

Kinetics of the oxidation of CuFeO_2 in Cu-Fe-O system

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Abstract. The oxidation kinetics of CuFeO_2 in Cu-Fe-O system have been studied between temperature range 500°C and 900°C in an ambient atmosphere containing constant oxygen partial pressure in the flowing nitrogen. Thermogravimetric analysis (TGA) technique was used as the main tool. The oxidation rate was found to decrease and the activation energy calculated from the oxidation rate constants for various composition increased from 8 to 45 k cal/mole on increasing the Fe_2O_3 content in the system. The value of exponent n in Avrami's equation $= 1 - \exp(-kt^n)$ also increased from 1.3 to 2.3. The microstructural changes associated with the oxidation have been studied using optical microscopy and correlated with results obtained from thermogravimetric analysis.

1. Introduction

Cu-Fe-O system is a double oxide system containing two transition metal elements. The valency states of the transition metal elements depend upon the sintering temperature and ambient atmosphere. Therefore in this system three phases, namely, CuFe_2O_4 , CuFe_5O_8 and CuFeO_2 exist. Although the phase transformation in this system under various equilibrium conditions have been studied, no correlation between the oxidation level, the temperature and phases present has been established in a systematic manner. The kinetics of phase transformation in this system have also not been clearly understood because of their dependence upon temperature, oxygen partial pressure and composition. These transformations occur due to the oxidation or reduction of copper ions in the Cu-Fe-O system.

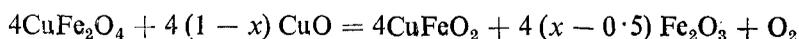
The present work deals with the kinetics of oxidation and mechanism of phase transformation in Cu-Fe-O system which occur due to the oxidation. For this study, CuFeO_2 has been chosen as the base material. A thermobalance has been used as the main tool to follow the kinetics of the oxidation. Besides studying the reaction kinetics, attempts have also been made to characterise the precipitation of second phase like Cu_2O , CuO , or Fe_2O_3 during oxidation. The precipitation of these phases have been explained with the help of x-ray diffraction analysis and optical microscopy.

2. Experimental procedure

CuO (Fe₂O₃)_x powder, whose composition is shown in table 1, was used as samples in a thermobalance to study the physico-chemical reactions in the Cu-Fe-O system. These powders were prepared by the usual ceramic technique (Snelling 1969) by prefiring at 800° C for 10 hr in air. The prefired samples were ball-milled again to get submicron size powders of homogeneous composition. X-ray analysis of these powders revealed that CuFe₂O₄ was the common phase along with CuO or Fe₂O₃ depending upon composition, i.e., whether *x* is less than or greater than 1 respectively. To obtain powders of CuFeO₂, the prefired powders of all the compositions of table 1 were heated in nitrogen atmosphere at 900° C in the thermobalance until they were reduced to CuFeO₂. The weight loss in each sample compared well with the calculated weight loss for one of the reduction reactions.



$$\text{for } x \leq 0.5,$$



$$\text{for } 0.5 \leq x \leq 1,$$



$$\text{for } x \geq 1.$$

Thus CuFeO₂ with Cu₂O or Fe₂O₃ as a second phase was obtained. This was further checked by x-ray analysis of the quenched samples held at 900° C in nitrogen atmosphere.

Table 1. Chemical composition of the samples.

Batch No.	Value of 'x' Mole	Composition	General formula
1.	0.3	CuO : 0.33 Fe ₂ O ₃	} (CuO (Fe ₂ O ₃) _x)
2.	0.5	CuO : 0.5 Fe ₂ O ₃	
3.	1.0	CuO : Fe ₂ O ₃	
4.	1.5	CuO : 1.5 Fe ₂ O ₃	
5.	2.0	CuO : 2.0 Fe ₂ O ₃	
6.	2.5	CuO : 2.5 Fe ₂ O ₃	

3. Different analyses

Thermogravimetric analysis technique was used to study the kinetics of the oxidation of CuFeO_2 in the stoichiometric and nonstoichiometric compositions of Cu-Fe-O system. For these studies, samples were cooled from 900°C in nitrogen atmosphere to various temperatures. Such a cooling under nitrogen atmosphere caused no increase in the weight of the sample, indicating that samples were not oxidised on cooling to the temperature of interest. A fixed amount of oxygen was added to the flowing nitrogen and gain in weight was monitored isothermally till the weight remained constant.

In support of the TGA results, x-ray diffraction analysis was used to investigate the various phases in the powders. For this purpose the samples, which were heat-treated at different temperatures and in various atmospheres, were powdered and prepared in a cylindrical shape using an adhesive. The Debye-Scherrer photographs of the powder were taken in a 11.46 cm diameter camera using FeK_α radiations. The interplanar spacings were calculated and compared with the ASTM cards.

The nature of precipitation of the second phase in the matrix and interdiffusion between two phases was studied through metallographic analysis of the samples. For optical metallography the prefired powders shown in table 1 were pressed in the form of discs and sintered in identical conditions similar to thermogravimetric analysis. The surface of the discs was ground by $\sim 0.5\text{ mm}$ and polished well using the method of Jain *et al* (1977). The polished samples were etched in a solution of (50% $\text{HCl} + \text{FeCl}_3$) or thermally at 900°C in oxygen atmosphere whenever needed.

4. Results and discussion

The isothermal plots of oxidation of CuFeO_2 in the stoichiometric composition at various temperatures and in non-stoichiometric compositions at 600°C in constant oxygen partial pressure are shown in figures 1 and 2 respectively. Figure 1 shows that the oxidation rate increased on increasing the temperature and reached a maximum value at a temperature $T_{k(\text{max})}$. If the temperature was further increased,

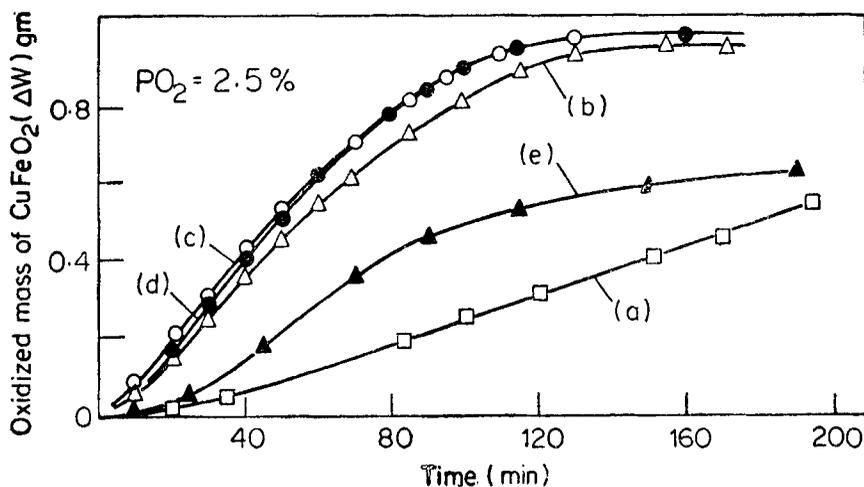


Figure 1. Oxidation of CuFeO_2 as a function of time and temperature.

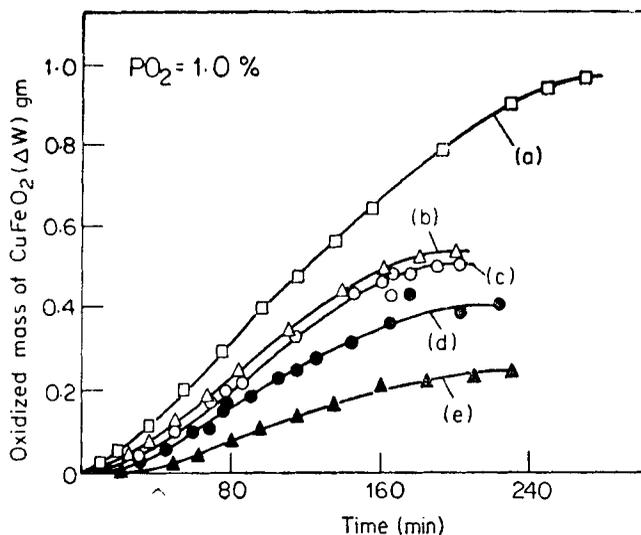


Figure 2. Oxidation of CuFeO_2 as a function of time and composition ($\text{CuO}(\text{Fe}_2\text{O}_3)_x$) at 600°C . (a) $x = 0.5$, (b) $x = 1.0$, (c) $x = 1.5$, (d) $x = 2.0$ and (e) $x = 2.5$.

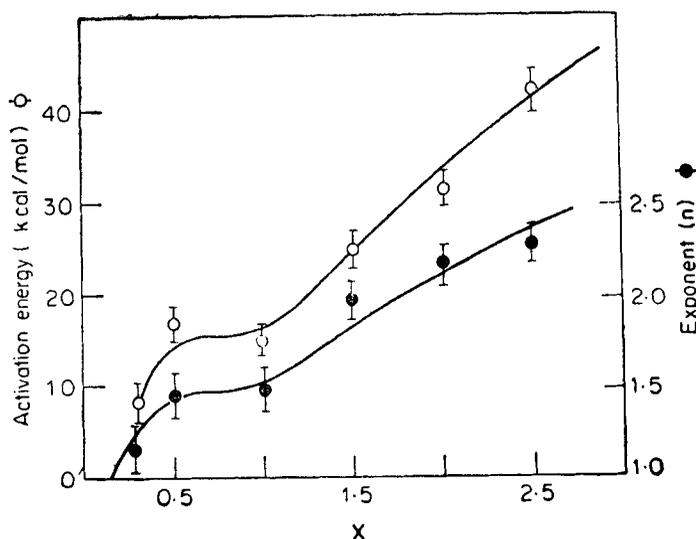
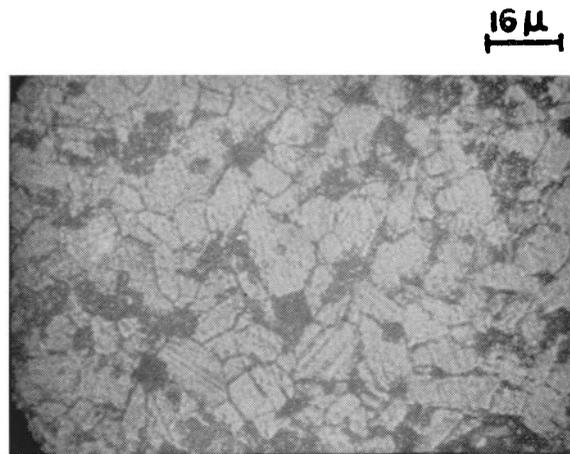


Figure 3. Plots of exponent (n) and activation energy versus x .

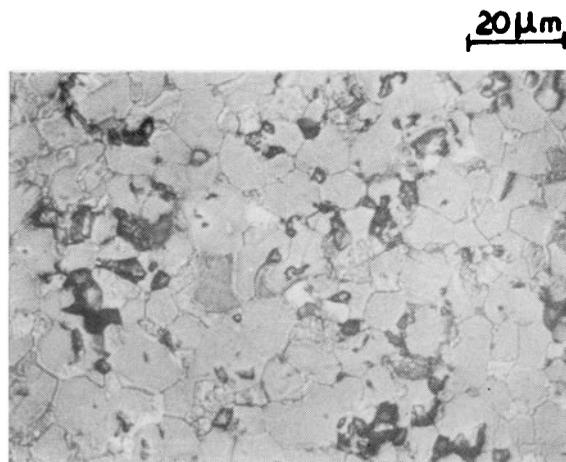
the oxidation rate decreased. Oxidation rate also decreased on increasing the Fe_2O_3 content in Cu-Fe-O system as shown in figure 2. These oxidation data agreed with Avrami's equation (Avrami 1939, 1940, 1941)

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

where f = fraction mass oxidised, k = oxidation rate constant, t = time and n = exponent. The intercepts and slope of the plots of $\ln \ln [1/(1-f)]$ versus $\ln(t)$ gave $\ln k$ and n . The value of n for a single composition remained constant with temperature. The activation energies for various compositions were calculated from the Arrhenius plots of the rate constants. The dependence of the activation energies and the exponent n on the composition is shown in figure 3. In



(a)



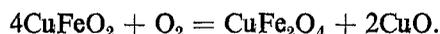
(b)

Figure 4. (a) Microstructure of the oxidised surface of a sample. (b) Microstructure of the sample 4 (a) after complete oxidation.

this figure both the activation energy and the exponent n seem to be constant in the composition range $0.5 \leq x \leq 1.0$ and increase on increasing x above one. Such a variation in the activation energy and n indicates the change in the oxidation mechanism.

It is surmised that in the stoichiometric composition of CuFeO_2 , initially, the surface adsorbs oxygen and forms a metastable phase which is rich in oxygen and subsequently the metastable phase transforms eutectoidally to give a lamellae of CuFe_2O_4 and CuO .

A micrograph of the oxidised surface of CuFeO_2 (figure 4a) shows this behaviour. Inside the grains of oxidised CuFeO_2 some grey and white lines are seen which would be CuFe_2O_4 and CuO according to the reaction



On prolonged heating in the oxygen atmosphere lamellae of both the phases which were observed simultaneously after chemical and thermal etching spheroidised as shown in figure 4 (b). In the non-stoichiometric samples, having excess Fe_2O_3 , CuO was not seen, because the precipitated CuO reacted with the Fe_2O_3 already present adjacent to the CuFeO_2 grains.

The constant values of activation energy and exponent n between the composition range $0.5 \leq x \leq 1.0$ indicate that the mechanism of oxidation remains the same for the said composition range. But above $x = 1$ the variation in both values indicates a change in oxidation mechanism, which can be explained as follows.

In the stoichiometric composition the metastable phase decomposes into two phases, namely, CuFe_2O_4 and CuO in the form of lamellae. For further oxidation Cu^{2+} and O^{2-} ions diffuse through CuO layer because the activation energy for ionic diffusion through CuO is less than CuFe_2O_4 (Jain *et al* 1979). Such a diffusion of ions causes an one-dimensional growth of new (CuFe_2O_4) phase. In the nonstoichiometric compositions for $x \geq 1$ the diffusion mechanism can be presented according to figure 5. In these compositions the interdiffusion between

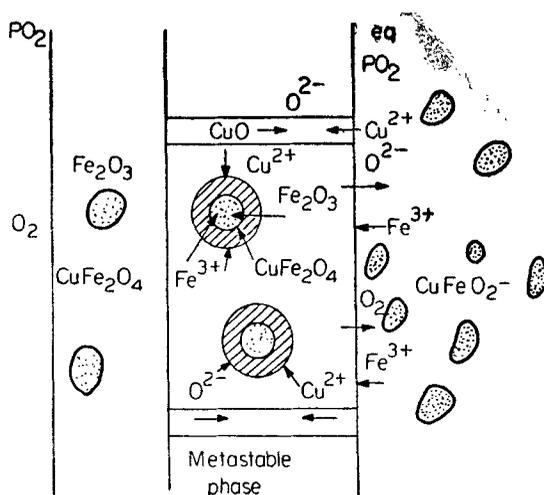


Figure 5. Schematic representation of the oxidation of CuFeO_2 in the nonstoichiometric composition.

Fe_2O_3 , which was in excess and metastable oxygen-rich phases starts causing a two-dimensional growth. On increasing the Fe_2O_3 content, the interdiffusion process between Fe_2O_3 and metastable phase starts to overcome the precipitation of CuO from the metastable phase. Therefore, the value of n changes from 1.3 to 2.3.

The activation energy of oxidation process of CuFeO_2 , obtained from stoichiometric composition, is nearly equal to the activation energy for diffusion of Cu^{2+} and O^{2-} ions through CuO phase which would explain that Cu^{2+} and O^{2-} diffuse through CuO phase. On increasing Fe_2O_3 (x) content, the concentration of CuO phase decreases, which would cause a diffusion of some Cu^{2+} and O^{2-} ions through CuFe_2O_4 . The activation energy of oxidation process of CuFeO_2 is the average of the activation energies of all the process, accruing simultaneously. Hence, on increasing the Fe_2O_3 concentration the diffusion through CuFe_2O_4 phase becomes dominant.

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