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Preparation and characteristics of Ni-ferrite powders obtained in the presence of fused salts

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This paper describes Ni-ferrite formation in the presence of Li_2SO_4–Na_2SO_4 molten salts, and in particular the effects of the raw materials, amount of salts, heating temperature and time on the size and shape of the ferrite powders, as well as on the rate of ferrite formation. The molten salts accelerate ferrite formation and complete ferrite formation is attained at lower temperatures than in solid state reactions. Ferrite powders with two types of shapes are obtained from NiO with different particle sizes and aggregation states; one is similar to the starting Fe_2O_3 particles and the other has an octahedral crystal habit. The difference follows from the different dissolution rates of Fe_2O_3 and NiO. Growing particles in molten salts have a crystal habit, but the most stable particle shape is rounded.

1. Introduction

The importance of powder characteristics has long been recognized in ferrite technology and various processes have been developed for preparing ferrite powders [1, 2]. One extreme is the conventional powder metullurgical method using solid state reactions, in which the composition control is easy but constituent element distributions is less uniform. The other extreme is the co-precipitation method, in which mixing on an atomic scale is achieved, but composition control is rather difficult. There is a modified powder metallurgical method which uses fused salt. This gives increased reaction rates and improved uniformity. Mg-ferrite, for instance, is formed at lower temperatures in the NaCl–KCl melt [3] and other ferrites are prepared with the aid of Li_2SO_4–Na_2SO_4 fused salts [4]. It is felt that little information is available on the characteristics of ferrite powders so obtained. The present study was undertaken to characterize the ferrite powders obtained in the presence of Li_2SO_4–Na_2SO_4 fused salts. This paper describes the effects of the amount of salts, heating temperature and time on the size and shape of the ferrite powders, and on the rate of ferrite formation. Effects of aggregation state of the starting raw materials have also been studied. On the basis of the results obtained, the mechanism of ferrite formation is discussed.

2. Experiments

The starting materials were of chemical pure grade. Fig. 1 shows SEMs of the oxide powders, the particle sizes of which are given in Table I. The oxides in stoichiometric composition and sulphates containing 36.5 mol% Na_2SO_4 were mixed in an agate mortar for 30 min. The amount of sulphate salts was defined by F, where

$$F = \frac{\text{total moles of sulphates}}{\text{total moles of oxides}}.$$

The mixtures were heated in a platinum crucible isothermally for a fixed period of time and then

TABLE I Particle size of raw materials, in which Fe_2O_3(c) and NiO(f) are aggregate powders, as checked by SEM and TEM

	Particle size (μm)	
	Primary particle	Secondary particle
Fe_2O_3(f)	0.2	10
Fe_2O_3(c)	0.4	0.2
NiO(f)	0.03	
NiO(c)	1	

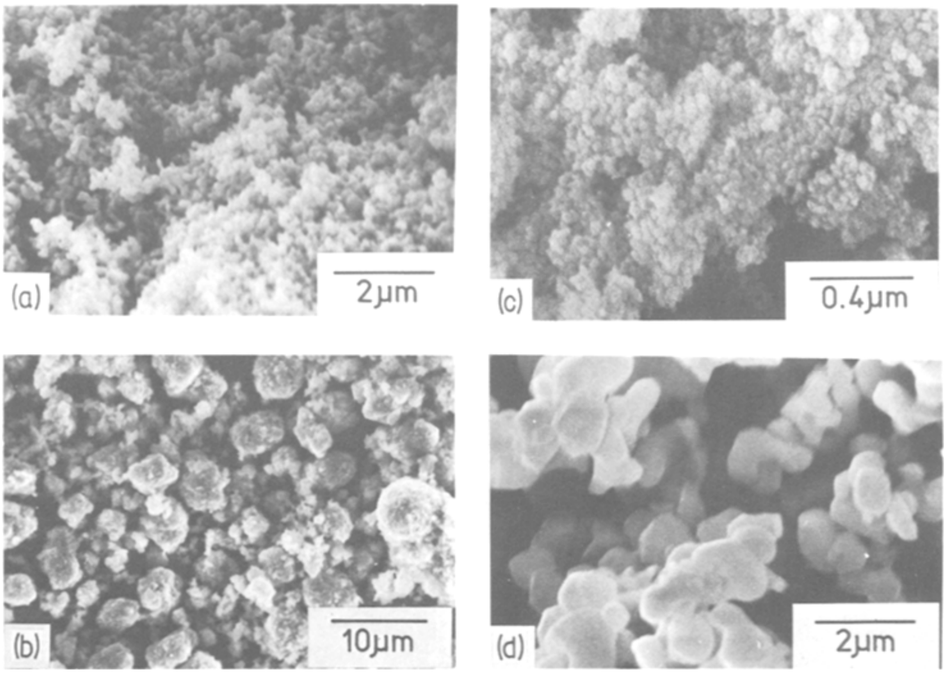

Figure 1 SEMs of raw materials, (a) Fe_2O_3(f), (b) Fe_2O_3(c), (c) NiO(f) and (d) NiO(c).

cooled in air. The firing temperature was chosen between 600 and 900° C, because the sulphate mixture of this composition melted at 594° C, as determined by DTA. The sulphates were washed out with de-ionized water several times until the aliquot became free from SO_4^{2-}, as checked by a $Ba(NO_3)_2$ solution.

The degree of ferrite formation was determined by X-ray diffraction analysis using Fe$K\alpha$; the amounts of unreacted Fe_2O_3 and ferrite formed were obtained from the peak area ratio of Fe_2O_3 (104) and ferrite (220) using a calibration curve prepared with known compositions. The fraction reacted, α, is

$$\frac{1 - \text{amount of unreacted } Fe_2O_3}{\text{amount of initial } Fe_2O_3} .$$

The size and shape of the particles were examined using an SEM.

3. Results

3.1. Rate of ferrite formation

Fig. 2 shows the relation between the fraction reacted and the temperature at which the mixtures of Fe_2O_3(f) and NiO (f and c) with and without sulphate salts were heated for 1 h. In both cases fused salts increased the reaction rates and complete ferrite formation was attained at lower temperatures than in solid state reactions. NiO(f) gave a higher reaction rate than NiO(c). Fig. 3 shows the relation between fraction reacted and the amount of salt (F) for a heating time of 1 h. The results indicate that the fused salts accelerate the ferrite formation. When NiO(f) was used, the reaction rate increased with increasing F and reached 100% completion at $F = 0.8$. When NiO(c) was used, however, the reaction rate increased with increasing amount of salts, but decreased after it passed through a maximum at $F = 0.16$.

X-ray diffraction analysis revealed that NiO and $NiFe_2O_4$ existed in the lower part of the crucible and that Fe_2O_3 and $NiFe_2O_4$ in the upper part. In the flux method of single-crystal formation, ferrite-forming constituents are completely dissolved into the flux. In the present case, however, the solubilities of the oxides into salts are small and oxide particles and molten salts co-existed. The molten salts exist between the oxide particles, and a free liquid phase was not observed, from the appearance of samples. Nevertheless, sedimentation of particles occurred. While Fe_2O_3 particles could be distributed all over the sample, NiO particles would sediment, as the true density of NiO is high and NiO(c) particles are large. The greater the amount of salts present, the more freely the particles will move. While the presence of salts may

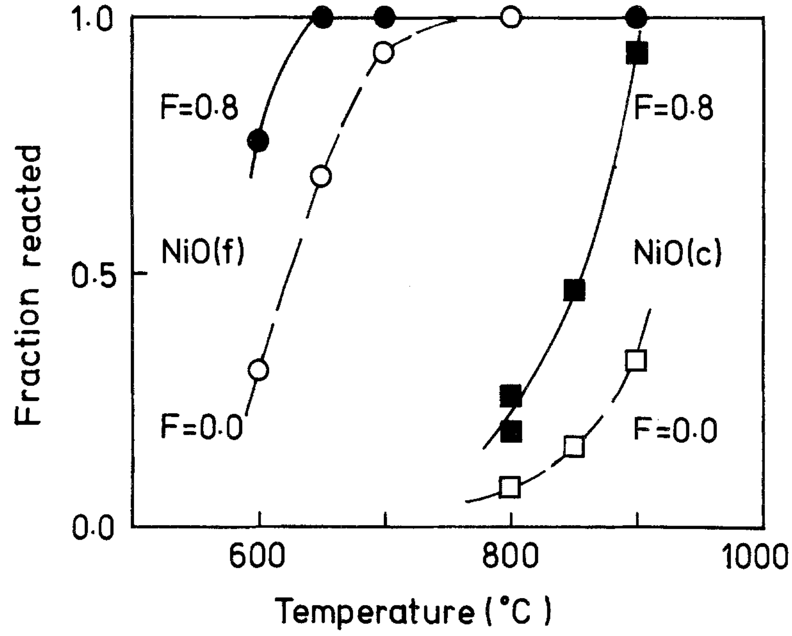

Figure 2 Fraction reacted attained by 1 h heating of mixtures of Fe_2O_3(f) and NiO(f and c) with $F = 0.0$ and 0.8 at various temperatures. ●, ○, NiO(f); ■, □, NiO(c).

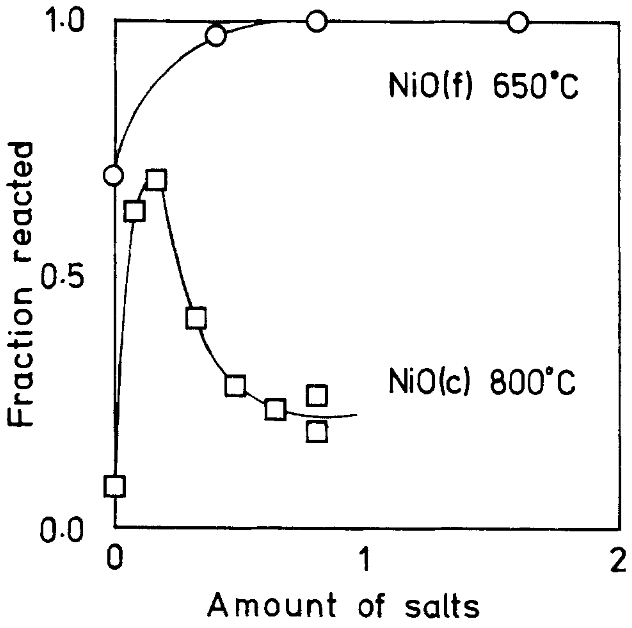

Figure 3 Effect of the amount of salts on the fraction reacted attained by 1 h heating of mixtures of Fe_2O_3(f) and NiO(f and c).

promote the reaction, it would also separate the reacting particles, thus the observed maximum in the relation between fraction reacted and the amount of salts would be explained.

3.2. Size and shape of ferrite powders

3.2.1. Ferrites obtained by reaction between Fe_2O_3 (f and c) and NiO(f)

Fig. 4 shows SEMs of ferrites obtained from Fe_2O_3(f) and NiO(f) at various temperatures and time periods. The ferrite powders obtained by 1 h heating had a shape similar to that of Fe_2O_3(f). They were slightly larger than the starting Fe_2O_3(f) irrespective of the reaction temperature. The shape and size of the ferrites obtained by 1 h heating were independent of the amount of salts. Prolonged heating at 900° C yielded a few particles which had an octahedral crystal habit.

Fig. 5 shows the ferrite obtained from Fe_2O_3(c) and NiO(f) 900° C for 1 h and indicates that the

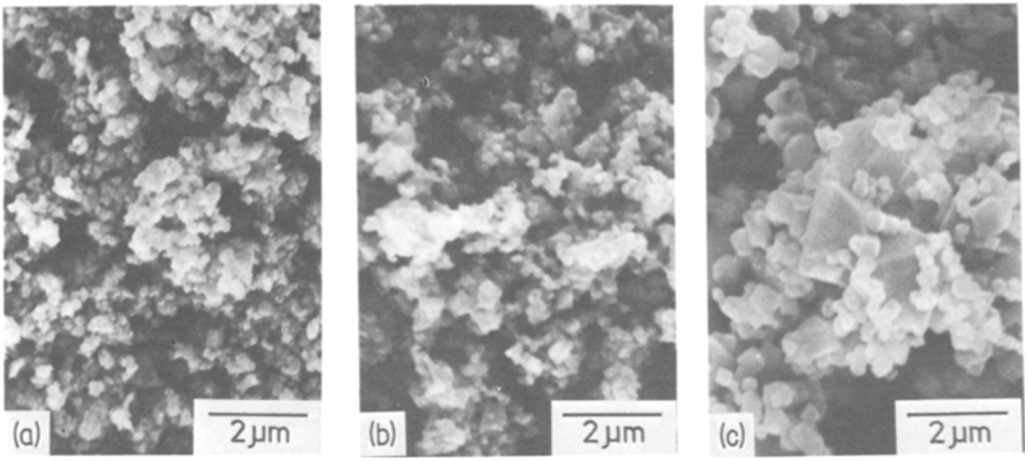

Figure 4 SEMs of powders obtained from Fe_2O_3(f) and NiO(f) with $F = 0.8$ at 700° C for 1 h (a), 900° C for 1 h (b), and 900° C for 18 h (c). In all cases ferrite formation was completed.

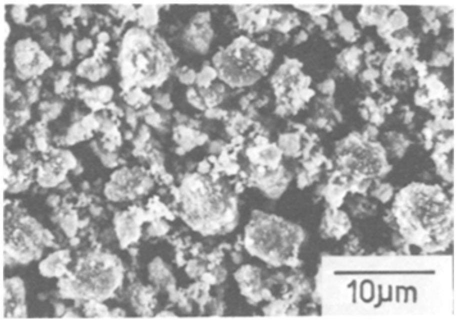

Figure 5 SEMs of the powder obtained from Fe_2O_3(c) and NiO(f) with $F = 0.8$ at 850° C for 1 h. The fraction reacted was 0.99.

appearance of Fe_2O_3(c) was maintained. From the fact that the ferrites had an appearance similar to the starting Fe_2O_3, it is inferred that ferrites formed at Fe_2O_3 particle surfaces.

3.2.2. Ferrites obtained by reaction between Fe_2O_3(f and c) and NiO(c)

Fig. 6 shows SEMs of powders obtained from Fe_2O_3(f) and NiO(c) at 850° C for different time periods, where the particles with a crystal habit are ferrite and the rounded particles are the raw materials. The ferrite particle had an appearance different from that of the raw materials. Increasing the heating time increased the size and number of ferrite particles. The crystal habit disappeared on prolonged heating at high temperatures as shown in Fig. 7.

Fig. 8 shows the effect of the amount of salts on the appearance of ferrite obtained at 800° C for 1 h. The size of the ferrite particles increased as the amount of salts increased. The increase in size would be related to the formation rate, since the

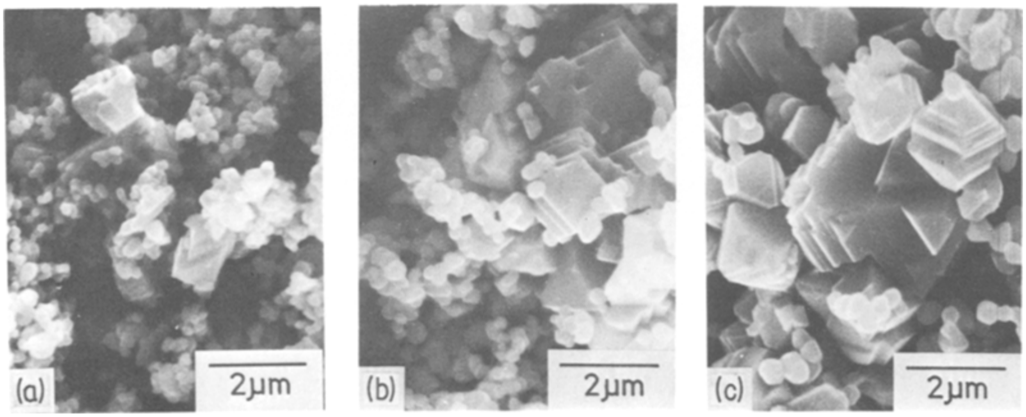

Figure 6 SEM photographs of powders obtained from Fe_2O_3(f) and NiO(c) with $F = 0.8$ heated at 850° C for: 1 h (a), $\alpha = 0.25$; 4 h (b) $\alpha = 0.50$; and 16 h (c) $\alpha = 0.87$.

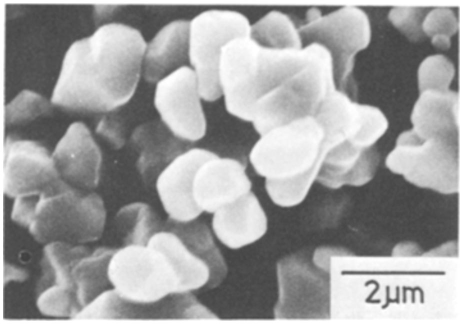

Figure 7 SEMs of the powder obtained from Fe_2O_3(f) and NiO(c) with $F = 0.8$ heated at 900° C for 18 h. Ferrite formation was completed.

reaction rate of this system had a maximum as shown in Fig. 3.

Fig. 9 shows the particles obtained from Fe_2O_3(c) and NiO(c) at 900° C for 1 h with $F = 0.8$. The major part was composed of unaggregated ferrite powder with a crystal habit, and the minor part was composed of aggregated powder, which retained characteristics of Fe_2O_3(c), although each particle of aggregates had a crystal habit. The latter would have formed on Fe_2O_3 particles.

4. Discussion

4.1. Mechanisms of ferrite formation in the presence of fused salts

Wickham postulated that NiO is soluble in Li_2SO_4–Na_2SO_4 melt but Fe_2O_3 is not [4]. DTA measurement showed that the ternary eutectic temperatures in the Fe_2O_3– and NiO–Li_2SO_4–Na_2SO_4 systems were lower than the eutectic temperature in the Li_2SO_4–Na_2SO_4 system. This means that both Fe_2O_3 and NiO dissolve in the sulphate melt.

The shape difference of ferrite particles obtained using NiO(f) and NiO(c) is probably explained from the difference in the dissolution rate of oxides into melt.

Case 1. This is the case when NiO(f) was used. When the dissolution rate of NiO is larger than that of Fe_2O_3, the dissolved NiO diffuses through molten salts, reaches the surface of Fe_2O_3 and forms the ferrite, before the dissolution of Fe_2O_3 occurs. Once the ferrite layer is formed at the Fe_2O_3 surface, Fe_2O_3 will not dissolve because Fe_2O_3, which diffuses through the ferrite layer, would be caught by NiO to form ferrite. Thus, ferrite powders with an appearance similar to Fe_2O_3 particles would result. The independence of particle size and shape on reaction temperature and amount of sulphate salts, which influence the formation rate, supports this view. The ferrite formation mechanism would be the same as that in solid state reactions, in which ferrite is formed, for instance, by counter-diffusion of Ni and Fe ions [5]. The increase in the formation rate (Figs. 2 and 3) may have resulted from an increase in the contact area of oxides, as the reaction would occur at the Fe_2O_3 surface and a larger area is available for the reaction than in solid state reactions [6].

Case 2. This is the case when NiO(c) was used. When the dissolution rates of NiO and Fe_2O_3 are comparable, dissolved NiO would react with dissolved Fe_2O_3 in the melt before reaching the Fe_2O_3 surface, and ferrite separates from the melt. It is well known that ferrite single crystals with an

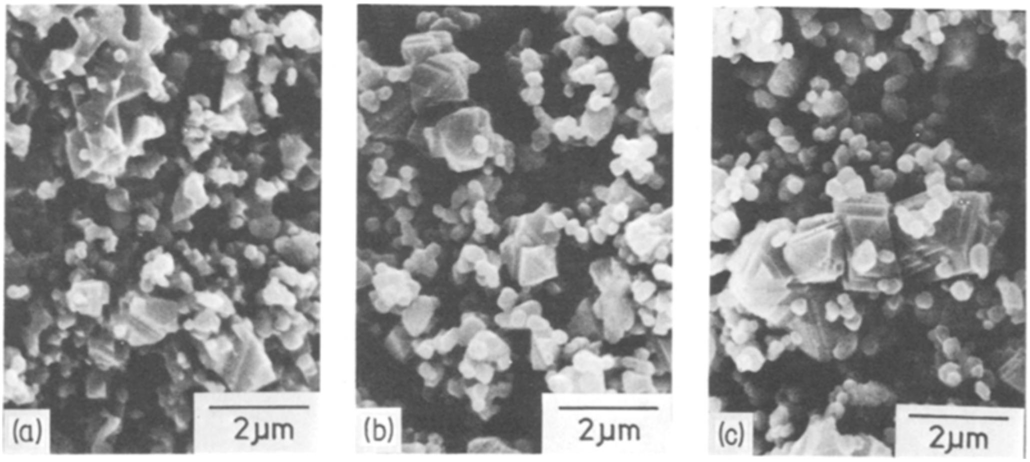

Figure 8 SEMs of powders obtained from Fe_2O_3(f) and NiO(c) heated at 800° C for 1 h with $F = 0.16$ (a), 0.48 (b), and 0.80 (c). Refer to Fig. 3 for fraction reacted.

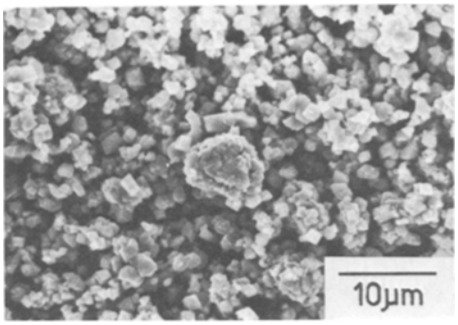

Figure 9 SEMs of the powder obtained from Fe_2O_3(c) and NiO(c) with $F = 0.80$ at 900° C for 1 h. Fraction reacted was 0.96.

octahedral crystal habit are obtained by flux methods, where ferrite precipitates from the flux containing ferrite-forming oxides. Also in the present case, Fe_2O_3 and NiO would dissolve in the melt and form nuclei of ferrite somewhere in the melt. Further dissolution would cause the particles to grow. Formation of ferrites in the molten salt would cause dependence of ferrite particle size on heating period (Fig. 6), amount of flux (Fig. 8) and temperature (data are not shown), which influence supersaturation and number of ferrite nuclei. As the reaction occurs in the melt, the formation is accelerated more than in solid state reactions.

Two experiments were made in order to confirm the above mechanisms. Fe_2O_3(f) was sintered at 1300° C for 3 h, crushed and heated with NiO(c) at 900° C for 1 h with $F = 0.8$. Fig. 10 shows the starting Fe_2O_3 powder and that obtained. The starting Fe_2O_3 powder was composed of large and small particles of about 20 and 0.5 μm, respectively. The obtained powder was composed of large ferrite particles probably formed on large and small Fe_2O_3 particles, both showing a crystal habit. The latter would have been formed in the melt from small Fe_2O_3 particle and NiO(c) as in the case shown in Fig. 7. The large ferrite particles would have been formed at the surface of the Fe_2O_3 particles, since large Fe_2O_3 would dissolve more slowly so that NiO is supplied from NiO(c) particles. Evidence that the ferrite layer was formed at the surface of the Fe_2O_3 particle was obtained by X-ray diffraction analysis. The intensity ratio of Fe_2O_3 (104) and ferrite (220) of the as-heated powder was 0.73, but increased to 1.15 by grinding it thoroughly. Thus, in the as-heated powder, Fe_2O_3 particles are covered with a ferrite layer and its intensity was decreased by absorption of X-rays by the ferrite layer. These facts indicate that the decrease in dissolution rate of Fe_2O_3 would change the mechanism from Case 2 to Case 1.

The second experiment was the ferrite formation from a mixture of Fe_2O_3(f), NiO(c) and NiO(f). The stoichiometric mixture of Fe_2O_3(f)–0.5 NiO(c)–0.5 NiO(f) with $F = 0.8$ was heated at 900° C for 1 h. The ferrite powder had an appearance similar to Fe_2O_3(f) and no particles with a crystal habit were observed. The results are explained as follows. As the reaction rate of NiO(f) is larger than that of NiO(c), Fe_2O_3(f) reacts with NiO(f) before reacting with NiO(c). As the Fe_2O_3 particles are covered with a ferrite layer, Fe_2O_3 does not dissolve into the melt, so the particles with a crystal habit are not formed. NiO(c) reacts with Fe_2O_3 by diffusion through the ferrite layer or by reacting with Fe_2O_3, which diffuses to the surface of particles through the ferrite layer. Therefore, particles with an appearance similar to Fe_2O_3(f) may have been obtained. These additional experiments would support the proposed mechanisms.

4.2. Discussion on the change of shape by prolonged heating at high temperature

The crystal habit was developed on prolonged heating at 900° C for NiO(f) and disappeared

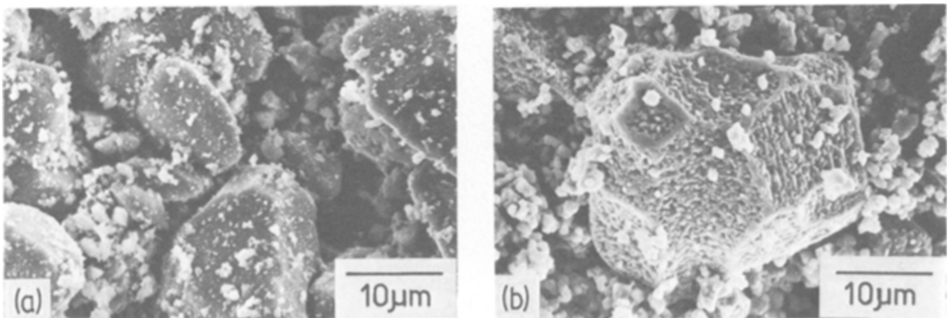

Figure 10 SEMs of the starting Fe_2O_3 (a), and the obtained ferrite powder (b), in which the fraction reacted was 0.59.

when NiO(c) was used, as shown in Figs. 4 and 7. Although, at first sight, the results seem imcompatible with each other, they are explained by assuming that the growing particles have a crystal habit and that particles which cease growth have a rounded shape. This assumption would be supported by the observation of pore shape in the sintered ferrites [7, 8]. A growing closed pore is octahedral in shape but the pore shape changes to spherical when growth stops. The pore is considered to be a negative image of a particle. In the present case, the growing particle had a crystal habit, as shown in Figs. 4c and 6. Prolonged heating of the particles obtained from NiO(c) would slow down particle growth and eliminate the crystal habit, as is the case in pores. These considerations were confirmed by the following evidence. Ferrite shown in Fig. 7 was mixed with another Ni-ferrite (shown in Fig. 4a) in fused salts with $F = 0.8$ and heated at 900° C for 1 h. The obtained ferrite had a crystal habit, which supports the above view.

Change of shape by prolonged heating indicates that the equilibrium shape of ferrites in molten salts is spherical rather than octahedral. Calculation of the surface energy of different faces shows that the surface energy of (1 1 1) of spinels is much smaller than those of (1 1 0) and (1 0 0) [9]. The surface energy of a curved surface oriented near the (0 0 1) plane in $Cu_{0.75}Fe_{2.25}O_4$ at 1100° C is 1.29 times larger than that of (1 1 1) [10]. Consideration of the suface energy proposes that the octahedron is the most stable shape, but additional contributions of edges and apices to the total surface energy has to be taken into account. On the other hand, the rounded particle has no edges or apices. The total surface energy of the octahedron would be larger than that of a sphere so that the latter may have resulted from prolonged heating.

5. Conclusions

Ni-ferrite is formed more rapidly in the presence of Li_2SO_4–Na_2SO_4 melt than in solid state reactions, because fused salts accelerate the transport of ferrite constituent oxides. Raw materials with large differences in particle size and in true density are not suitable for this method because sedimentation of the large and heavy particles causes inhomogeneous mixing. The shape of ferrite particles depends on the dissolution rates of the oxides. When the dissolution rate of NiO is larger than that of Fe_2O_3, ferrite with an appearance similar to Fe_2O_3 is obtained. When the dissolution rate of Fe_2O_3 is larger than or comparable to that of NiO, ferrite with an octahedral crystal habit is obtained. Prolonged heating results in a morphological change. Growing particles have an octahedral crystal habit but particles which cease growing are spherical.

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