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KINETICS AND MECHANISM OF COPPER FERRITE FORMATION

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ABSTRACT

The kinetics and mechanism of copper ferrite formation were investigated at different temperatures (up to 1100°C). A new method was applied to determine the reaction kinetics and its activation energy from DTA curves The formation of such a ferrite in the range 1010—1090°C seems to obey the equation of a phase boundary reaction with cylindrical symmetry $[1-(1-\alpha)^{1/2}=kt]$, where its activation energy amounts to 361 kcal mole^{-1} The reaction extent was also followed by means of chemical and X-ray diffraction analyses. The dissolution of cupric or ferric oxides, as excess in the formed ferrite, was found to be possible, but they separated on cooling. Under oxidizing atmospheres, and at temperatures $\leqslant$1100°C, $Cu_2O \cdot Fe_2O_3$ or $Cu_2O \cdot Fe_3O_4$ compounds are unstable.

INTRODUCTION

Copper ferrites are usually formed during the roasting processes of copper sulphide ores contaminated with pyrite. They also exist in both copper mattes and slags during the smelting process [1], but mainly in the form of cuprous ferrite. The economic importance of extracting copper from the slags containing copper ferrites [2] provides incentive to study the kinetics of such ferrite formation.

Some authors prepared copper ferrite at 500°C [3] and in the range 600—750°C [4,5], while others [6—8] considered that stable ferrite can only be produced after several hours sintering at 1000°C. Kushima and Amanuma [7] found that the formed ferrite can dissolve either ferric of cupric oxides in amounts exceeding the equimolecular ratio for temperatures higher than 1100 and 1150°C, respectively. Gadalla and others [9,10] prepared an extra pure copper ferrite by repeated heating of a 1 : 1 oxide mixture at 1050°C under fully oxidizing conditions. They also found that heating at temperatures higher than 1077°C leads to the production of $Cu_2O \cdot Fe_3O_4$ (which is an oxygen deficient compound), contradicting the results given by others [7,11,12] who suggested the identified phase $Cu_2O \cdot Fe_2O_3$ in this temperature range.

The present investigation comprises a study on the preparation of synthetic copper ferrite and the mechanism of its formation. This work is an extension of a previous one [13] in which the kinetics and mechanism of zinc ferrite formation were studied. The favourable temperature for copper ferrite formation was investigated on the basis of differential thermal and X-ray analyses, which aid in clarifying the discrepancies regarding the formed compounds and throw light on the mechanism of leaching processes [14].

EXPERIMENTAL

Materials

Pure cupric oxide was heated in air at 650°C to remove any volatiles [10], whereas pure iron oxide was prepared by precipitation and ignition methods [13].

Apparatus and technique

All are described in a previous publication [13].

RESULTS AND DISCUSSION

Chemical analysis

Using an equimolecular mixture of Fe_2O_3 and CuO analysis of samples sintered for 300 min at different temperatures (Table 1) shows that increasing the sintering temperature leads to a considerable decrease in the amount of CuO remaining unreacted. This amount is unchanged up to 600°C and cannot be identified beyond 1100°C where the reaction is complete and copper ferrite is formed.

X-Ray analysis

The X-ray diffraction analyses of the reaction products are shown in Fig. 1. The results are in agreement with those of chemical analysis. However, at 1000°C, the patterns of both Fe_2O_3 and CuO cannot be easily detected, where they could be dissolved as solid solutions in the formed ferrite. This achievement was also considered by Gadalla and White [10] who detected a series of solid solutions at this temperature. The compound $Cu_2O \cdot Fe_2O_3$ is also not identified, as established by some authors [7,12], where the only possibility of its formation is in reducing atmospheres [15].

DTA studies

An equimolecular mixture of CuO and Fe_2O_3 was thermally analyzed using a heating rate of 2.5°C min^{-1} (Fig. 2). Curve A shows that the reaction seems to start at 780°C at a very slow rate, and extends up to 1010°C. This may indicate that copper ferrite is formed with very small amounts at these relatively low temperatures, despite the slow heating rates. This achievement agrees with the results of chemical analysis, as well as those given by Saull et

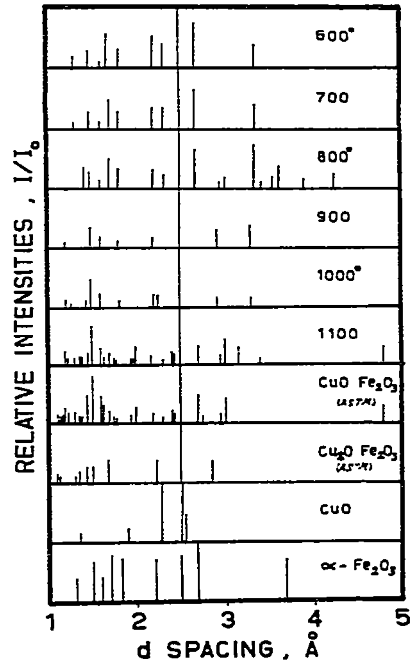
TABLE 1

Analysis of samples sintered for 300 min at different temperatures

Sintering temperature (°C)	600	700	800	900	1000	1100
Amount of CuO unreacted (%)	100	96	84	36	12	0

al. [16] who succeeded in preparing copper ferrite at 780° C, where only a yield of 75% was obtained after 48 h heating. The main endothermic peak displayed at 1010—1090° C is very sharp with a maximum at 1045° C, which indicates the vigorous rate of this reaction. Although the reaction seems to be accomplished at 1090° C, recrystallization of the formed ferrite may take place as depicted from the small peak displayed just beyond that temperature. Melting of the formed ferrite starts at 1115° C, as may be explained from the sharp drop in the DTA curve at this temperature. This result is in agreement with that given by Gadalla and White [10].

It is found that increasing the CuO content in the oxide mixture gives nearly the same DTA curve (Fig. 2 B and C) as that of the equimolecular ratio, i.e. it starts at 780° C and ends at 1100° C, with a slow reaction rate in



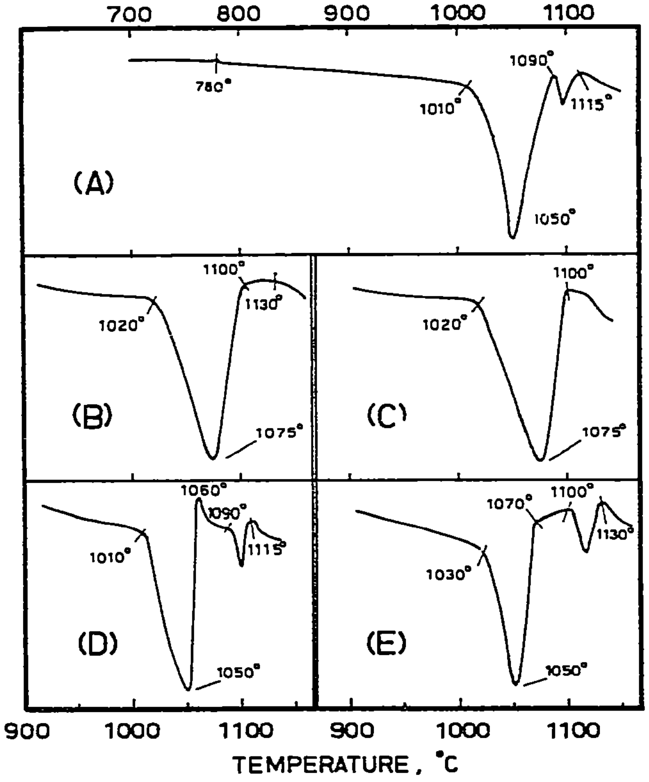


Fig. 1. X-Ray Debyograms of copper ferrite prepared at different sintering temperatures. The ASTM patterns of the starting materials and copper ferrite are included.

Fig. 2. The DTA curves of mixtures of CuO and Fe_2O_3 having the following molar ratios: A, 1 : 1; B, 1.5 : 1; C, 2 : 1; D, 1 : 1.5; E, 1 : 2.

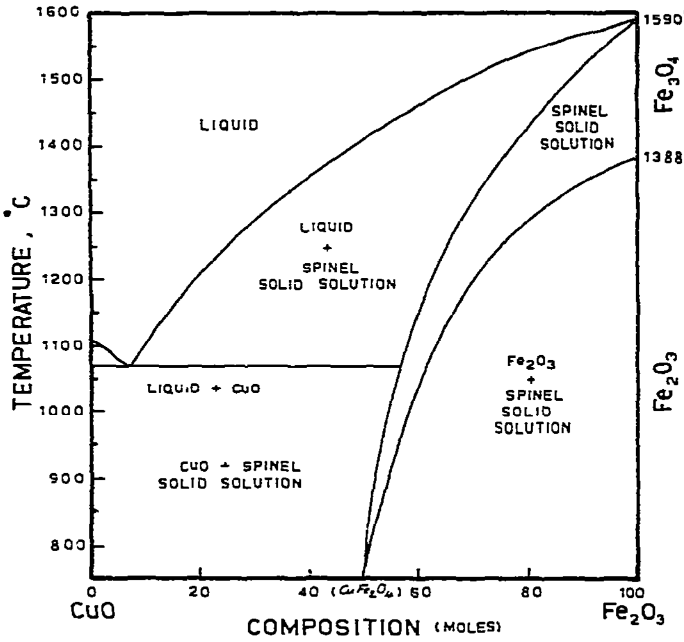


Fig 3 Phase diagram of CuO and Fe_2O_3 (molar basis).

the 780—1020°C region. It is noticed that the small peak following the sharp one is not detected, because the formed ferrite which melts at 1100°C dissolves the excess CuO. Also, the main endothermic peak becomes broader and its maximum is obtained at 1075°C (25°C higher).

On the other hand, on using mixtures containing excess Fe_2O_3, more sharp endothermic peaks are detected (Fig. 2D, E), where their maxima occur at 1050°C (as that of the equimolecular ratio). This sharp peak is also proceeded by a shallow slope starting at 780°C and followed by another endothermic peak in the range 1090—1130°C. The latter peak is shifted towards higher temperatures at an oxide ratio as high as 1 : 2 (curve E). This peak may be considered as phase transformation of the excess Fe_2O_3 to Fe_3O_4, where the latter form can increase the melting point of the formed ferrite and consequently a solid solution of $CuO \cdot Fe_2O_3$ and Fe_3O_4 might be obtained. This assumption is based on the phase diagrams established by Gadalla and White [10] (Fig. 3).

Mechanism of copper ferrite formation

This mechanism is rather more complicated than that of zinc ferrite formation [13]. As depicted by the chemical analysis and the DTA results, the reaction proceeds at two temperature ranges (780—1010°C and 1010—1090°C) with two different rates; the former is relatively slow (within 230°C) and covers 31% of the reaction extent on applying a low heating rate (2.5°C min^{-1}). The second rate is markedly very rapid and accomplished within 80°C to achieve 100% ferrite formation. This may indicate that the reaction can proceed at a temperature as low as 780°C, but several days are needed. Even so, it is necessary to sinter the pressed samples at 1000° C for 5 h in order to produce 88% copper ferrite. The incomplete formation of copper ferrite at this sintering temperature was proved by previous authors [6,8]. The vigorous reaction rate can only be achieved at temperatures $<1010°$C. This abrupt change in the reaction rate can be attributed to the partial fusion of CuO which increases its mobility and reactivity with Fe_2O_3. Accordingly, the reaction can be accomplished within 1 h at 1100° C.

The probable kinetic equation which controls the reaction rate is difficult to determine below 1010°C because of the very slow reaction rate and its low extent. In addition, the slow reaction obtained below 1010°C is overlapped by the fast endothermic one, where the end limit of the first reaction is not well defined. Therefore, in this investigation, the reaction kinetics are devoted to the extent of reaction at temperatures $>1010°$C (the well-defined DTA peak). The calculations were carried out with the aid of some recommendations [13,17—20] applying the following steps:

(i) the area surrounded by the sharp DTA peak on one side and its baseline on the other was measured by a planimeter and considered as unity, resembling the complete reaction extent;

(ii) this area was divided into small batches by parallel lines perpendicular to the temperature axis (5° in succession), and the reaction extent (fraction α) at each respective temperature was determined as the measured area ratio;

(iii) on plotting the fraction α vs. its respective absolute temperature, the curve shown in Fig. 4 was obtained which is similar to a conventional TGA curve;

(iv) applying the different kinetic equations for a solid state reaction

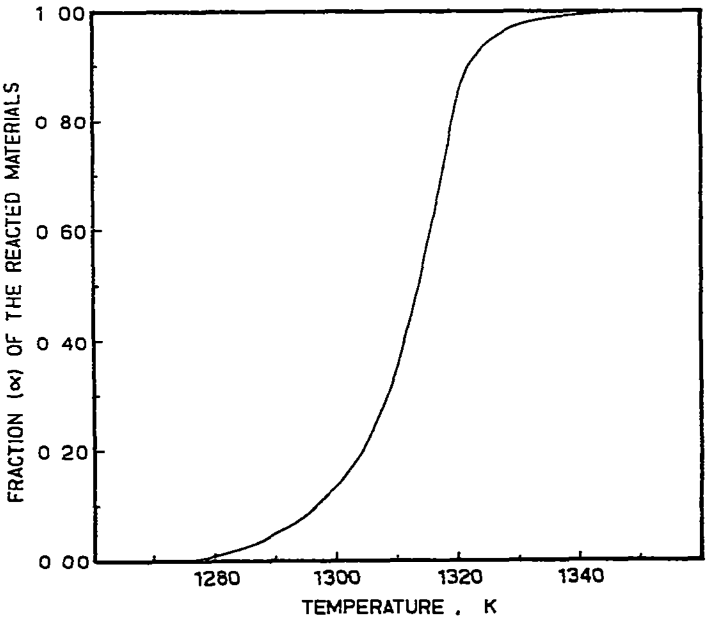


Fig. 4. The relationship between the fraction, α, of materials reacted and temperature for copper ferrite formation.

TABLE 2

The kinetic equations applied for solid state reactions [20]

Function	Equation	Rate controlling process
D_1	$\alpha^2 = kt$	One-dimensional diffusion.
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	Two-dimensional diffusion, cylindrical symmetry.
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation.
D_4	$(1-2/3\alpha)-(1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling—Braunshtein equation.
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle.
A_2	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation, Avrami equation I.
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation, Avrami equation II.
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundry reaction, cylindrical symmetry.
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundry reaction, spherical symmetry.

(Table 2) and the method of calculation recommended by Šatava [20] for TGA results, the most probable kinetic equation is that which gives a straight line on the log g(α) vs. $1/T$ plot (Fig. 5).

It is seen from Fig. 5 that the function R_2 "phase boundry reaction,

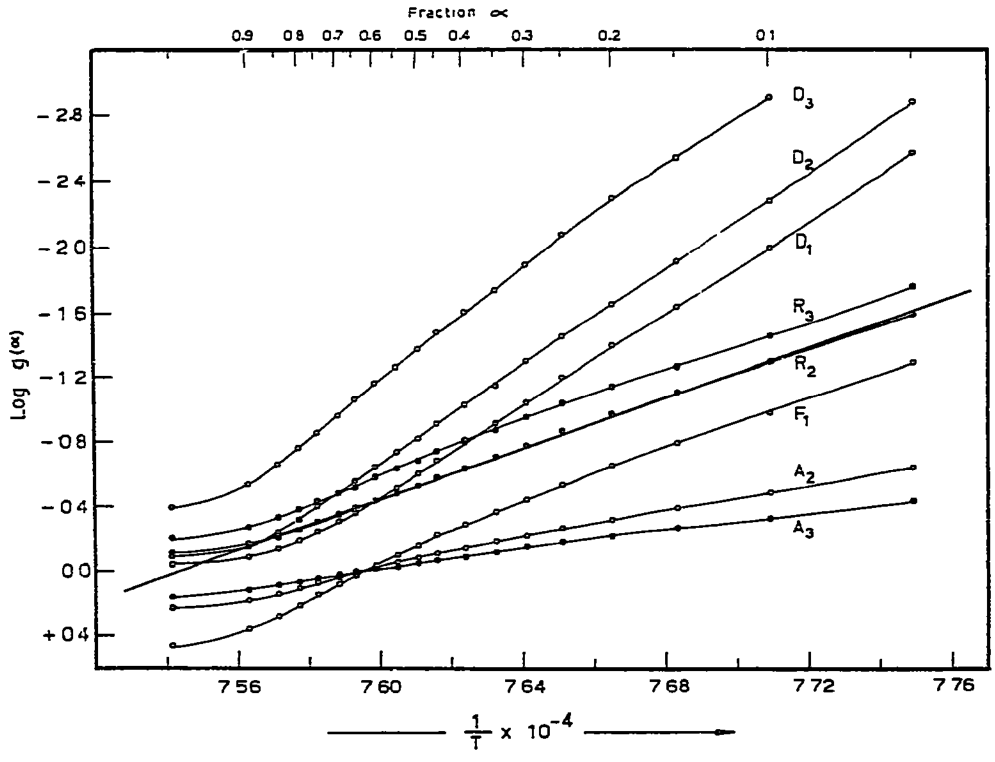


Fig. 5. Plot of log g(α) vs. $1/T$ for the formation of copper ferrite, applying the various functions of a solid state reaction.

cylindrical symmetry" is the only applicable equation for copper ferrite formation (especially in the temperature range in which the reaction proceeds vigorously). This function gives a satisfactory straight line on the log g(α) vs. $1/T$ plot, where its slope amounts to -7.86×10^4 d log g(α)/$d1/T$. The function R_2: $1 - (1 - \alpha)^{1/2} = kt$.

Using the calculation method suggested by Šatava [20], the above-mentioned slope value predicts an activation energy of 361 kcal mole^{-1}. It should be noted that this value is relatively too high in comparison with those given for zinc ferrite formation [13,21,22].

One may conclude that the nucleation process during the formation of copper ferrite is relatively unaffected by increasing the amount of CuO in the oxide mixture compared with the 1 : 1 ratio, where similar DTA peaks are obtained. The excess of CuO only affects the melting of the formed ferrite as it starts 15°C earlier, without showing the peak of recrystallization. However, the excess of Fe_2O_3 brings about a lowering of the DTA peak maximum by 20—30°C. This is due to the formation of spinel and γ-Fe_2O_3 solid solution in the temperature range 1050—1070°C (Fig. 3). The formation of the compound $Cu_2O \cdot Fe_3O_4$ may exist at higher temperatures, in accordance with some investigators [9,12], where it is represented by the sharp peak appearing in the temperature ranges 1090—1115°C and 1100—1130°C on using oxide mixture ratios 1 : 1.5 and 1 : 2 of CuO : Fe_2O_3, respectively (Fig. 2). The formation of such a compound cannot be investigated by X-ray analysis (Fig. 6) where it is re-oxidized when cooled to room

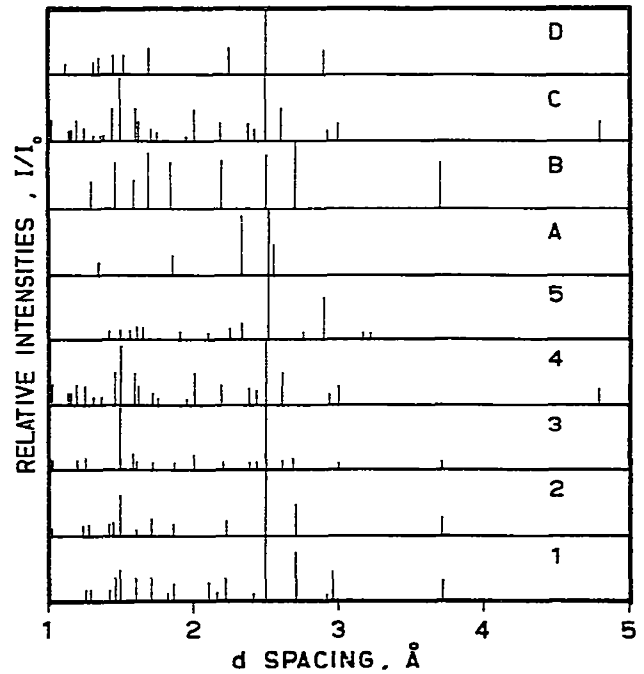


Fig. 6. X-Ray Debyograms of copper ferrite prepared at 1100°C for 300 min, using different CuO . Fe_2O_3 molar ratios. 1, 1 : 3; 2, 1 : 2; 3, 1 : 1.6; 4, 1 : 1; 5, 2 : 1. The X-ray patterns, taken from the ASTM cards, are A, CuO; B, Fe_2O_3; C, $CuO \cdot Fe_2O_3$; D, $Cu_2O \cdot Fe_2O_3$.

temperature. The decomposition of CuO to Cu_2O and Fe_2O_3 to Fe_3O_4 is well known [23], where it depends on the partial pressure of oxygen in the reaction system [9,10].

Finally, one may consider that there is no evidence of the formation of the compound $CuO \cdot 2\,Fe_2O_3$ already mentioned by some authors [7,23], where X-ray analysis of the product prepared from the 1 : 2 oxide mixture reveals the presence of copper ferrite admixed with Fe_2O_3. This is in good agreement with that investigated by Gadalla and others [9,10] who found that the excess Fe_2O_3 was separated in the form of Fe_2O_3 dissolved in the spinel solid solution, especially at temperatures >1100°C. On the other hand, the X-ray patterns of the oxide mixture containing excess CuO (2 : 1 molar ratio of CuO : Fe_2O_3) are more or less identical with that of the compound $Cu_2O \cdot Fe_2O_3$ (Fig. 6D and 5). Accordingly, one may assume that the reaction at this high temperature (where melting does occur) proceeds according to the following equation

$$CuO \cdot Fe_2O_3 + CuO \rightarrow Cu_2O \cdot Fe_2O_3 + 1/2O_2$$

Although this achievement confirms the conclusions found by some authors [7,11,12], it contradicts the results found by others [9,10] who assumed the formation of a mixture of CuO and $CuFe_2O_3$. The formation of the compound $Cu_2O \cdot Fe_2O_3$ was found to take place during copper smelting, as one of the main components [1], where it is admixed with copper matte in the slags obtained from copper smelters.

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