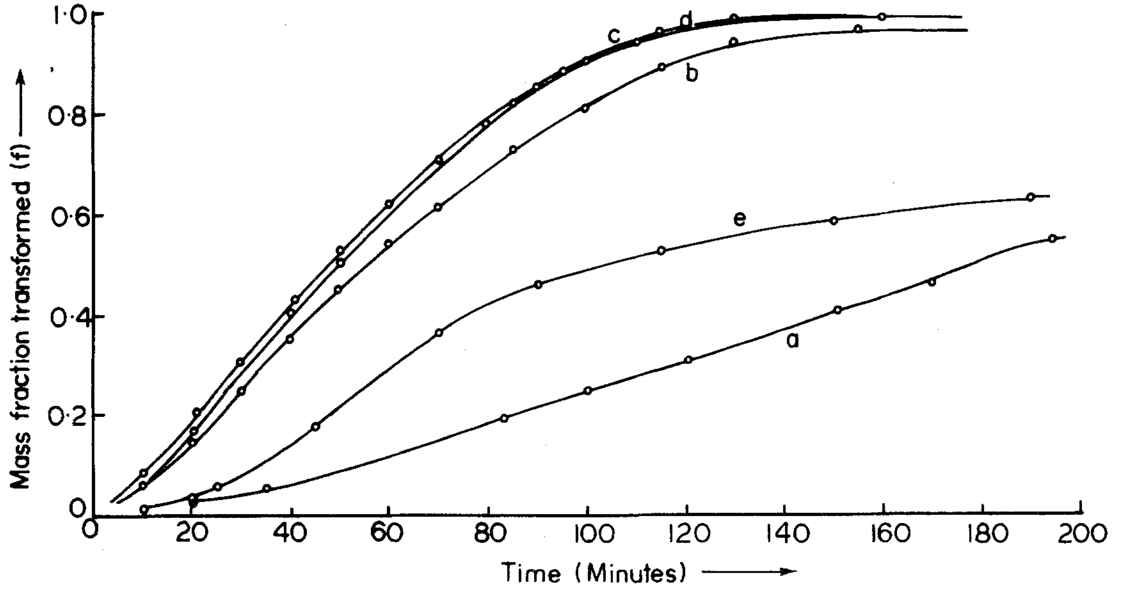

Figure 3 TGA plot of mass fraction transformed f versus time t; (a) 900, (b) 800, (c) 700, (d) 600, and (e) 500° C.

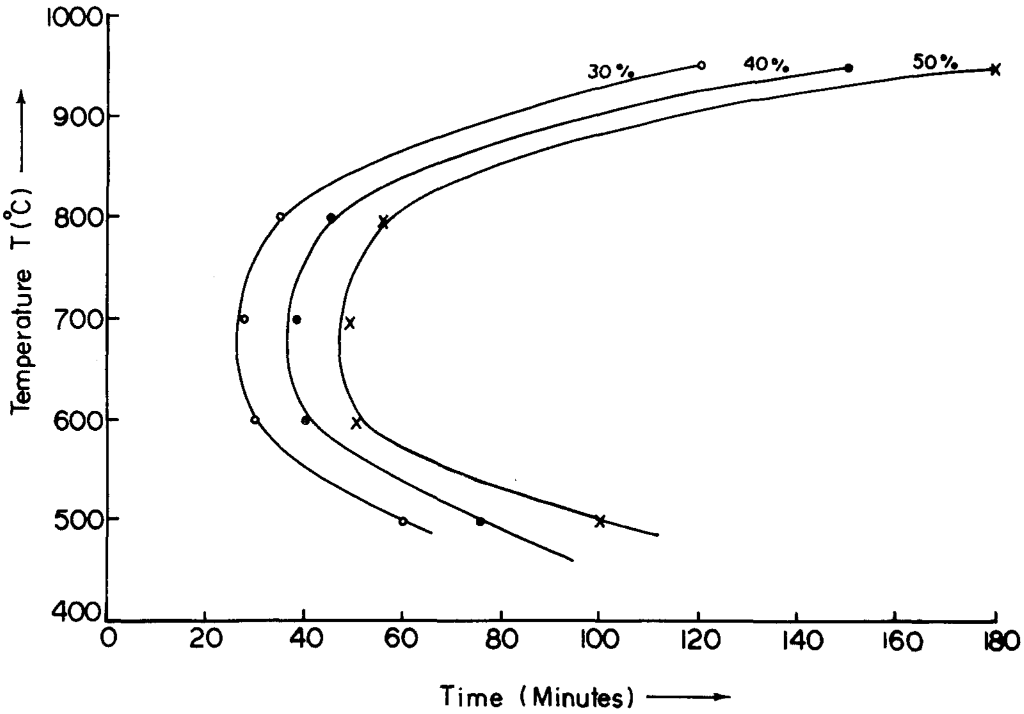

Figure 4 Time–temperature – transformation diagram of $CuFeO_2$ of constant percentage of oxidation. ○ 30%, ● 40%, and X 50%.

slope at lower temperatures. At lower temperature, the activation energy was estimated to be $\sim 18 \pm 2\,\text{kcal mol}^{-1}$.

3.3. Metallographic observation of precipitates

Fig. 8a shows the $CuFeO_2$ sample; Fig. 8b shows the same sample oxidized to $CuFe_2O_4$ and CuO. The CuO has precipitated rather homogeneously in Fig. 8b. It may be noted that the grain boundaries are not revealed in Fig. 8b, since they could only be delineated under prolonged etching, resulting in etching away of the CuO precipitates leaving pores (Fig. 8c), which could not be distinguished from the natural pores occurring in the sample.

3.4. Mechanism of oxidation

Any mechanism of oxidation to be suggested should explain two typical characters of oxidation of $CuFeO_2$. They are (1) the reduction in rate of oxidation at higher temperature (Fig. 7), and (2) the low activation energy for oxidation at low temperature. In oxidation of metals [10], the oxide layer grows due to diffusion of either metal ions towards the oxide–atmosphere interface or oxygen ions towards the metal–oxide interface (with corresponding electron transport to neutralize the charge). In this case where two oxides are products of the oxidation of $CuFeO_2$, the oxidation can proceed according to any of the two schemes given in Fig. 9. In scheme 1 (Fig. 9a), CuO precipitates homogeneously and in scheme 2 (Fig. 9b), there is a lamellar growth akin to pearlite in steels.

In either scheme there is a chemical free-energy gradient established between the $CuFeO_2$–$CuFe_2O_4$ + CuO and $CuFe_2O_4$ + CuO–atmosphere interfaces, which governs the flux of ions and hence the rate of oxidation.

$$J = -M\frac{d\mu}{dx} = -M\frac{\Delta\mu}{x}$$

and

$$-\Delta\mu = RT\ln - \frac{p_{O_2}}{p_{O_2}^{eq}}$$

where M = a mobility related term, μ = chemical potential, p_{O_2} = partial pressure of oxygen in atmosphere, $p_{O_2}^{eq}$ = equilibrium partial pressure of oxidation from Equation 5.

At low temperatures, mobility approaches zero and hence the oxidation rate decreases. As the temperature of oxidation is increased, the rate increases. But as the temperature is further increased, the free-energy gradient approaches zero

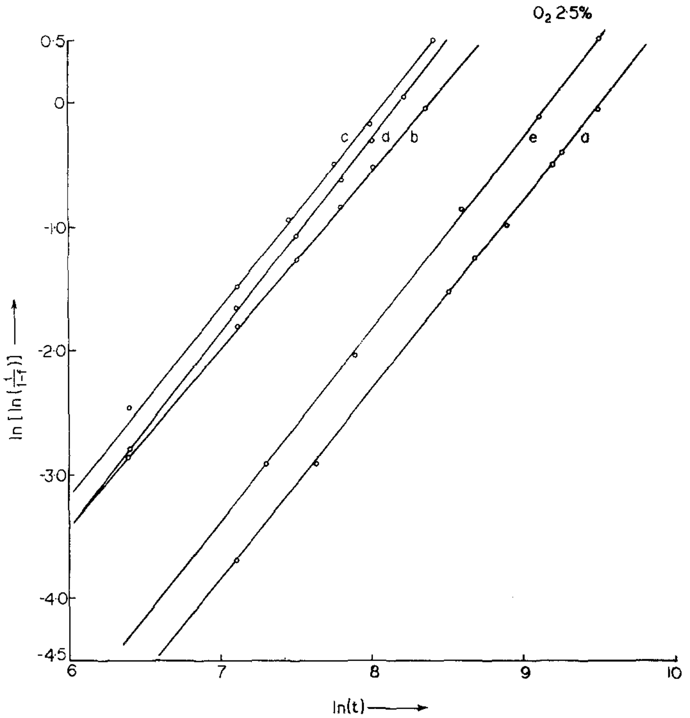

Figure 5 Plot of $\ln[\ln(1/1-f)]$ versus $\ln(t)$; (a) 900, (b) 800, (c) 700, (d) 600 and (e) 500° C.

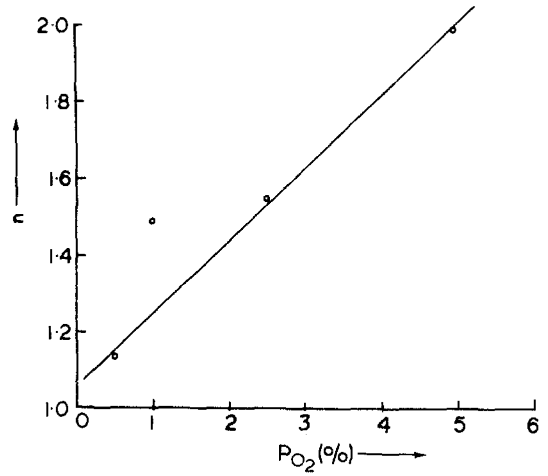

Figure 6 Plot of n versus partial pressure of oxygen p_{O_2}.

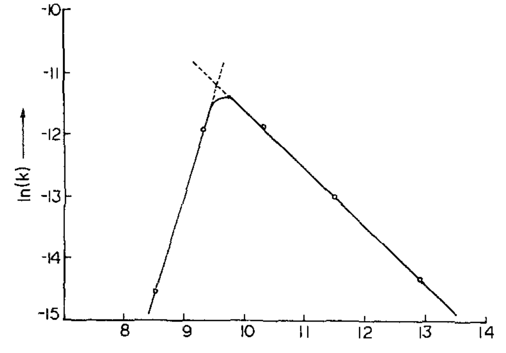

Figure 7 Arrhenius plot of rate constant, $\ln k$ versus $1/T$.

as $p_{O_2}^{eq}$ approaches p_{O_2}. Hence the rate of oxidation goes through a maximum and then decreases to zero as the temperature of oxidation is increased.

The activation energy for oxidation of $CuFeO_2$ was estimated to be $\sim 18 \pm 2$ kcal mol^{-1}. It is much less than the activation energy for self-diffusion of cations through spinels which varies between 50 and 150 kcal mol^{-1} [11]. The activation energy for self-diffusion of oxygen ions in spinels is more than that of cations, so that diffusion of copper or oxygen ions through $CuFe_2O_4$ is a rather slow process. Any grain-boundary diffusion can also be eliminated since oxidation of powders, each of which was a single crystal, was studied by TGA. The activation energy for oxidation of $CuFeO_2$ is however comparable to the activation energy for oxidation of copper metal to CuO [12, 13], which is $\sim$20.14 kcal mol^{-1} where diffusion of the Cu ions through CuO is the dominant process. Such a diffusion can only be possible if there is lamellar precipitation of CuO via scheme 2 (see Fig. 9b). Metallographic examination of oxidized polycrystalline sample shows a rather homogeneous precipitation, but a polycrystalline sample is not a true representation of the single crystal since oxygen can diffuse through grain boundaries in a polycrystalline sample.

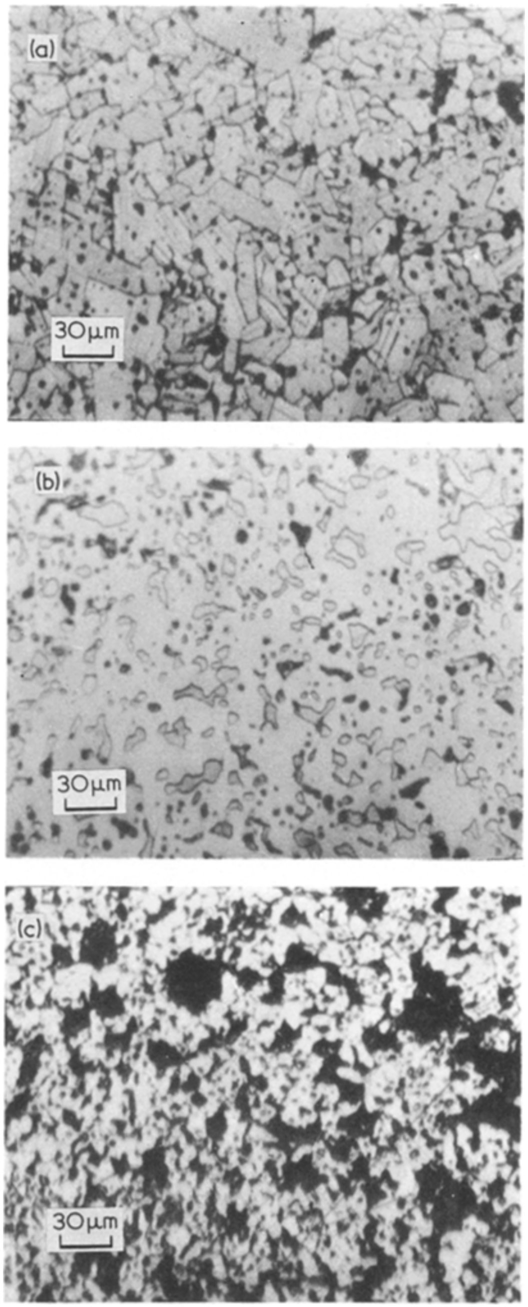

Figure 8 Photomicrographs of polished and etched section of $CuFeO_2$; (a) $CuFeO_2$ (b) Sample a Oxidised to $CuFe_2O_4$ + CuO, (c) Etched sample b.

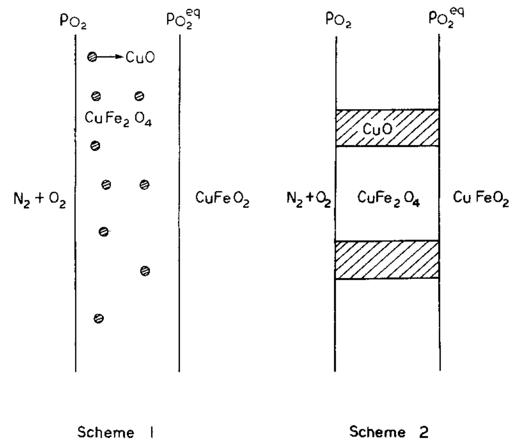

Figure 9 (a) Schematic representation of the continuous precipitation of CuO in the $CuFe_2O_4$–CuO region. (b) Schematic representation of the dis-continuous precipitation of CuO in the $CuFe_2O_4$–CuO region.

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