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DILATOMETRIC INVESTIGATION OF THE PHASE TRANSITION IN COPPER FERRITE

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ABSTRACT

Thermal expansion measurements on quenched copper ferrites revealed that the kinetics of the cation rearrangements in the spinel phase depend on the oxygen stoichiometry, which is in turn depending on the quenching temperature. The tetragonal distortion of the spinel structure is primarily determined by the octahedral Cu^{2+}-concentration and only indirectly by oxidation of the sample. The tetragonal to cubic transition in copper ferrite is of a diffusionless type when the transition temperature is lower than 300°C; above that temperature the ionic rearrangement between the sublattices interferes with the transition.

INTRODUCTION

Copper ferrite, $CuFe_2O_4$, is reported to exist in two crystallographic forms, a tetragonally distorted and a cubic spinel structure, depending on the concentration of the distorting Jahn-Teller Cu^{2+}-ions present on the B-sites of the spinel structure[1,2]. The cation distribution, i.e., the concentration of octahedral Cu^{2+}-ions, can be changed by thermal treatments, which makes it possible to relate the crystal structure and the transformation temperature to the thermal history of the material. A number of authors[1–4] attributed the distribution changes to a simple thermal effect due to the mixing-entropy[5]. However, O'Bryan et al.[6] found indications, that the distribution is not determined merely by the quenching temperature, but is also influenced by the oxygen stoichiometry. Ohbayashi et al.[7] concluded from the identical properties of samples sintered at 1200°C, in 100 atm oxygen and at 500°C in air, that the normal inverse change of the cation distribution is only due to a change of the oxygen stoichiometry, i.e., the appearance of Cu^{+}-ions.

Another problem concerning copper ferrite often overlooked in the literature is that pure copper ferrite is difficult to prepare. Mexmain[8] found that pure $CuFe_2O_4$ can only be prepared by a special oxidizing sintering procedure below 850°C. However, the phases in the samples were checked with X-ray diffraction, which does not exclude the presence of a small amount of a second phase. Yamaguchi[9] found by careful microscopic investigation that "pure" $CuFe_2O_4$ contains CuO as a second phase and that the spinellic phase has the composition $Cu_{0.91}Fe_{2.09}O_{4\pm\gamma}$.

To investigate and elucidate the relation between oxidation, cation distribution and crystal structure of copper ferrite further, we measured the thermal dilatation of a number of samples $Cu_xFe_{3-x}O_{4\pm\gamma}$ ($0.84 \leq x \leq 1.0$) which were annealed at different temperatures before the measurements.

EXPERIMENTAL

A number of polycrystalline samples $Cu_xFe_{3-x}O_{4\pm\gamma}$, with $x = 0.84$; 0.88; 0.92; 0.96 and 1.0, were prepared from mixtures of CuO and Fe_2O_3. These mixtures were preheated for 4 h at 800°C in air, pressed in the form of bars and sintered 2 h at 920°C in 1 atm. oxygen. Rods (with dimensions $2 \times 2 \times 30$ mm) cut from these bars, were annealed in oxygen for 65 h at 700°C, then 24 h at 920°C and subsequently quenched to room temperature. The samples $x = 1.0$ contained traces of CuO, detectable with X-ray diffraction and the samples $x = 0.92$, 0.88 and 0.84 contained α-Fe_2O_3 as a second phase. The samples $x = 0.96$ showed only the spinel phase in the X-ray diagram. By microscopic investigations it was hard to detect a second phase in this material because of the microcrystalline and porous nature of the samples. After the annealing procedure at 920°C a number of samples was heated again at various temperatures in oxygen for 24 h and water quenched to room temperature. Chemical analysis indicated that the copper–iron ratios were correct within 1%. The thermal dilatation of these quenched specimens was measured from room temperature up to 700°C with a dilatometer described elsewhere[10]. The X-ray measurements were performed with Cu-Kα radiation on a Philips diffractometer.

RESULTS AND DISCUSSION

As was already recognized by Mexmain[8] the formation at 900°C of a pure spinel $CuFe_2O_4$ from CuO and Fe_2O_3 is hampered by a reduction during the beginning of the sinterprocess. At the first stage of the process a spinellic phase is formed with an excess of iron ($Cu_xFe_{3-x}O_4$, $x < 1$), which implies the presence of monovalent copper ions in the spinel phase and a loss of oxygen of the sample[8]. In the second stage of sintering, oxygen has to be dissolved in the sample. We observed that re-oxidation of the sample is very difficult if the sample has a high density. For this reason, it is not desirable to carry out the whole sinterprocess at 900–920°C because the densification of the samples to about 95% of the theoretical value is reached at that temperature within 5 h. Re-oxidation of dense samples takes place slowly, which was proved by the presence of large amounts of CuO in samples $x = 1.0$ sintered for 24 h at 920°C. After 2 h sintering in oxygen at 920°C, the density of the material was about 75%; if these samples were annealed in oxygen for 65 h at 700°C, and afterwards sintered again for 24 h at 920°C, hardly detectable traces of CuO were observed. For the compositions $0.84 \leq x \leq 1.0$ we applied now an oxidation at 700°C after the first stage of sintering, as indicated under "Experimental".

After preparation the samples $0.84 \leq x \leq 1.0$ were annealed at 620°C in 1 atm.

oxygen for 24 h, quenched to room temperature and examined by X-ray diffraction. The compositions 0.92, 0.88 and 0.84 consisted of α-Fe_2O_3 and a tetragonal spinel phase with c/a ratio of 1.043. The composition $x = 1.0$ contained a tetragonal spinel with the same c/a ratio of 1.043 and CuO as a second phase; for $x = 0.96$ no second phases could be detected. From these observations we concluded that the stability region of the spinel structure in oxygen at 620°C is very small and limited around the composition $Cu_{0.96}Fe_{2.04}O_4$, which deviates somewhat from the phase diagram by Yamaguchi[9]. We prepared the same compositions also by the wet chemical method according to[11] and found essentially the same results as in the case of the ceramic preparation. From these experiments one may expect that, if a single phase ferrite with composition $x = 0.96$ is heated at temperatures above 620°C, reduction takes place which decreases the Cu^{2+} concentration in the spinel structure and which supports the idea of Ohbayashi et al.[7], that the changes in cation distributions and cubic–tetragonal transition are due to the change in degree of oxidation.

To investigate this further we annealed rods of the prepared copper ferrites in oxygen at temperatures of 800, 740, 680 and 620°C for 24 h, followed by quenching. The thermal dilatation of these samples showed a remarkable behaviour. Between the compositions there were no large differences in thermal dilatation, which supports the idea that in all the samples a spinel phase with fixed composition $\sim Cu_{0.96}Fe_{2.04}O_{4\pm\gamma}$ was present in addition to small amounts of a second phase of CuO or Fe_2O_3, and that the anomalies in the thermal dilatation are only caused by the spinel phase. Because of the uncertainty in the exact Cu–Fe ratio of the spinel phase, the Fe^{2+} content of the sample (active oxygen content) is not a good measure for the cation vacancy concentration. For this reason no systematic analysis could be made of the cation vacancy concentration, although this concentration is very important for the kinetics of the rearrangement of the cations as will be discussed later on. The samples, which were quenched from temperatures below 800°C contained tetragonally distorted spinels with axial ratios increasing with decreasing quenching temperature.

In the dilatation curves (in Fig. 1 the results are given for the composition $x = 0.96$) an anomaly was observed in the temperature region 80–250°C, which can be attributed to the tetragonal→cubic transition; the transition temperature (T_{tr}) increases more or less linearly with the axial ratio, which was also observed in other Jahn-Teller deformed spinel systems[12]. In the temperature region 250–450°C, the dilatation behaviour is more complicated. The specimens quenched from 800°C showed a dent in the dilatation curve near 400°C, which broadened for the lower quenching temperature; for the temperature 620°C even a splitting is observed. This complex behaviour can be explained by the exchange of cations between the octahedral and tetrahedral sublattices: $Fe_{oct} + Cu_{tetr} \rightleftarrows Fe_{tetr} + Cu_{oct}$ and the influence of the oxidation degree of the samples on the kinetics of this cation exchange. If the samples were quenched after a dilatation measurement up to 450°C, the crystal structure turned out to be tetragonal with c/a value between 1.050 and 1.055, which is much higher than those of the materials before the measurements. The dilatation measurements were carried out in air with a heating rate of 2°C min^{-1}, which makes it

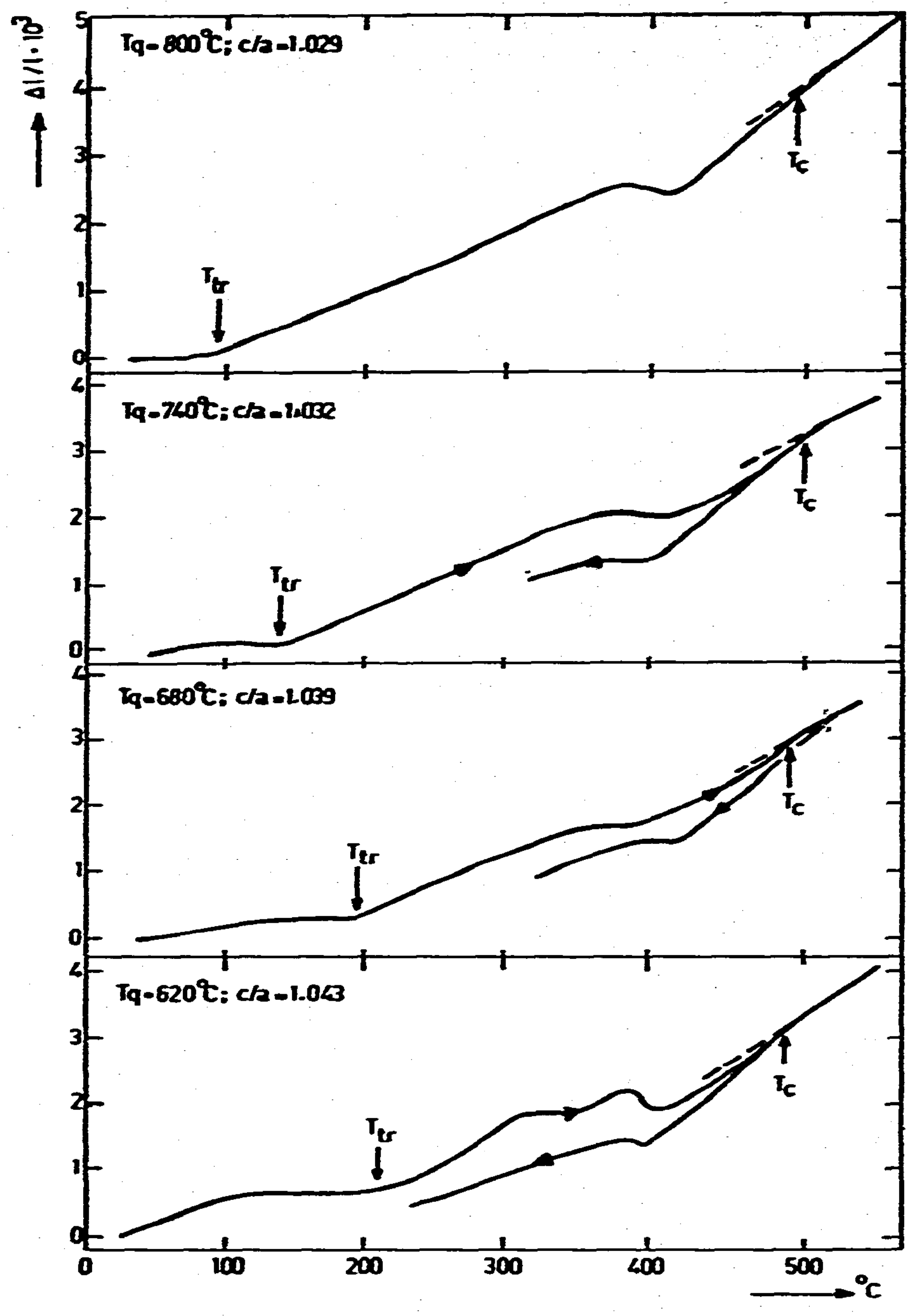

Fig. 1. Thermal expansion of quenched $Cu_{0.96}Fe_{2.04}O_4$ specimens. Quenching temperatures and axial ratios of the quenched samples are indicated in the figure.

improbable that the change of the *c/a* ratio is caused by oxidation. This change has to be due to the cation exchange between the sublattices.

It is known that in copper ferrites, the Cu^{2+} ions have a preference to be located on the octahedral sites at low temperatures, and that the cation distribution is temperature dependent[2]. Below ±300 °C the cation exchange is too slow to achieve the equilibrium distribution[12]. By quenching from temperatures above 300 °C, too many copper ions are frozen on tetrahedral sites; so there is a shortage of Cu^{2+} ions on octahedral sites which results in a lower value of the tetragonal axial ratio, or even a cubic structure is obtained. When increasing the temperature again, equilibrium will be retained in the temperature region where the cation exchange can go on. Consequently, for the specimens with low c/a values, i.e., low temperatures at which the transition from the tetragonal to the cubic structure appears, we will find again at somewhat higher temperatures a transition from the cubic to a tetragonal structure caused by the increased concentration of octahedral Cu^{2+} ions. At still higher temperatures the tetragonal structure will become cubic again because of the destruction of the alignment of the Jahn-Teller distorted $Cu^{2+}O_6^{2-}$ octahedra[13] and because of the gradual decrease of the octahedral Cu^{2+} concentration with increasing temperature. Whether all these effects can be observed separately by thermal expansion measurements depends on the temperature where the cation exchange becomes noticeable. The velocity of the cation exchange at a certain temperature is strongly enhanced by the presence of cation vacancies, which was proved by the authors by means of creep measurements[14] on magnesium ferrites[15]; with increasing vacancy concentration, the temperature region, where the cation exchange occurs, shifts to lower temperature.

The explanation of the complex dilatation curves above 250 °C is now based on the idea that with increasing quenching temperature, the number of cation vacancies decreases. For materials quenched from 800 °C, the exchange of cations starts at ±400 °C. This temperature coincides with the tetragonal–cubic transition of a material slowly cooled to room temperature[16], having the equilibrium cation distribution at the transition temperature. This gives the anomaly in the dilatation near 410 °C, which takes place in a temperature interval of about 25 °C. By decreasing the quenching temperature, the samples will be more oxidized and the migration will occur at lower temperatures. The result is that the anomaly in the thermal expansion is spread over a large temperature interval.

The broadening of the anomaly is indeed observed and for $T_q = 620$ °C even a separation of the two effects occurs. At 300 °C the cation exchange starts, and near 340 °C the equilibrium distribution of that temperature is retained. If the sample is quenched to room temperature after a dilatation measurement up to 340 °C, the c/a value turned out to be increased from 1.043 to 1.058. An estimation[12] of the tetragonal–cubic transition temperature from the c/a–T_{tr} relation gives ± 400 °C, which fits in with the observed phenomena. From these dilatation experiments it follows also that between 300 and 400 °C, the structure which changed at 210 °C from tetragonal into cubic, becomes again tetragonal as a consequence of the cation redistribution, and at ±410 °C the structure turns again into a cubic one.

Another problem, which was noted by O'Bryan et al.[6] concerns the different room temperature structures of samples quenched from different temperatures. The kinetics of the ion rearrangement are rapid above ±400 °C and one would expect that

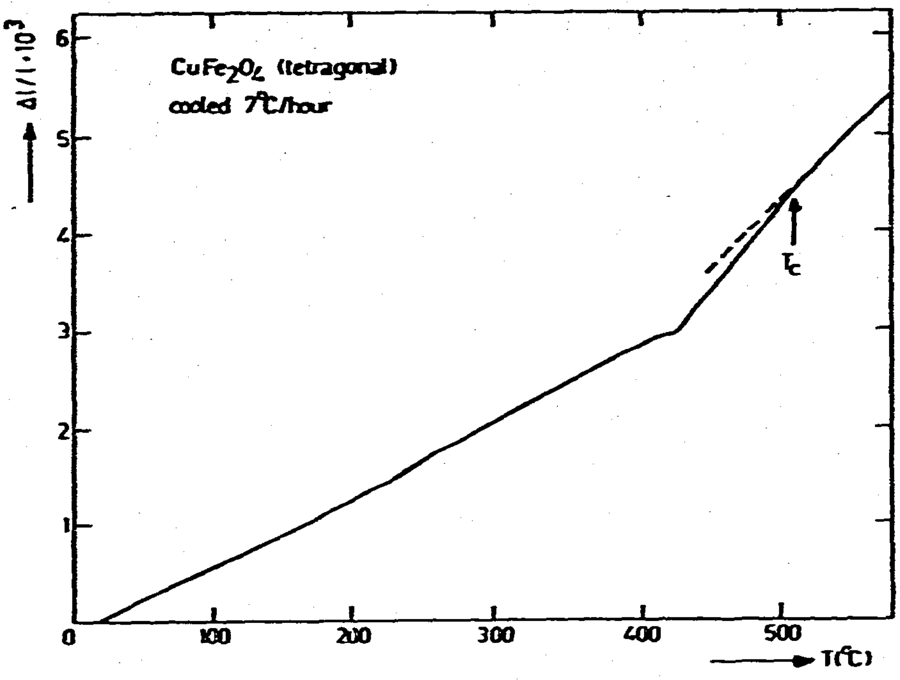

Fig. 2. Thermal expansion of a specimen $CuFe_2O_4$, sintered at 900 °C in 1 atm. O_2 and slowly cooled to room temperature.

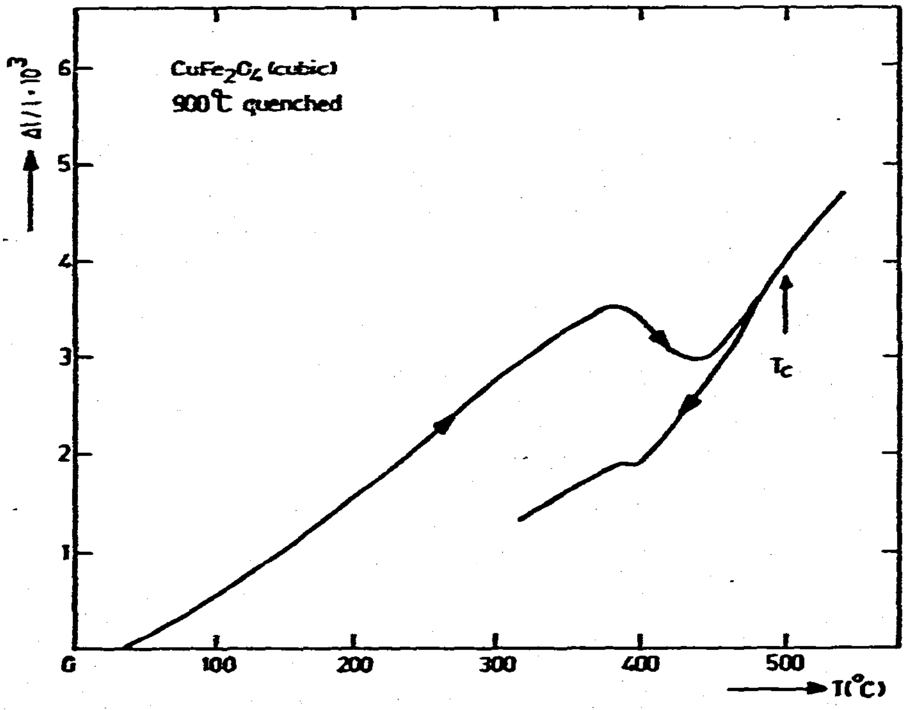

Fig. 3. Thermal expansion of a specimen $CuFe_2O_4$, sintered at 900 °C in 1 atm. O_2 and quenched to room temperature.

quenching from different temperatures would produce the same forms. However, if one takes into consideration the influence of the vacancy concentration upon the kinetics, the occurrence of different c/a values can be related to variation of the oxygen stoichiometry of the spinel phase. By quenching from various temperatures, the oxygen stoichiometry will change and as a consequence the temperature region where the velocity of the cation exchange becomes substantial shifts to lower values. This means that the equilibrium distribution of different temperatures will be preserved, depending on the vacancy concentration. The variation in c/a value for the specimens quenched from different temperatures supports now the idea that between 620 and 900°C a reduction of the spinel phase takes place with increasing temperature. However, this reduction has not the direct influence on the cation distribution and crystal structure as was stated in literature[7] but has an indirect influence by means of the kinetics of the cation rearrangements.

A further proof that between 300 and 400°C a cation rearrangement takes place without interference with the atmosphere was found in the thermal dilatation of two samples $x = 0.96$, measured in 1 atm. nitrogen; one sample was heated in pure oxygen and quenched from 900°C into water, the other slowly cooled in oxygen at a rate of 7°C h^{-1}. The measurements are presented in Figs. 2 and 3. The slowly cooled sample was tetragonal with $c/a = 1.058$ and showed the phase transition at 415°C, which is much higher than the usually reported[2,8] value of 360°C, although a value of 405°C is also reported[17]. The quenched sample was cubic and showed a large anomaly near 400°C. As the structure at room temperature is cubic, this anomaly cannot be due to the tetragonal → cubic transition. Further, if the thermal expansion of the quenched sample was also measured with decreasing temperature (see Fig. 3), about the same curve was obtained as for the slowly cooled sample and the structure changed into a tetragonal one with $c/a = 1.056$. Only the transition temperature was ca. 10°C lower. As oxidation during the measurement is ruled out by the N_2 atmosphere only the cation rearrangement can be the origin of the observed effects.

A final remark is that we observed in all the samples a small anomaly near 500°C, which is due to the ferrigmanetic → paramagnetic transition at the Curie temperature T_c.

CONCLUSIONS

(i) The dilatation measurements on quenched copper ferrites prove that the crystal structure is primarily determined by the octahedral Cu^{2+} concentration and only indirectly by the oxidation of the samples. The oxygen stoichiometry has a large influence on the kinetics of cation rearrangements in the spinel phase, which is the origin of the scattering of the experimental data reported in literature.

(ii) The compound $CuFe_2O_4$ which is reported in literature consists of a spinel phase $\sim Cu_{0.96}Fe_{2.04}O_{4\pm\gamma}$ with CuO as a second phase.

(iii) Between 300 and 400°C, the velocity of the cation exchange between the sublattices becomes substantial so that for the tetragonal → cubic transition in copper ferrites a diffusionless transition is only possible if the transition temperature is lower than 300°C, and above that temperature the ionic rearrangement between the sublattices will interfere with the transition.

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