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Phase Relations in the Ferrite Region of the System Cu-Fe-O in Air*

(Received November 28, 1966)

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Abstract

Phase equilibria in the ferrite region of the system Cu-Fe-O have been investigated in air. Phases present in the system CuO-Fe₂O₃ are given as a function of temperature together with liquidus and solidus temperatures. The three most important features of the equilibria are as follows:

- (1) In the true binary system CuO-Fe₂O₃, single-phase copper ferrite deviates from the equimolar composition to Fe₂O₃ and is expressed by CuFe₂O₄ · (Fe₂O₃)_x, where $x = 0.160 \pm 0.005$.
- (2) The spinel solid solution including CuFe₅O₈ decomposes into two or three phases below $890 \pm 5^\circ\text{C}$ under the non-oxidizing conditions. The existence of the oxygen-deficient copper ferrite has been suggested.
- (3) Cuprous orthoferrite CuFeO₂ was determined to have both a stability minimum and maximum in air at 1015 ± 2 and $1090 \pm 5^\circ\text{C}$ respectively.

I. Introduction

The present investigation was undertaken to determine the phase relations in the ferrite region of the system Cu-Fe-O in air with particular emphasis on the spinel solid solution including CuFe₅O₈. Copper ferrite plays an important role in electronic engineering, but it is felt that the preparation of well-defined polycrystalline materials suffers from the lack of phase equilibria data. Cubic-tetragonal transition of copper ferrite has been studied extensively and is interpreted in terms of cupric ion concentration in the tetrahedral site of the spinel structure¹⁾. It must be mentioned, however, that little attention has been paid to the effect of compositional and phase changes during heat treatment. Another feature to be added in the system Cu-Fe-O is the existence of the compounds CuFeO₂ and CuFe₅O₈. (The existence of the latter is doubtful in view of the present findings, but it will be assumed to exist for preliminary discussions.) Although many publications are

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1) A. Ohnishi and T. Teranishi, "Crystal Distortion in Copper Ferrite-Chromite Series", J. Phys. Soc. Japan, **16** [11] 35-43 (1961).

found on these compounds²⁾, informations on the chemical and physical properties seem controversial especially on CuFe_5O_8 , again due to the lack of phase equilibria data. One of the evidence in favor of this point of view would be recognized by the wide variation in the published data on the ferromagnetic Curie temperatures of copper ferrite and CuFe_5O_8 .

Kushima and Amanuma³⁾ studied the system $\text{CuO-Fe}_2\text{O}_3$ in air, but their data are rather puzzling probably due to inadequate quenching of the specimens. Toropov and Borisenko⁴⁾ report a wide range of spinel solid solution in the system $\text{CuO-Fe}_2\text{O}_3$ at 1000°C in air. Earlier studies, together with above mentioned ones, seem to have paid little attention to the change in valence state of copper and iron ions. Schmahl and Müller⁵⁾ made an extensive study on the system Cu-Fe-O and determined the phase boundaries from the equilibrium oxygen pressure in the subsolidus region. Recently, Jefferson⁶⁾ studied the system $\text{CuFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ from magnetic and crystallographic points of view.

II. Experimental

(1) General Procedure

Phase equilibria were determined mainly by quenching method. Samples in a known Cu/Fe ratio were held at constant temperature in platinum crucible until equilibrium was reached among the gas, liquid, and crystalline phases, and quenched into water. Phase identification was accomplished by microscopic examination of polished quenched samples and X-ray diffraction using Fe-K_α radiation. Solidus and liquidus temperatures were determined by visual and microscopic examinations. Tips (3–4 mm large) were prepared from both melted specimens and sintered bodies of a known Cu/Fe ratio by crashing, the latter having been previously heated just below the solidus or liquidus temperature for a sufficiently long time (more than 5h) to attain the equilibrium. The tip was suspended in a vertical tube furnace with

- 2) (a) F. Bertaut and C. Delorme, "Study on Fe_5CuO_8 ", *Compt. rend.*, **236**, 74–6 (1953).
- (b) J. Théry and R. Collongues, "On the Properties of Cuprous Ferrite", *ibid.*, **254**, 685–7 (1962).
- (c) E. Kordes and E. Röttig, "New Mixed Oxides with the Spinel Structure", *Z. anorg. allgem. Chem.*, **264**, 34–47 (1951).
- 3) I. Kushima and T. Amanuma, "On the Constitution of Copper Ferrite", *Mem. Fac. Eng., Kyoto Univ.*, **17**, 290–310 (1955); *Chem. Abstr.*, **50**, 6993c (1956).
- 4) N. A. Toropov and A. I. Borisenko, "The System $\text{CuO-Fe}_2\text{O}_3$ ", *Doklady Acad. Nauk. SSSR*, **71**, 69–71 (1950); *Chem. Abstr.*, **44**, 6329f (1950).
- 5) N. G. Schmahl and F. Müller, "Equilibria in the System Copper-Iron-Oxygen", *Arch. Eisenhüttenw.*, **35** [6] 527–532 (1964).
- 6) C. F. Jefferson, "The Constitution of CuFe_5O_8 ", *J. appl. Phys.*, **36** [3] 1165–6 (1965).

a platinum boat. The furnace temperature was raised in increments of several degrees and held for 20–30 min. After each increment the sample was removed from the furnace and the tip was examined. The solidus and liquidus temperatures were determined as those at which a “rounding off” and “complete flattening” of the tip were first observed respectively. Although these temperatures were checked by microscopic examination of the quenched samples, high accuracy cannot always be claimed especially with solidus temperature. A special care was taken to prevent oxidation in the heat treatment and in the Curie temperature measurement. This was accomplished by using sintered bodies or evacuated capsules containing powdered specimens.

(2) Starting Materials

Starting materials having six representative compositions in the system $\text{CuO-Fe}_2\text{O}_3$ were prepared by usual ceramic techniques. Mixtures of reagent-grade oxides with a known Cu/Fe ratio were thoroughly mixed in an agate mortar and heated for 20 h at 800°C , and then ground to -200 mesh. Heating and regrinding were repeated several times finally followed by slow cooling. The absence of cuprous and/or ferrous ion was verified by KMnO_4 titration. Copper/iron ratios of these starting materials were determined by chemical analysis. Additional mixtures were prepared from the two neighboring compositions including CuO and Fe_2O_3 .

(3) Furnace and Temperature Control

The resistance winding of the vertical tube furnace employed in quenching was an 80 % platinum, 20 % rhodium alloy. Temperature constancy was maintained by means of a regulator connected to a Pt-13 % Rh · Pt thermocouple in the hot zone of the furnace. Actual temperatures were measured by a second thermocouple placed just below the platinum crucible containing samples. After reaching equilibrium, the furnace temperature could be held to within $\pm 2^\circ\text{C}$ in the 1300°C region.

III. Results and Discussion

Fig. 1 shows the phase diagram in the ferrite region of the system Cu-Fe-O constructed from the experimental data. The diagram in Fig. 1 consists of two parts, (A) and (B), with (A) showing the phases present as a function of temperature for the binary system $\text{CuO-Fe}_2\text{O}_3$ in air. Although it appears here as a binary system, it is actually an isobaric section through the ternary system Cu-Fe-O projected along the constant Cu/Fe lines. In Fig. 1 (B), phases present in the part of the composition diagram of the system Cu-Fe-O are given as a function of the solid composition. Thus, the temperatures at which the mixture of a given Cu/Fe ratio is stable in each phase field are readily known from Fig. 1 (A). The horizontal lines in Fig. 1 (A) denote the univariant reactions, since three condensed phases are in equilibrium under the constant oxygen pressure. Cupric oxide was found to react with spinel to form CuFeO_2 at $1015 \pm 2^\circ\text{C}$ by high temperature X-ray

diffraction, in good agreement with that given by Schmahl and Müller⁵⁾. X-ray diffraction revealed also that Cu_2O was absent during the reaction and that the reaction was virtually reversible. In addition, the mixture with Cu/Fe equal to 3/2 indicated an abrupt weight loss of 2.8 % at 1015°C. Cupric oxide was found unstable in air above $1028 \pm 2^\circ\text{C}$ by high temperature X-ray diffraction. This is comparable with 1026°C obtained with CuO ⁷⁾, suggesting that the oxygen potential

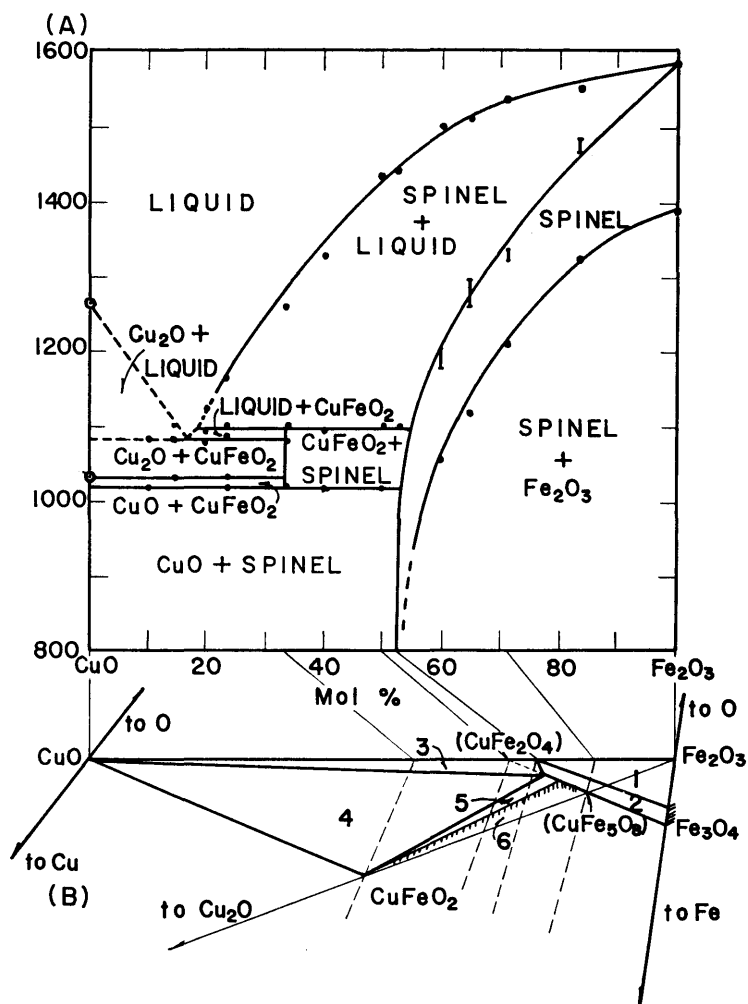


Fig. 1. Diagram Illustrating Phase Relations in the System $\text{CuO}-\text{Fe}_2\text{O}_3$ in Air.

----- : Constant Cu/Fe line

⊙ : by Roberts and Smyth (footnote 7)

1 : S + Fe_2O_3 , 2 : S, 3 : S + CuO , 4 : S + CuO + CuFeO_2 ,

5 : S + CuFeO_2 , 6 : S + Liq. (S : Spinel).

7) H. S. Roberts and F. H. Smyth, "The System Copper : Cupric Oxide : Oxygen", J. Am. Chem. Soc., 43, 1061-79 (1921).

of CuO is little affected by the existence of CuFeO₂. The eutectic temperature between Cu₂O and CuFeO₂ was at 1085±5°C. Although it might be in error as mentioned before, it may not be very far from 1080.2°C, the eutectic temperature between CuO and Cu₂O at the oxygen pressure of 402.3 mmHg⁷⁾. Cuprous ortho ferrite melted incongruently at about 1095±5°C. The liquid phase was supposed to contain more oxygen than solid phases, since the mixture falling at this Cu/Fe ratio indicated a pronounced weight gain (1.9 % of starting mixture) at about 1090°C.

Now, the phase changes of a typical mixture on the CuO-Fe₂O₃ join, e. g., 1>Cu/Fe>1/2 (initially CuO plus spinel) are illustrated. When heated at progressively increasing temperatures, total composition of the solid phases moves away from the CuO-Fe₂O₃ join along the constant Cu/Fe line. Within the two-phase field 3 in Fig. 1 (B), the spinel composition in equilibrium with CuO, which is known from the conjugate line connecting CuO and the total composition under consideration, becomes rich in iron separating CuO simultaneously. The amount of CuO increases gradually until 1015°C is reached, at which CuO reacts with spinel to form CuFeO₂. By phase rule, the composition of the spinel remains fixed during the reaction at 1015°C. Above 1015°C the spinel composition moves again toward Fe₃O₄ until the liquid phase appears.

In addition to the phase diagram presented in Fig. 1, essential features in the system Cu-Fe-O are as follows: First, it was found that the composition of single-phase copper ferrite on the CuO-Fe₂O₃ join contains excess amount of Fe₂O₃ over the equimolar composition, though exaggerated a little in Fig. 1 (B) for clarity. Several mixtures containing excess amounts of Fe₂O₃ over the equimolar composition (CuFe₂O₄) were heated at 900°C for 80 h, and then slow-cooled so that the low valent cations might be oxidized. Instead of two phases, spinel plus CuO or Fe₂O₃ as expected from Fig. 1, all the mixtures consisted of three phases, i. e., spinel, CuO and Fe₂O₃†. (This will be referred to and discussed later in this paper.) Then free CuO and free Fe₂O₃ were determined by chemical and X-ray diffraction analyses respectively, and the composition giving single-phase copper ferrite on the CuO-Fe₂O₃ join was estimated assuming that either of the oxides should vanish under the true equilibrium. Thus, it is predicted that the single-phase copper ferrite without low valent cations is given by CuFe₂O₄ · (Fe₂O₃)_x, where $x=0.160\pm 0.005$. This means that under the equilibrium, a starting composition of an equimolar mixture of CuO and Fe₂O₃ would consist of CuO in equilibrium with CuFe₂O₄ · (Fe₂O₃)_{0.16}. Judged from the various experimental observations, the width of the spinel field on the CuO-Fe₂O₃ join, if any, would be very narrow. An attempt to obtain another evidence in favor of this finding from the lattice constants has been unsuccessful.

† Considerable efforts were devoted to obtain CuO-free sample. In order to avoid possible dissociation, the mixtures were heated at 700°C in oxygen for 20 h. In spite of regrinding and heating repeated several times, the solid state reaction was found incomplete, and essentially the same results were observed.

Another feature to be mentioned is that the spinel solid solution could be divided into two based on the results of additional experiments, in which a number of sintered specimens † consisting of single-phase spinel solid solution with various Cu/Fe ratios were held at 850°C for 3 h followed by slow cooling, then, they were subjected to microscopic examination and X-ray diffraction as well as to Curie temperature measurement. For the composition to the left of the $\text{Cu}_2\text{O-Fe}_2\text{O}_3$ join, the phases present after the heat treatment were copper ferrite, Fe_2O_3 and CuFeO_2 , while for those to the right, Fe_3O_4 †† was detected instead of copper ferrite. It must be mentioned here that the copper ferrite obtained in this heat treatment was different from aforementioned one ($\text{CuFe}_2\text{O}_4 \cdot (\text{Fe}_2\text{O}_3)_{0.16}$), as distinguished by their Curie temperatures; 450 and 490°C respectively⁸⁾. Although the exact composition has not been determined, copper ferrite with lower Curie temperature was assumed to lie somewhere on the lower boundary of the spinel field in Fig. 1 (B). Probably, this may contain some oxygen deficiencies, since it could not be obtained by the same heat treatment under the oxidizing conditions.

It is well known^{2a)} that the compound CuFe_5O_8 is unstable at low temperatures even under the non-oxidizing conditions. The critical temperature above which it is stable was found $890 \pm 5^\circ\text{C}$. No significant change in the critical temperature was observed in both sides of the $\text{Cu}_2\text{O-Fe}_2\text{O}_3$ join. Although the existence of CuFe_5O_8 has been assumed in the preceding discussion, it must be stressed that no significance attaches to the formula CuFe_5O_8 . Strictly speaking, the composition having Cu/Fe equal to 1/5 has both a stability minimum and maximum in air at 1210 and 1350°C respectively.

In view of the present findings, the somewhat unusual fact that an additional phase CuO was present in mixtures containing excess amounts of Fe_2O_3 over the equimolar composition, might be interpreted as being due to the formation of CuO and Fe_2O_3 at different parts of the sample in slow cooling. Change of the spinel solid solution during the slow cooling in air is supposed to consist of the following two processes; decomposition of the spinel solid solution into oxygen-deficient copper ferrite, Fe_2O_3 and CuFeO_2 , and the oxidation of CuFeO_2 to form CuO and copper ferrite, thus resulting in the three phases. †††

IV. Summary

Phase equilibria have been studied in air and the phases present in the binary

† With sintered specimens, oxidation during heat treatment could be virtually prevented except at the surface layer.

†† This phase was identified by the characteristic Curie temperature, 575°C.

8) S. Sahara and T. Yamaguchi, "Effect of Oxygen Deficiency on the Phase Transition of Copper Ferrite", J. appl. Phys., 37 [8] 3324. (1966).

††† Although the oxidation of the oxygen-deficient copper ferrite must be taken into account, this would be not predominant in the present discussion.

system $\text{CuO-Fe}_2\text{O}_3$ are given as a function of the temperature. The temperatures of four univariant reactions in air were determined by quenching method and by high temperature X-ray diffraction.

It was shown that under the equilibrium, the simple ferrite (CuFe_2O_4) consists of two phases, CuO and $\text{CuFe}_2\text{O}_4 \cdot (\text{Fe}_2\text{O}_3)_{0.16}$. The spinel solid solution was studied and it was found that below $890 \pm 5^\circ\text{C}$ and under the non-oxidizing conditions, the spinel solid solution including CuFe_5O_8 decomposes into CuFeO_2 , Fe_2O_3 and either Fe_3O_4 or oxygen-deficient copper ferrite.

The data obtained in the present investigation complete the general picture of phase relations in the ferrite region of the system Cu-Fe-O in air, though detailed informations are required for the lattice defect consideration of copper ferrites.

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