Journal of Thermal Analysis, Vol. 3 (1971) 17–23

INVESTIGATION OF THE PHASE TRANSITION IN $Cu_{0.5}Fe_{2.5}O_4$ BY DTA

Z. ŠIMŠA and P. HOLBA

Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

(Received May 21, 1970)

The DTA curves of the quenched ferrites $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ displayed both an exothermic peak at 500—740° and an endothermic peak at about 1000° while slowly cooled samples showed only the high-temperature endothermic peak. It was confirmed by X-ray diffraction studies that the exothermic peak is due to the decomposition of the ferrite at these temperatures into hematite and delafossite. On the other hand, the endothermic peak was found to be caused by re-formation of the ferrite above 1000°. A tentative phase diagram of the ferrites $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ is presented.

Data on the existence and stability regions of the ferrite $Cu_{0.5}Fe_{2.5}O_4$ are rather controversial. In some papers [1–4], this ferrite is considered as a member of the solid solution series between magnetite, Fe_3O_4, and copper ferrite, $CuFe_2O_4$. In other papers [5–7] this ferrite is treated as a definite compound, $CuFe_5O_8$, possessing specific physical properties. Although some authors consider $Cu_{0.5}Fe_{2.5}O_4$ to be constituted primarily from Cu^{2+}, Fe^{2+} and Fe^{3+} ions [1, 2, 8] others claim that only Cu^{1+} and Fe^{3+} ions are present [3, 5–7].

Recently, by a simultaneous investigation of the electrical and magnetic properties [9] and by X-ray investigation [10], the distributions of cations and their valencies in the quenched samples of the ferrites $Cu_{0.52}Fe_{2.48}O_4$ were established. On heating samples to higher temperatures irreversible changes in the temperature dependences of electrical [8, 9] and magnetic [11] properties were observed. The anomalous changes were attributed to the decomposition of the ferrite into delafossite, $CuFeO_2$, and hematite, α-Fe_2O_3. This decomposition, originally proposed by Bertaut and Delorme [1], was later doubted by Gadalla and White [4], but was confirmed by Wiedersich et al. [12].

It seemed worth while to study the decomposition of the ferrite $Cu_{0.5}Fe_{2.5}O_4$ by means of DTA and X-ray diffraction methods in order to obtain new information on the phases and processes involved.

Experimental

Polycrystalline samples of the ferrite with a final chemical composition $Cu_{0.52}Fe_{2.48}O_{4+\gamma}$ were prepared from mixtures of pure CuO and Fe_2O_3 by the usual ceramic procedure. The first sintering at 800° in air for 20 hours was fol-

lowed after grinding and pressing into pellets by a second firing under the conditions shown in Table 1. After the firing the samples were quenched in water or quickly taken out of the furnace and cooled in air. With these samples the oxygen content expressed be means of the oxygen non-stoichiometry parameter γ was determined by a modification of Gorther's method [13, 14].

The differential thermal analysis of the polycrystalline samples was performed in static air by means of the apparatus described in [15]. The temperature was usually raised at a rate of 5–10°/min, but no substantial changes in DTA curves were observed with different heating rates. The apparatus permitted the sampler to be taken out of the furnace at any desired temperature and quenched in water. Phases in quenched samples were determined by the Debye–Scherrer powder technique using Fe K_α X-radiation. Some of the samples were also investigated with a metallographic microscope.

Results

Typical DTA curves for some of the samples of the ferrite $Cu_{0.52}Fe_{2.48}O_{4+\gamma}$ are represented in Fig. 1. On heating the quenched samples, exothermic peaks with maxima between 500–740° and endothermic peaks with maxima at 1000° are observed (see curve 1 in Fig. 1). The areas of both peaks are practically the same.

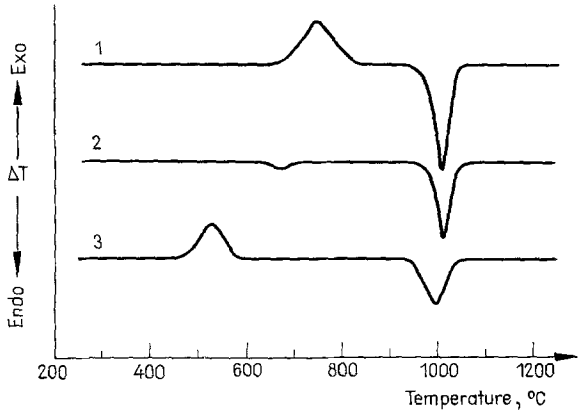

Fig. 1. DTA curves of the ferrite $Cu_{0.52}Fe_{2.48}O_4$. Curve 1: original sample No. 2 quenched from 1255°. Curve 2: sample slowly cooled from 1250°. Curve 3: sample quenched from 1050°

On the other hand, the slowly cooled ferrites or the ferrites quenched from the temperature region between the exothermic and the endothermic peaks (i.e. between approx. 500–1000°) display only an endothermic peak at 1000°

(see curve 2 in Fig. 1) and in some cases also a much smaller endothermic peak at 660°. (The origin of the endothermic peak at 660° is not fully understood. It might be due to the transition from the antiferromagnetic to the paramagnetic state of the precipitated hematite.) However, once the temperature of the ferrite is raised above 1000° and the ferrite is quenched to room temperature, the low

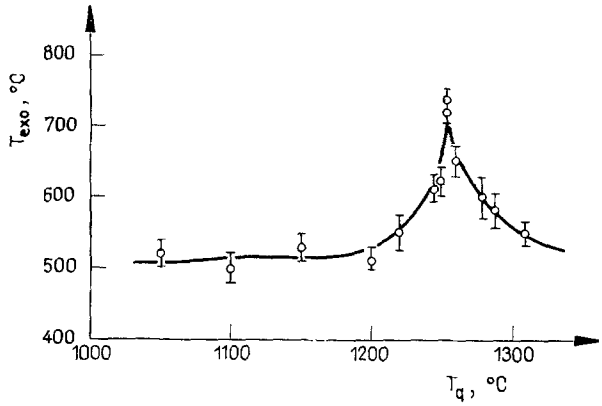

Fig. 2. Position of the low-temperature exothermic peak as a function of the quenching temperature T_q

temperature exothermic peak (at 500–740°) reappears on the DTA curve (see curve 3). The position of the maximum of the low-temperature exothermic peak is influenced by the quenching temperature and this dependence is represented in Fig. 2. Here the temperatures of the maxima of the exothermic peaks are plotted since they can be determined more accurately from DTA curves than can the temperatures of the beginnings of the peaks which are some 50–60° lower and which would correspond better to the real decomposition temperatures.

In contrast, the position of the endothermic peaks is found to be independent of the preparation conditions. The beginnings of the peaks are at 950± 20° and the maxima at 1000 ± 10°.

The above mentioned DTA investigation seemed to support the earlier suggested decomposition of the quenched ferrite $Cu_{0.5}Fe_{2.5}O_4$ into hematite and delafossite [1, 8, 9]. To confirm this decomposition scheme a series of X-ray diffractograms was taken of suitably heat-treated and quenched samples. In Fig. 3a is shown a schematic representation of the main diffraction lines of the original sample No. 2, together with its decomposition (Figs. 3b, 3c and 3d) into hematite (Fig. 3e) and delafossite (Fig. 3f). It should be noted that the X-ray patterns of our samples of quenched ferrite, hematite and delafossite are in full agreement with the ASTM data for these compounds.

From Fig. 3 it can be seen (and the photometry of the respective diffraction ines confirms it) that after 15 minutes of annealing at 730° approx. 60% of the

original spinel has decomposed. Similarly, annealing for 75 minutes and 22 hours respectively at the same temperature leaves less than 5% of the spinel phase unchanged.

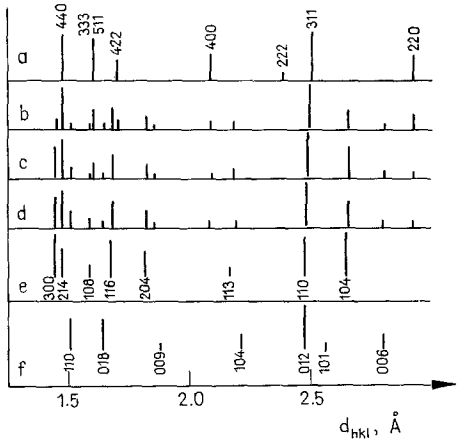

Fig. 3. Schematic representation of the main diffraction lines of *a)* original quenched sample No. 2, *b)* sample No. 2 after 15 minutes' heating at 730° in air, *c)* sample No. 2 after 75 minutes' heating at 730° in air, *d)* sample No. 2 after 22 hours' heating at 730° in air, *e)* hematite (commercial pure Fe_2O_3), *f)* delafossite (prepared from a mixture of CuO and Fe_2O_3 by firing for 65 hours at 1100° in argon, and quenched)

A metallographic examination of the polished and etched surfaces of the annealed samples revealed a lamellar structure (characteristic of a eutectoid decomposition in accordance with the recent results obtained by Yamaguchi and Shiraishi [16].

Discussion

DTA curves presented in Fig. 1, together with X-ray and metallographic examinations, confirm previous ideas on the decomposition of the ferrite $Cu_{0.5}Fe_{2.5}O_4$ [1, 9, 16]. In the samples quenched from high temperatures a metastable cubic spinel structure is retained. On heating this metastable ferrite to higher temperatures, the spinal starts to decompose;

$$2\,Cu_{0.5}Fe_{2.5}O_4 \text{ (spinel)} \rightleftarrows 2\,Fe_2O_3 \text{ (hematite)} + CuFeO_2 \text{ (delafossite)} \quad (1)$$

This process is accompanied (at 500–740°) by a release of heat which is indicated by an exothermic peak on the DTA curves. When the temperature is raised further, the two phases (hematite and delafossite) coexist until 950°. Here the opposit reaction (from right to left in Eq. (1)) begins which leads to the re-for-

mation of the ferrite $Cu_{0.5}Fe_{2.5}O_4$. This reaction, however, requires the absorption of heat causing an endothermic peak on the DTA curve. As the same substances play a part in both reactions the heat changes involved should be the same. The latter conclusion was confirmed by experiment.

In Fig. 4 is a tentative phase diagram of the ferrites studied which represents a join in the system Cu–Fe–O corresponding to the ratio Cu : Fe = 1 : 5. Above 1000° there are three regions: spinel + delafossite, spinel, and spinel + hematite, in agreement with the results of Bergstein [17]. Below 1000° a three-phase equilibrium region of spinel + delafossite + hematite exists. The presence of the three-phase region can be understood if one admits that the

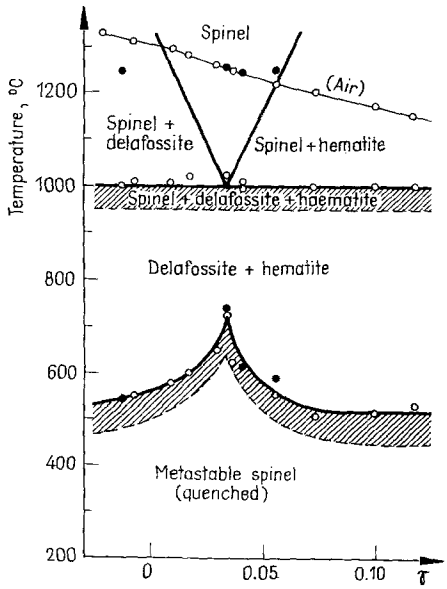

Fig. 4. Tentative phase diagram of the ferrites $Cu_{0.52}Fe_{2.48}O_{4+\gamma}$. The oxygen non stoichiometry parameter γ of our four samples (●) was found by chemical analysis (see Table 1) while the other values (○) were determined from the quenching temperature and the isobar (air) drawn in the diagram according to our data and in good agreement with [4]

invariant point of the eutectoid decomposition is shifted outside the join plane. In this case the decomposition (or recombination) in an isolated ternary system may occur in a certain temperature interval (causing a broad DTA peak). This latter conclusion is also supported by the decomposition curves given by Yamaguchi and Shiraishi [16] where the fact that the ferrite $Cu_{0.5}Fe_{2.5}O_4$ does not decompose even after several hours of heating at 980° can be explained on the same basis.

On further inspection of the phase relations in Fig. 4 we can see that at low temperatures a metastable single-phase cubic spinel is retained when samples

are quenched from high temperatures. The transition from the metastable phase into a two-phase region is accompanied by an exothermic peak on the DTA curves. This transition was found to be dependent on the quenching temperature (see Fig. 2). It seems to be reasonable to ascribe this dependence to the influence of the oxygen content in the samples. Taking into account Gadalla and White's results [4] of the equilibrium oxygen content as a function of the firing temperature in air for $Cu_{0.53}Fe_{2.47}O_{4+y}$ and also our data (see Table 1), we can transform the dependence as represented in Fig. 2 into a dependence of the position of the exothermic peaks as a function of the oxygen content γ. In Fig. 4 the lower hatched area (instead of a single boundary) represents the temperature intervals in which metastable spinel changes into the two phases.

Table 1

Firing conditions and oxygen content of the samples $Cu_{0.52}Fe_{2.48}O_{4+\gamma}$

Sample No.	Firing temp., °C	Firing atm., % O_2	Firing time, hours	γ
1	1250	2	20	−0.013
2	1255	21 (air)	22	+0.033
3	1245	21 (air)	14	+0.040
4	1250	100	18	+0.055

Further, it is expected that the oxygen content corresponding to the maximum temperature of the exothermic peak should be the same as that corresponding to the lowest temperature of the homogeneous spinel region. For other compositions the presence of traces of a non-spinel phase (delafossite or hematite) formed in samples during firing at high temperatures or during quenching promotes the decomposition of the metastable spinel phase, thus decreasing the transition temperatures.

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RÉSUMÉ — Les courbes d'ATD des ferrites trempées, de type $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ présentent un pic exothermique à 500—740° et un autre, endothermique, vers 1000°. Seul ce dernier pic apparaît dans le cas d'échantillons refroidis lentement. D'après les études par diffraction de rayons X, l'effet exothermique est dû à une décomposition de la ferrite en hématite et en delafossite. L'effet endothermique correspond à une nouvelle formation de ferrite au-dessus de 1000°. Essai pour représenter le diagramme de phase des ferrites $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$.

ZUSAMMENFASSUNG — Die DTA Kurven von schnell abgekühlten Ferriten der Zusammensetzung $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ enthielten die exothermische Spitze zwischen 500—740°, sowie die endothermische Spitze bei ungefähr 1000°, während langsam abgekühlte Proben nur die letztere aufwiesen. Die Röntgendiffraktionsanalyse zeigte, daß die exothermische Spitze durch Umlagerung des Ferrits in Hämatit und Delafossit, die endothermische Spitze hingegen durch die Neubildung des Ferrits bei ungefähr 1000° hervorgerufen wird. Es wurde ein Versuch zur Darstellung des Phasendiagramms der Ferrite des Typs $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ unternommen.

Резюме — На ДТА кривых быстро охлажденных ферритов $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ имеется два экзотермических пика при 500—740° и эндотермический пик около 1000°, в случае же медленно охлажденных образцов обнаружен только высокотемпературный эндотермический пик. Методом диффракции рентгеновских лучей подтверждено, что экзотермические пики проявляются в результате превращения феррита в хематит и делафоссит, которое происходит при вышесказанных температурах. Эндотермический пик указывает на образование нового вида феррита выше 1000°. Показана диаграмма фазы феррита $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$