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Polymorphic Transformation in Copper Ferrite and Manganite by Grinding

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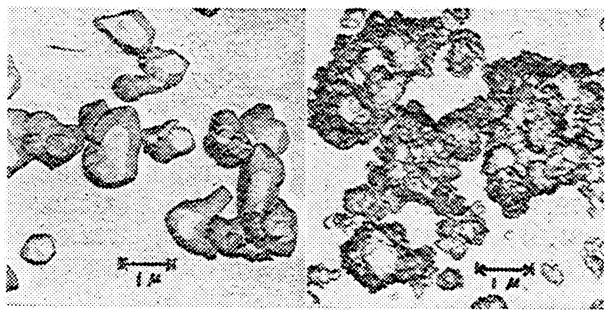
Many spinels such as $CuFe_2O_4$ and Mn_3O_4 have a tetragonally-distorted structure. The origin of the tetragonal distortion is the cooperative Jahn-Teller ordering of Cu^{2+} or Mn^{3+} at octahedral sites of the spinel structure. The tetragonality $\sigma=(c-a)/a$ is about 6% for $CuFe_2O_4$ and about 16% for Mn_3O_4 at room temperature. The variation of the tetragonality, σ, with the temperature has been studied by Ohnishi and his co-workers[1] for $CuFe_2O_4$ and by McMurdie and his co-worders[2] for Mn_3O_4. The transformation from the tetragonal to the cubic structure occurs at 360°C for $CuFe_2O_4$[1] and at 1170°C for Mn_3O_4.[2] The observation to be described here is that $CuFe_2O_4$ can be transformed from the tetragonal to the cubic structure by mechanical grinding at room temperature, while Mn_3O_4 can not be transformed by the same procedure.

$CuFe_2O_4$ was prepared from powders of CuO and Fe_2O_3 by heating at 930°C for 3 hr and by subsequent cooling to room temperature. Mn_3O_4 was prepared from powder of MnO_2 by heating at 1000°C for 3 hr and by subsequent quenching in water. These samples were ground in a ball mill with water for intervals up to 190 hr. The ground samples were examined by means of an electron microscope and by the X-ray diffraction method, using Mn-filtered Fe$K\alpha$ radiation.

The electron micrographs of the tetragonal $CuFe_2O_4$ particles before and after grinding are shown in Fig. 1. Before grinding, each particle is fairly rounded in shape and has a size between 0.5 and 1.0 μ. As the grinding progresses, the particles became smaller and irregular and the amount of small-size chipping increases.

X-Ray diffraction diagrams of the tetragonal $CuFe_2O_4$ at various stages of grinding are given in Fig. 2. As the grinding increases, the (311) peak of the cubic structure appears, in the intermediate-time grinding it is seen that both tetragonal and cubic structures existing, while in long-time grinding the tetragonal structure is almost entirely transformed into the cubic one. Such changes in diffraction lines by grinding are similar to those caused by heating.[3]



Original Ground for 190 hr

Fig. 1. Electron micrographs of $CuFe_2O_4$ particles before and after grinding.

X-Ray diffraction lines gradually broaden with grinding, as is shown in Fig. 2. Such a fact was more clearly seen in the experiment of grinding cubic $CuFe_2O_4$ (quenched from 930°C). The analysis of line-broadening using Hall's method[4] revealed that the strain increased and the crystallite size decreased with grinding. The increased strain might be described in terms of large dislocation density, whereas the small crystallite might be due to multiple twinning.[5] Therefore, it can be presumed as the main effect of polymorphic transformation that the cooperative Jahn-Teller ordering is destroyed by lattice imperfections, such as dislocation and stacking fault generated by grinding. As the another factor in the transformation, the change in the surface energy should also be considered. However, since there are no suitable methods for the measurement and theoretical calculation of the surface energy, it is beyond the scope of this discussion to consider the contribution of surface energy to the transformation.

On the other hand, Mn_3O_4 could not be transformed by grinding, even after 100 hrs' grinding. In the case of the transformation of Mn_3O_4, a greater amount of energy will be required, because Mn_3O_4 has a much higher transition temperature than $CuFe_2O_4$.

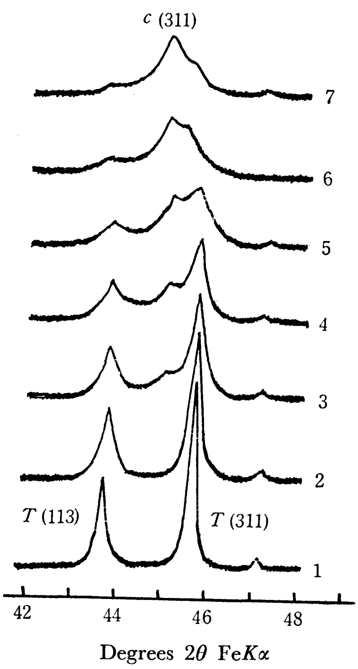


Fig. 2. X-ray diffraction diagrams of tetragonal $CuFe_2O_4$ after grinding.
Time of grinding 1: 0 hr, 2: 5 hr, 3: 20 hr, 4: 40 hr, 5: 70 hr, 6: 110 hr, 7: 190 hr.

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