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Study of copper ferrite formation reaction

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The reaction by which copper ferrite is formed was studied in the temperature interval 800 to 950°C. The composition and the thickness of the reaction layer were obtained by electron probe microanalysis. The equilibrium concentrations of copper and iron at the reaction-layer boundaries and the concentration gradient across the layer were determined. The kinetic parameters of the reaction were calculated. The mechanism of the reaction was discussed on the basis of the observations.

1. Introduction

Copper ferrite, a typical inverse ferrite, when added to some other ferrites improves their magnetic characteristics. Its extensive application has initiated a detailed investigation of this system. The formation reaction of copper ferrite has been studied by many authors [1-9]. Most of these investigations were related to the study of the conditions of copper ferrite production, determination of the temperatures at which the reaction starts, and the analysis of the products formed, thus leaving the reaction mechanism and kinetics insufficiently explained. The purpose of the present work was to contribute to a better understanding of the kinetics and mechanism of copper ferrite formation by studying the reaction between CuO and Fe_2O_3 in the temperature interval 800 to 950°C, using an electron-probe microanalyser.

2. Experimental Part

2.1 Sample Preparation

The composition of the reaction layer was investigated using specimens in which a CuO/Fe_2O_3 interphase boundary was produced. The starting raw materials were pure CuO(BDH) and Fe_2O_3(Bayer) powders. The CuO powder was pressed at 1000 kg/cm^2 into tablets 8 mm in diameter and 10 mm thick. These were then sintered at 850°C for 20 h, pulverised and passed through sieves to obtain a fraction with granules 200 to 300 μm in diameter. The CuO granules were then mixed with Fe_2O_3 powder (having an average particle size of 1 μm) in a 20:80 weight ratio and the mixture homogenised. The mass was pressed at 1000 kg/cm^2 into tablets 9 mm in diameter and 10 mm thick. The resulting specimens were composed of large CuO particles surrounded by fine-grained iron oxide. The specimens were fired at 800, 850, 900 and 950°C for 1 to 7 h.

2.2 Composition of Reaction Layer

The Cu ferrite formation-reaction at a CuO/Fe_2O_3 interphase boundary was investigated, using an SEM-2 electron probe microanalyser. A standard metallographic procedure followed by the vacuum-evaporation of a thin carbon layer was used to prepare the specimens. CuKα and FeKα lines were used. An accelerating voltage of 25 kV was applied. The measurements were made with a LiF crystal and an X-ray proportional counter. The distribution of both Cu and Fe were determined along lines intersecting the reaction layer, formed at the CuO/Fe_2O_3 interphase boundary. The exact quantitative composition of the reaction layer was determined along these lines at every 3 to 5 μm. In these measurements pure elements were used as the standards. The results obtained were corrected for absorption by the method of Philibert [10]. Evaluation of corrections for fluorescence and atomic number effect has shown that in this system they are negligible.

2.3 Thickness of Reaction Layer

Optical microscopy was not suitable for determining the thickness of the reaction layer. The microstructure of the ferrite was not different from that of CuO and Fe_2O_3, thus making the interphase boundaries indistinguishable. Therefore an effort was made to obtain some information regarding the kinetics of this process on the basis of data obtained with the electron-probe microanalyser. To determine the thickness of the reaction layer, X-ray photographs as well as photographs showing the distribution of Cu and Fe along the layer, were used. In order to be sure that a realistic thickness of the layer is obtained, with a diametral cut of the grain instead of a peripheral cut which gives a higher value, the largest grains (about 300 μm) with the minimum layer thickness were selected. These grains were used to follow the distribution along lines intersecting the reaction layer perpendicularly. The electron-probe microanalysis showed that in the majority of the specimens, the unreacted parts of a CuO grain were torn out during metallographical preparation. Among the grains in which the unreacted CuO was not lost from the specimen, a cavity in the reaction layer/CuO interface was observed.

3. Results and Discussion

The secondary-electron photograph of a specimen "ferritised" at 950°C for 7 h, with the line along which the change in composition was observed, is shown in fig. 1. Figs. 2 and 3 show the distribution of Cu and Fe, respectively, in the specimen, and fig. 4 shows the distribution of Cu and Fe along the line indicated on the electron photograph. Specimens fired at other temperatures and times exhibit the same characteristics, except that the thickness of reaction layer increases as the temperature and time are increased.

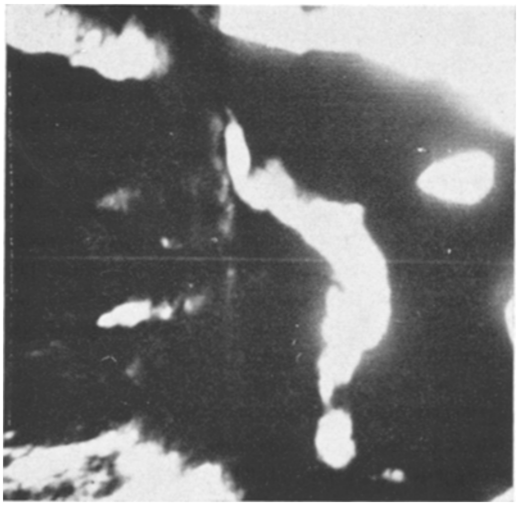

Figure 1 Electron picture on microprobe (× 250).

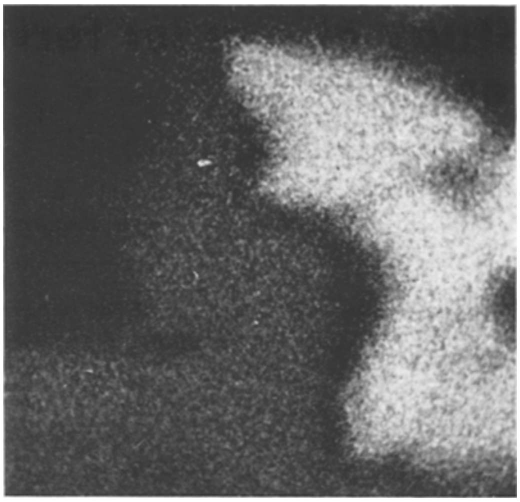

Figure 2 X-ray picture with CuKα (× 250).

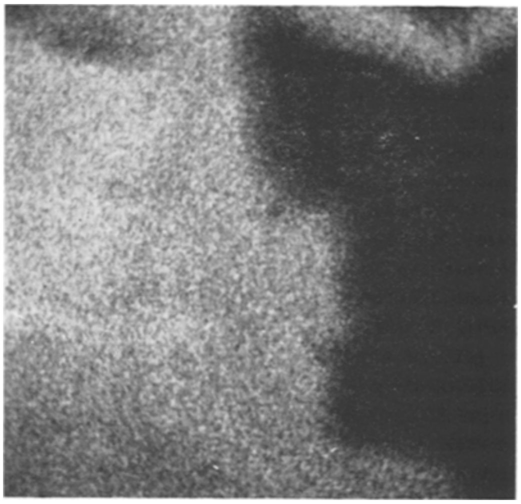

Figure 3 X-ray picture with FeKα (× 250).

A gradual linear change in concentration of Cu and Fe across the reaction layer, shown in fig. 4, but also evident in other specimens, indicates a continuous change in composition of the reaction layer going from CuO towards Fe_2O_3. A graphical representation of Cu and Fe content along the indicated line was obtained by measuring the Cu and Fe concentrations across the reaction layer at 3 to 5 μm intervals. Fig. 5 shows this relation for a specimen fired 7 h at 950°. From such diagrams, boundary concentra-

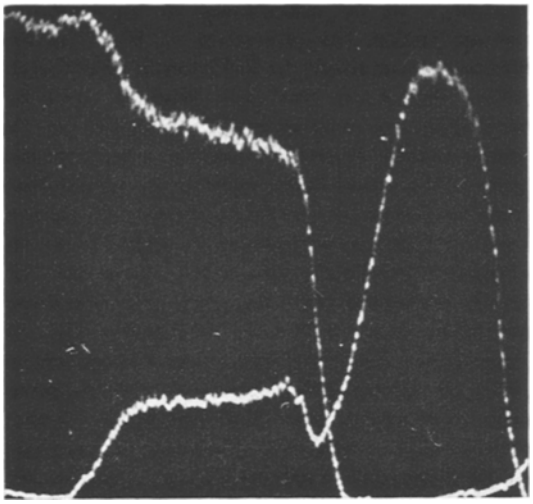

Figure 4 Distribution of Cu and Fe along the line in fig. 1 (× 250).

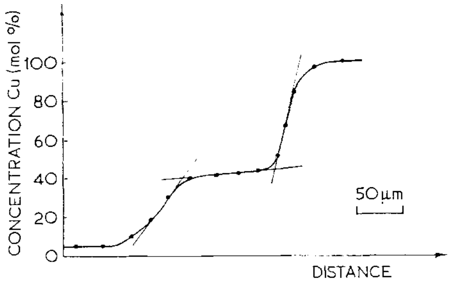

Figure 5 Determination of copper concentrations at the boundaries of the reaction-layer.

tions of Cu and Fe in the reaction layer are obtained by a tangent construction as indicated. These values are not affected by the time, providing the temperature of ferritisation was kept constant. This indicates that an equilibrium composition of the layer in contact with CuO or Fe_2O_3 phase is established at each temperature. The equilibrium concentration at different temperatures are given in table I.

TABLE I Concentration of Fe in Cu ferrite on the boundaries of the reaction layer (expressed as mol% Fe_2O_3).

Boundary	800°C	850°C	900°C	950°C
$CuFe_2O_4/CuO$	50.0	50.0	50.0	51.8
$CuFe_2O_4/Fe_2O_3$	50.0	50.9	52.5	56.8

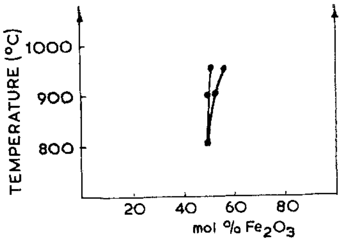

Figure 6 Boundary compositions of the reaction-layer for various temperatures.

On the basis of these values a graph showing the composition of the reaction layer as a function of temperature was constructed (fig. 6). This graph is actually a part of the CuO-Fe_2O_3 phase-diagram representing the range of spinel phase in the temperature interval investigated. The data of fig. 6 show that the boundary concentration of the reaction layer at its interphase boundary with CuO is not appreciably affected by temperature. Only in a specimen ferritised at 950°C is a slight increase of Fe_2O_3 concentration observed at this boundary. However, the composition of the reaction layer at its interphase boundary with Fe_2O_3 changes considerably with temperature. In the specimens fired at 950°C the content of Fe_2O_3 is as high as 56.8 mol%. The increased solubility of Fe_2O_3 in Cu ferrite at higher temperatures has been observed by other authors. Van Arkel [11] has shown that 30 mols of Cu ferrite can dissolve up to 40 mols of Fe_2O_3 at 1250°C. The results shown in fig. 6 are in good agreement with a previously published CuO/Fe_2O_3 phase diagram [12].

The results obtained show that the formation reaction of Cu ferrite proceeds identically to reactions taking place in the previously examined NiO/Fe_2O_3 and ZnO/Fe_2O_3 systems [13, 14]. In the very beginning of the reaction the equimolar ferrite is formed at the CuO/Fe_2O_3 interphase boundary. The ferrite formed establishes immediately separate interphase boundaries towards the CuO and Fe_2O_3 phases, at which further chemical reactions take place. Fe^{3+} and Cu^{2+} ions diffuse in opposite directions through the reaction layer and at the interphase boundaries react with starting oxides, forming ferrites with compositions corresponding to the left and right sides of the diagram in fig. 6, respectively. We have confirmed that the established concentration gradient is characterised by a linear variation in concentration of both elements across the reaction layer. As the concentration at the interphase boundaries is constant, an increase in thickness of the reaction layer causes a de-

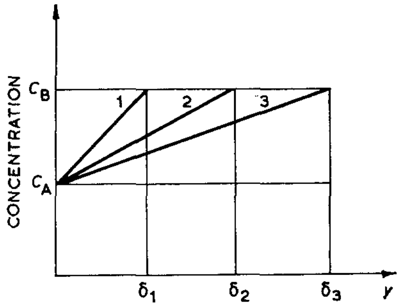

Figure 7 Change in concentration gradient of the reaction-layer as a function of thickness (Schematic).

crease in concentration gradient. This relation is schematically presented in fig. 7. The family of straight lines in fig. 7 (1, 2, 3 . . . *n*) may be expressed by the equation

$$c = c_A + k \cdot y \qquad (1)$$

where k = value of concentration gradient along the layer, given by the equation

$$k = \frac{c_B - c_A}{\delta} \qquad (2)$$

In equation 2, $(c_B - c_A)$ = difference in concentrations at interphase boundaries of the reaction layer, which is a constant for a given temperature and δ is the reaction layer thickness.

By combining equations 1 and 2, the equation

$$c = c_A + \frac{c_B - c_A}{\delta} \cdot y \qquad (3)$$

is obtained.

The equation 3 may be applied only if the condition $0 < y < \delta$ is satisfied.

Our results show that the layer thickness increases as the reaction of ferrite formation proceeds. The ferrite composition continuously changes with time at each point, so that the resulting layer exhibits a continuous transition of composition going from one boundary to the other. Accordingly, diffusion of Cu^{2+} and Fe^{3+} through the reaction layer takes place in a concentration gradient; the magnitude of this gradient affects the rate of these diffusion processes and, consequently, the rate of Cu-ferrite formation.

The formation of a solid solution of Fe_2O_3 in the spinel phase causes the formation of cation vacancies in both octahedral and tetrahedral positions of the spinel lattice. This considerable increase in the number of vacancies also accelerates the diffusion, i.e. the rate of spinel formation. We must point out that for electroneutrality to be maintained in an immobile anionic lattice, the migration of $3Cu^{2+}$ in one direction must cause the diffusion of $2Fe^{3+}$ in the other. Based on this fact Wagner [15] has developed his well-known hypothesis on the mechanism of ferrite formation, which necessitates a three times faster increase in the reaction-layer thickness at the Fe_2O_3 boundary than at CuO interphase boundary, in relation to the original CuO/Fe_2O_3 boundary. However, the results presented here, together with previously published data on Ni and Zn ferrites [13, 14] suggest that, due to the formation of a continuous series of ferrite solid solutions, the proposed ratio of reaction rates does not hold. Further, because of the formation of solid solutions Fe_2O_3 would disappear much earlier than CuO, in case equal amounts of CuO and Fe_2O_3 were provided for reaction. Any effort to study the reaction by following the disappearance of initial components or the formation of reaction products might result in a misleading interpretation of the reaction kinetics. This is particularly true if the magnetic properties were used to study the reaction kinetics, in which case the formation of a pure $CuO\text{-}Fe_2O_3$ is assumed. However, it is clear that the formation of a series of solid solutions would cause the magnetic properties of the reaction product to be very much different from that of pure $CuO\text{-}Fe_2O_3$.

The kinetics of spinel formation was followed by measuring the thickness of the reaction product as a function of time and temperature of ferritisation. A plot of layer thickness versus time at various temperatures gives a straight line in a log-log diagram (fig. 8). From this plot it may be

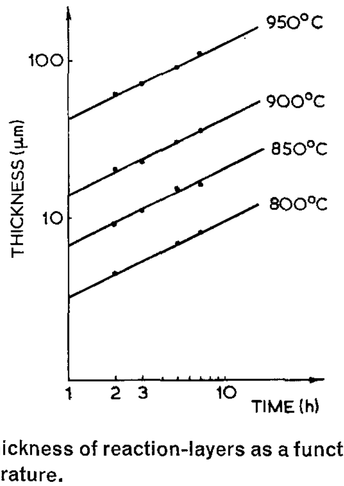

Figure 8 Thickness of reaction-layers as a function of time and temperature.

concluded that the thickness of the reaction layer increases according to the equation

$$x = (k \, . \, t)^n \qquad (4)$$

where x = reaction layer thickness, k = rate constant of layer thickening for a given temperature, t = time, and n = time exponent.

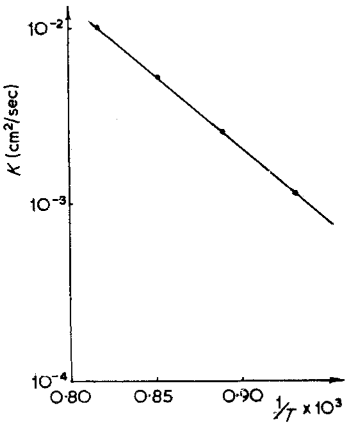

Figure 9 Rate-constant for thickening of the reaction-layer as a function of time.

The time exponent is constant at all temperatures, i.e. 0.5. Temperature dependence of the rate constant is given in fig. 9. and being rectilinear, follows the Arrhenius equation

$$k = k_0 \times e^{-Q/RT} \qquad (5)$$

A value of 75000 cal/mol was obtained for the energy of activation and 5.5×10^4 cm²/sec for the pre-exponential factor so that the law of Cu ferrite reaction layer growth may be expressed by the equation

$$x^2 = 5.5 \times 10^4 \, . \, \mathrm{e}^{-75\,000/RT} \, . \, t \qquad (6)$$

The square dependence on thickness obtained here confirms our previous assumption that the reaction proceeds by diffusion of Cu and Fe through the reaction layer. A comparison of activation energy of the reaction studied here with that for the diffusion of Cu and Fe in homogeneous stoichiometric ferrite would not provide an answer to the question, which of the two processes is the controlling one. (Besides, the data on the activation energies for Cu and Fe diffusion in ferrite are not, at present, available in the literature.) The results mentioned above, i.e. the formation of a continuous series of solid solutions instead of a homogeneous reaction layer, indicate that the diffusion of Cu and Fe in the reaction layer and pure ferrite may occur under considerably different conditions. For these reasons, we are unable to offer, at the present time, a theoretical explanation for the value of the activation energy governing Cu-ferrite formation.

The appearance of cavities at CuO, but not at Fe_2O_3 interphase boundary (probably responsible for the loss of many unreacted CuO grains) may be taken to indicate that Cu^{2+} diffuses faster through the reaction layer than does Fe^{3+}. However, this assumption cannot be presently proved, owing to the lack of ferrite self-diffusion coefficients.

4. Conclusion

The study of the Cu-ferrite formation reaction in 800 to 950°C temperature interval has shown that the ferrite formed is not of a constant composition. Two equilibrium compositions, one approximately corresponding to the equimolar stoichiometric Cu-ferrite, and the other reacher in Fe_2O_3, were established at CuO and Fe_2O_3 interphase boundaries, respectively. Between these two limiting values, a continuous series of solid solutions is formed.

The equilibrium concentration of Fe_2O_3 in ferrite at its boundary towards Fe_2O_3 increases with temperature. The reaction of Cu-ferrite formation consists of the two processes: chemical reactions at the interphase boundaries and Cu and Fe diffusion through the reaction layer having a concentration gradient. Thickening of the Cu ferrite layer may be expressed by equation 6.

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