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DISTRIBUTION OF MANGANESE IN MANGANESE FERRITE PARTICLES PREPARED BY AIR OXIDATION OF HYDROXIDE SUSPENSIONS

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The distribution of manganese in manganese ferrite particles prepared by the air oxidation of coprecipitated hydroxide suspensions has been investigated from the dissolution curves by using the core-model. The mole fraction of manganese increases gradually from the center to the surface of the particles and also increases abruptly near the particle surface.

The spinel type ferrites prepared by the air oxidation of suspensions of the coprecipitated hydroxide containing ferrous ions (wet method) are characterized by uniformity of particle size and shape. Moreover, high purity ferrites can be obtained if the purity of starting salts and water is taken into account.1) On the other hand, in the preparation of manganese ferrite by this method the inhomogeneity in the composition of each manganese ferrite particle is pointed out qualitatively from the following experimental results;2) (1) the particle size increases with increasing the oxidation temperatures and/or the alkali content, (2) during the course of oxidation the mean mole fraction of manganese in the ferrite particles increases with increasing the oxidation time. However, the details of manganese distribution in the radial direction in the ferrite particles have not been yet cleared.

In the present paper manganese ferrite has been prepared by the wet method and the distribution of manganese in the ferrite particles has been investigated quantitatively from the dissolution curves. The object of the present paper is in obtaining a fundamental knowledge to control cation distribution in the ferrite particles.

After manganese ferrites prepared under various conditions were confirmed as a single phase of spinel structure, the lattice parameter, the particle size and shape, and the specific surface area were measured. In the next place the cation distribution in the ferrite particles was obtained by dissolving them in hydrochloric acid at every predetermined period and determining the amount of iron and manganese with an atomic absorption spectrophotometer.

The conditions for preparing manganese ferrite are briefly described below and were determined by referring to those reported by Kiyama$^{3)}$ and Katsura et al.$^{4)}$

volume of reaction vessel : 2.5 dm^3
volume of suspension : 2.0 dm^3
initial pH : 11.0 to 12.0
concentration of [Fe^{2+}+Mn^{2+}] : 0.1 mol/dm^3
air flow rate : 3.0 dm^3/min
oxidation temperature : 70 to 80°C
oxidation time : 3 to 48.0 hr

The ferrites prepared under these conditions were filtered, washed with dil.H_2SO_4 (pH 4.0) and deionized water for several times. The product was stored in a vacuum dessicator at room temperature. The ferrite powder thus obtained was subjected to the electronmicroscopic observation, the measurement of surface area, X-ray diffractometry and the dissolution experiment.

The electronmicrographs showed that the mean particle size was about 0.1 μm. As the particle larger than 0.2 μm in diameter was scarecely observed in the micrographs, the particle size distribution seemed to be limited. The particle shape was round cube and could be regarded as sphere. The surface area measured with a surface area analyser model SA-1000 (Shibata Kagaku Kikai Co. Ltd.) ranged from 11.0 to 22.0 m^2/g depending on the preparation conditions and the initial composition. As the surface area of spherical particle of manganese ferrite with 0.1 μm diameter or cubic particle with 0.1 μm side is equal to 12.0 m^2/g, the ferrite particle obtained in this work would consist of the primary one without open pore. The lattice parameter was ranged from 8.423 to 8.443 Å by the preparation conditions even if the initial composition was stoichiometric (Fe/Mn=2/1) and the values were much smaller than that obtained by a solid state reaction (8.50 Å).$^{5)}$

The cation distribution in the ferrite particles from the dissolution experiment can be obtained in the following manner. As the particle size of the formed ferrite decreases during the course of dissolution, the reaction has been investigated by the core-model. The dissolution curves were found to fit the rate equation (1) in which the chemical reaction is a rate determining step.

$$1 - (1 - S)^{1/3} = k t \quad (1)$$

where S, t and k are mole fraction of dissolved ferrite, oxidation time and constant, respectively.[6)]

Fig.1 shows the relation between dissolution time and the amount of manganese or iron when 2.0 g of manganese ferrite was dissolved in 1M HCl at room temperature. The power regression curves are represented by solid lines. From the smoothed dissolution curves for each specimen, S values for each t are obtained by Eq.(1). When the concentration of acid is adequately chosen, t and $[1-(1-S)^{1/3}]$ show a good linear relationship up to S=0.4.

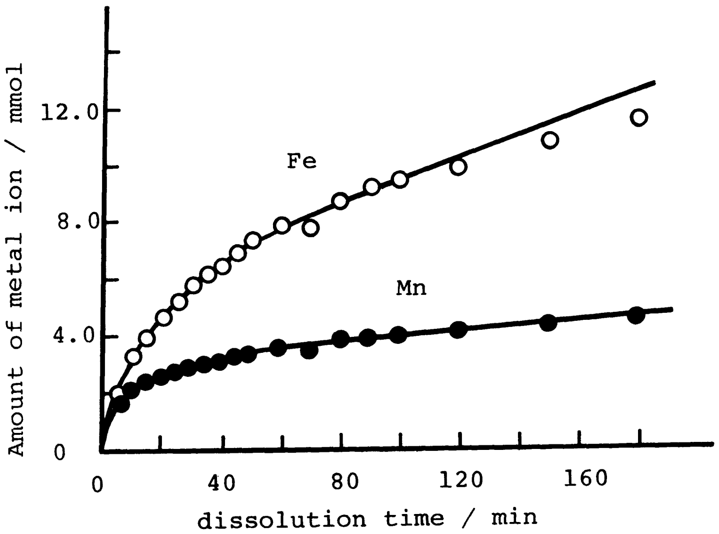

Fig.1 Dissolution behavior of manganese ferrite
Weight of sample: 2.00 g
Acid used: 1M HCl , 1
Preparation of Ferrite: initial pH; 11.0
oxidation temperature; 80°C
oxidation time; 3 hr

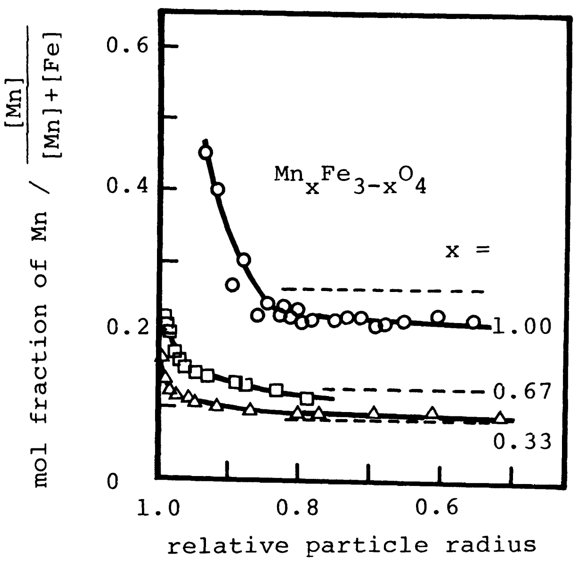

Fig.2 Manganese distribution in $Mn_xFe_{3-x}O_4$ in the radial direction
Preparation of ferrite:
initial pH; 11.0
oxidation temperature; 80°C
oxidation time; 3.0 hr

Fig.2 shows the manganese distribution in manganese ferrite particles before heat treatment. The left end of the abscissa indicates the surface of the ferrite particle. The dotted lines in the figure indicate the mean mole fraction of manganese ion when the whole sample powder was dissolved. As is obvious from the figure, high mole fraction region of manganese exists near the particle surface and it decreases gradually to the center of the particle.

The determination of manganese and iron, however, became very difficult when the particle size of the ferrite powder was smaller than that of half of its original radius because the residual ferrite particle behaved like a colloidal one. Therefore the distribution of manganese near the center of the particles was estimated from the change of the concentration of the solution which was obtained by dissolving the suspension at the early stage of ferrite formation. The concentration of both manganese and iron in the suspension at the early stage of ferrite formation decreased linearly with increasing time. This fact suggests that the ratio of the amount of both ions which are incorporated into the spinel type lattice may be constant. It has been ascertained from the preliminary experiment that manganese ferrite particles obtained by a solid state reaction have homogeneous manganese distribution.

Ferrites by the wet method is known to be formed by dissolution-segregation mechanism in which hydroxides or intermediate compounds such as green rust react with dissolved oxygen.[7] It is not obvious what is the rate determining step of ferrite formation among the dissolution of hydroxides into the solution, the transformation of hydroxides into green rust and the reaction of green rust with dissolved oxygen etc. However, if the reaction of the dissolved green rust with dissolved oxygen is the rate determining step, the mechanism of ferrite formation might be simplified as the precipitation reaction from the homogeneous solution.

As the conditions for preparing manganese ferrite are rather limited, namely, the oxidation temperature should above 70°C and the initial pH should be above 11.0, it is rather difficult to control the cation distribution by changing these parameters. Homogeneity of manganese ferrite particles can be considerably improved by the heat treatment of the product in an inert atmosphere around 500°C for a prolonged period. For example, the manganese distribution at the inner part of the particles was almost uniform irrespective of the initial composition by the heat treatment at 400°C for 72 hr or 500°C for 3 hr. However, the steep mole fraction gradient of manganese near the particle surface remained unchanged.

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