JOURNAL OF MATERIALS SCIENCE 21 (1986) 2876–2880

Preparation of acicular NiZn-ferrite powders

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Acicular NiZn-ferrite powder particles have been prepared from goethite-derived acicular Fe_2O_3 and spherical constituent oxides in the presence of molten chloride or sulphate. The morphology of NiZn-ferrite particles has been studied with reference to the effect of chemical species of molten salts, ferrite composition and particle size of constituent divalent oxides. Hence the best preparation conditions for acicular NiZn-ferrite powder with homogeneous composition have been determined; a mixture of acicular Fe_2O_3 and submicron constituent oxides is heated at 900° C in an amount of potassium chloride with four times the weight of ferrite. Electron diffraction analysis shows that the particle axes of acicular Fe_2O_3 and NiZn-ferrite are parallel to $[\bar{1}100]_{\text{haematite}}$ and $[\bar{1}01]_{\text{ferrite}}$ and that a topotactic relation is retained.

1. Introduction

Molten salt synthesis is one of the important fabrication methods to obtain particles with controlled shapes for grain-oriented ceramics [1]. Molten salt used as a solvent aids the formation of compounds from their constituent oxides. Reaction in molten salt consists of two processes [2]: complex oxide formation and particle growth. Platy and acicular particles of compounds with low crystal symmetry such as $BaFe_{12}O_{19}$ [3] and $PbNb_2O_6$ [4] are obtained in the presence of molten salt utilizing a large growth anisotropy. For compounds with high crystal symmetry, on the other hand, equiaxed particle shape is more stable [5]. Based on a careful study of reactions in molten salt, we have found that it is possible to control the particle shape of compounds with cubic symmetry [6] and have been successful in making rod-shaped $BaTiO_3$ particles by heating rod-shaped $TiO_2 \cdot nH_2O$ with equiaxed $BaCO_3$ in the presence of molten chloride [7]. Sulphate should not be used for preparing $BaTiO_3$ because of its reaction with $BaCO_3$.

This paper deals with preparation of acicular Ni-, NiZn- and Zn-ferrite powders from acicular Fe_2O_3 and equiaxed NiO and ZnO powders in the presence of molten chloride or sulphate, and the effects of flux species and ferrite composition on the particle morphology of reaction products were studied. Based on the experimental results, a reaction scheme in molten salt is discussed.

2. Materials and methods

Fig. 1 shows a scanning electron micrograph (SEM) of the raw material α-Fe_2O_3 particles derived from acicular α-FeOOH by heating at 600° C for 1 h in air. In addition to submicron ZnO(0.3 μm) and NiO(0.08 μm) powders, a coarse NiO(1.2 μm) powder was used. They were referred to as ZnO, NiO(f) and NiO(c), respectively. Acicular Fe_2O_3 was wet-mixed with a stoichiometric amount of constituent divalent oxides using a blender. The mixture was admixed with flux. The amount of flux, W, was defined here by the ratio (total weight of flux)/(total weight of oxides). In this experiment, four kinds of flux were used as shown in Table I.

The oxides–flux mixtures were heated at a temperature between 700 and 1000° C for 1 h in air, and then cooled. The flux was washed out with hot deionized water several times until the water became Cl^-- and SO_4^{2-}-free. The degree of ferrite formation was determined by X-ray diffraction analysis using a calibration curve prepared with known compositions [2]. The compositional changes of the NiZn-ferrite obtained was examined by thermomagnetic analysis [8]. The particle size and shape were examined by scanning electron microscopy. The orientation relation in a particle was determined by electron diffraction analysis.

Solubilities of constituent oxides, nickel- and zinc-ferrites in flux were determined as follows [9]. Single crystals of oxides and ferrites were embedded in a flux and heated at 900° C for 18 h. The amount of oxides or ferrites dissolved in the known weight of flux was determined by the weight difference of the single crystal before and after heating.

3. Results and discussion

3.1. Reaction in NaCl–KCl flux

When a 0.5NiO(f) + 0.5ZnO + Fe_2O_3 mixture was heated at 700° C for 1 h in NaCl–KCl flux ($W = 4.0$), the ferrite formation was completed. Fig. 2 shows SEMs of NiZn-ferrite obtained at 700 and 900° C. The acicular shape of the starting Fe_2O_3 particles was preserved in the 700° C product. The SEM appearance of the 800° C product was almost the same as that of the 700° C product. The product particles changed shape at 900° C. The particle deformation was also observed when the flux ratio, W, was small, i.e. the morphology of the 700° C product obtained with $W = 0.9$ is similar to that of the 900° C product with

TABLE I Chemical species of flux used in this experiment

Composition	$0.65Li_2SO_4$ $+ 0.35Na_2SO_4$	NaCl	0.5NaCl $+ 0.5$KCl	KCl
Melting point (° C)	598	800	650	774

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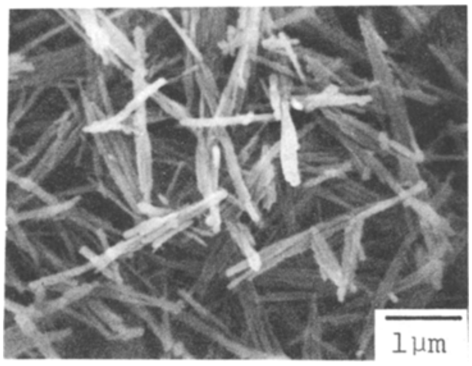

Figure 1 SEM of starting Fe_2O_3 powder.

$W = 4.0$ (Fig. 2b). Hence, the flux ratio W was fixed at 4.0 in the subsequent experiments.

The particle morphologies of zinc- and nickel-ferrites obtained at 700° C were similar to that of NiZn-ferrite obtained at 700° C as shown in Fig. 2a. However, at elevated temperature a significant effect of ferrite composition x in $Ni_xZn_{(1-x)}Fe_2O_4$ was observed on the particle morphology. Fig. 3 shows the SEMs of zinc-, NiZn- and nickel-ferrite powders obtained at 900° C for 1 h. The degree of particle deformation increases with decreasing x. At 900° C the ferrite formation was completed in 4 min heating, irrespective of the ferrite composition, and acicular ferrite particles were obtained. This means that in the presence of NaCl–KCl flux, the acicular shape of Fe_2O_3 particles is preserved during ferrite formation, and that the acicular ferrite particles obtained undergo deformation to equiaxed ones on annealing. In summary, the deformation rate depends on the heating temperature, amount of flux and ferrite composition.

3.2. Reaction in Na_2SO_4–Li_2SO_4 flux

The same experiment as described above was repeated using Na_2SO_4–Li_2SO_4 flux. When $W = 4.0$, formation was completed in 1 h heating at 700° C irrespective of ferrite composition. Fig. 4 shows the SEMs of zinc-, NiZn- and nickel-ferrite powders obtained at 700° C. Zinc-ferrite particles barely preserved the acicular shape of Fe_2O_3, but careful comparison of zinc-ferrites obtained in sulphate and NaCl–KCl fluxes at 700° C revealed that the particles obtained in sulphate flux have thickened to some extent. In sulphate flux, partial substitution of NiO(f) for ZnO resulted in the deformation of particles. The nickel- and NiZn-ferrite powders obtained at 700° C were mixtures of equiaxed particles of about 0.1 μm and rounded acicular particles. A slight increase in temperature caused extensive particle deformation.

In order to find out the origin of deformation, the starting Fe_2O_3 powder and acicular zinc-, NiZn- and nickel-ferrite powders obtained at 700° C in NaCl–KCl flux were annealed in sulphate flux at 700° C for 1 h. No significant change in the particle shape was observed. This fact indicates that particle deformation in sulphate flux occurs during the ferrite formation. Perhaps, the different roles of flux observed between chloride and sulphate fluxes could be explained in terms of the relative solubility as well as the dissolution rate of oxides, on which the subsequent sections have focused.

3.3. Effect of particle size of NiO on the reaction

In NaCl–KCl flux, 1 h heating at 700° C was sufficient for nickel-ferrite formation from fine NiO(f), and acicular nickel-ferrite powder was obtained. Coarse NiO(c), however, required 1 h heating at 1000° C for the complete reaction. The result of SEM observation as shown in Fig. 5 has revealed that the nickel-ferrite powder obtained is a mixture of rounded acicular and large octahedral particles. A fractional reaction of 0.66 was obtained with coarse NiO(c) by 1 h heating at 900° C, and large octahedral particles were observed. Hence it is considered that large octahedral particles were formed during reaction with coarse NiO(c).

3.4. Reaction mechanisms in flux

The original shape of Fe_2O_3 particles will be retained if the ferrite formation takes place on the Fe_2O_3 surface, the dissolution of Fe_2O_3 particles into flux thus being prevented. In Section 3.3, it was shown that an increase in particle size of NiO suppressed the reaction rate and yielded large equiaxed particles. The increase in particle size of NiO would slow down the dissolution rate of NiO into the flux so increasing the possibility of Fe_2O_3 dissolving in the flux. Thus, a possible reaction mechanism with coarse NiO(c) is as follows. A part of Fe_2O_3 dissolves in the flux and reacts with dissolved NiO, and then ferrite precipitates out.

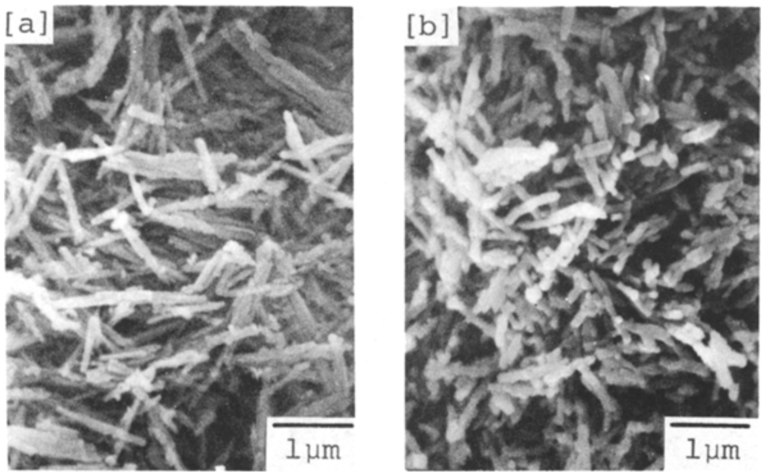

Figure 2 SEMs of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders obtained from NiO(f) and ZnO in NaCl–KCl flux ($W = 4.0$), heated at (a) 700° C and (b) 900° C.

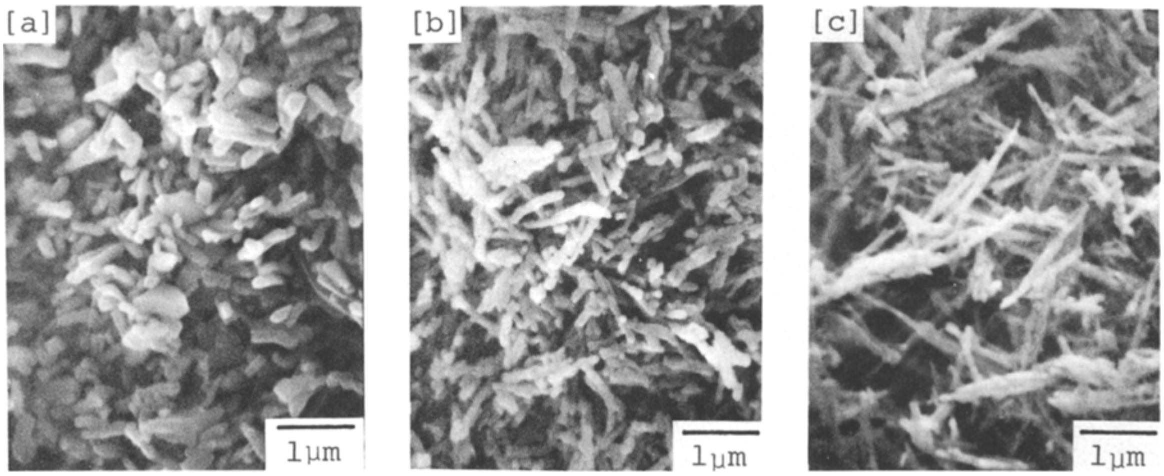

Figure 3 SEMs of (a) $ZnFe_2O_4$, (b) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $NiFe_2O_4$ powders obtained at 900° C for 1 h in NaCl–KCl flux ($W = 4.0$).

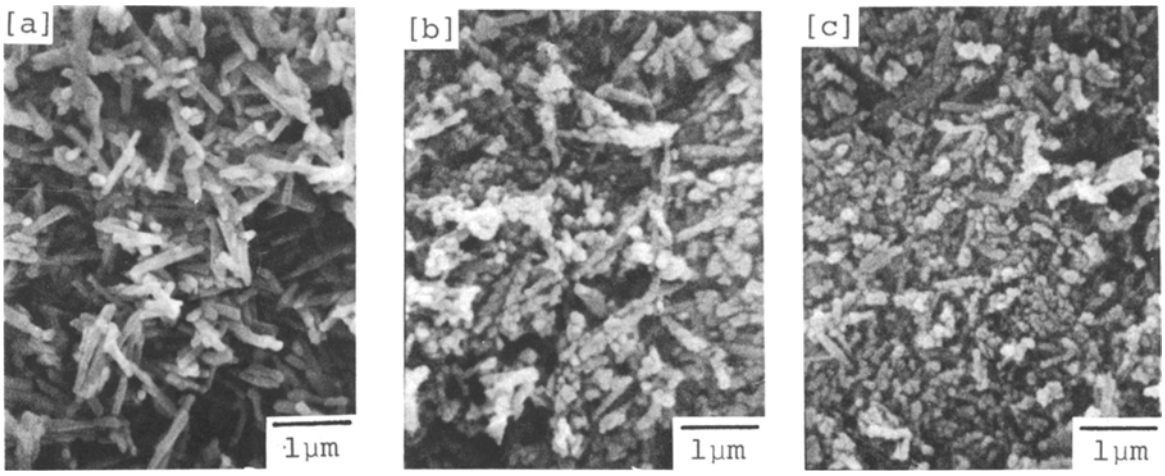

Figure 4 SEMs of (a) $ZnFe_2O_4$, (b) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $NiFe_2O_4$ powders obtained by 1 h heating at 700° C in Na_2SO_4–K_2SO_4 flux ($W = 4.0$).

The relative dissolution rate of Fe_2O_3 depends on the relative solubility in flux. Table II lists the solubilities of oxides and ferrites in four types of fluxes at 900° C. Irrespective of flux composition, the solubility of ferrites are always one order of magnitude smaller than that of constituent oxides. The same tendency is expected at other temperatures used in this experiment. The solubility of Fe_2O_3 in Na_2SO_4–Li_2SO_4 flux is much larger than that of Fe_2O_3 in NaCl–KCl flux. This would explain why the particle deformation is more extensive in Na_2SO_4–Li_2SO_4 flux than in NaCl–KCl flux as shown in Figs 4 and 2a. Namely, the relatively large solubility of Fe_2O_3 in sulphate flux accelerates the dissolution of Fe_2O_3, resulting in ferrite formation by the solution-precipitation process and a considerable change in particle shape. In sulphate flux, partial substitution of NiO(f) for ZnO accelerated the particle deformation during ferrite formation as described in Section 3.2. As the solubility of NiO in sulphate flux is almost the same as that of ZnO, the solubility difference between nickel- and zinc-ferrites would be responsible for their particle morphologies. A possible explanation is that larger solubility of ferrites would require an extensive time for saturation with ferrite, giving a greater opportunity for the Fe_2O_3 to dissolve. In addition to the above explanation, differences of powder characteristics and chemical properties between NiO(f) and ZnO would also affect the relative dissolution rates in sulphate flux.

In NaCl–KCl flux, acicular ferrite particles deformed into rounded ones on annealing, and the deformation rate increased with decreasing x in $Ni_xZn_{(1-x)}Fe_2O_4$ as

TABLE II Solubilities of nickel-, zinc-ferrites and constituent oxides in fluxes

Oxides	Solubility (mol/g salt)			
	$0.65Li_2SO_4$ $+0.35Na_2SO_4$	NaCl	0.5NaCl +0.5KCl	KCl
NiO	1.6×10^{-6}	6.7×10^{-7}	6.7×10^{-7}	6.7×10^{-7}
ZnO	1.5×10^{-6}	1.7×10^{-6}	1.2×10^{-6}	9.1×10^{-7}
Fe_2O_3	4.8×10^{-6}	1.9×10^{-6}	2.2×10^{-6}	1.2×10^{-6}
$NiFe_2O_4$	5.1×10^{-7}	7.7×10^{-8}	9.8×10^{-8}	5.1×10^{-8}
$ZnFe_2O_4$	1.6×10^{-7}	2.4×10^{-7}	1.8×10^{-7}	5.0×10^{-8}

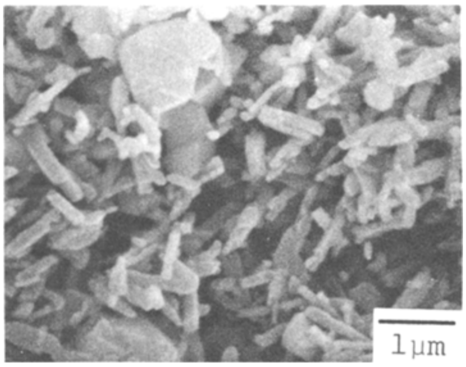

Figure 5 SEM of a $NiFe_2O_4$ powder obtained from NiO(c), heated at 900° C for 1 h in NaCl–KCl flux ($W = 4.0$).

shown in Fig. 3. In NaCl–KCl flux, the solubility of zinc-ferrite is larger than that of nickel-ferrite as shown in Table II, implying that the solubility of $Ni_xZn_{(1-x)}Fe_2O_4$ increases with decreasing nickel-content. As deformation of acicular ferrite particles in molten salt proceeds in the same manner as Ostwald ripening, the increase in the solubility of ferrite would yield particle deformation of acicular ferrite particles. To confirm the above point of view, the effect of flux composition on the deformation rate of acicular zinc-ferrite particles was examined. Zinc-ferrite formation at 900° C was completed in 4 min heating, irrespective of flux species, and acicular zinc-ferrite particles were obtained. Fig. 6 shows the SEMs of zinc-ferrite powders obtained by 1 h heating at 900° C in NaCl, NaCl–KCl and KCl fluxes. Apparently, the degree of particle deformation increases with increasing solubility of zinc-ferrite in flux as shown in Table II. When KCl flux was used, acicular NiZn- and nickel-ferrite particles, similar to zinc-ferrite particles as shown in Fig. 6c, were obtained at 900° C.

Essentially, there are two possible mechanisms of particle deformation:

1. ferrite formation occurs by solution-precipitation process;
2. acicular ferrite particles deform into rounded ones on annealing in flux.

A smaller size of constituent divalent oxides and smaller solubility of Fe_2O_3 in flux suppress a chance of Fe_2O_3 dissolution, preventing particle deformation by mechanism 1. The low solubility of ferrite in flux prevents the particle deformation by mechanism 2.

3.5. Characterization of acicular shaped ferrite particles

Fig. 7 shows the effect of heating temperature on the compositional homogeneity of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders obtained in NaCl–KCl flux. As the Curie temperature of NiZn-ferrite depends on the concentration of Ni^{2+} relative to Zn^{2+}, the shape of the thermomagnetic curve reflects compositional fluctuation in the obtained NiZn-ferrite powder. Magnetization of the 900° C product changes sharply at the Curie temperature of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, indicating compositional homogeneity. Decreasing the heating temperature causes a relatively low magnetization at room temperature and a broad distribution of Curie temperature indicative of the large compositional fluctuation. This result shows that 900° C heating is required to obtain a homogeneous NiZn-ferrite powder. But NiZn-ferrite particles obtained at 900° C in NaCl–KCl flux, as shown in Fig. 2b, deformed into rounded ones. Acicular $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles, on the other hand, were obtained at 900° C in KCl flux as shown in Fig. 8. Thermomagnetic analysis of this NiZn-ferrite powder revealed that the composition is satisfactorily homogeneous.

Fig. 9 shows electron diffraction patterns of acicular Fe_2O_3 and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles obtained at 900° C in KCl flux. Particle axes were found to be parallel to $[\bar{1}\,1\,0\,0]_{\text{hexagonal}}$ and $[\bar{1}\,0\,1]_{\text{spinel}}$. Thus, the orientation relation between Fe_2O_3 and NiZn-ferrite is expressed as follows:

$$[\bar{1}\,1\,0\,0]_{\text{haematite}} \parallel [\bar{1}\,0\,1]_{\text{ferrite}}$$

The obtained relation agreed well with the topotactic relation between Fe_2O_3 and spinel-type ferrite, implying that the ferrite formation takes place by the topotactic reaction.

Acknowledgement

The authors thank Dr Jan Willem Martens of Philips

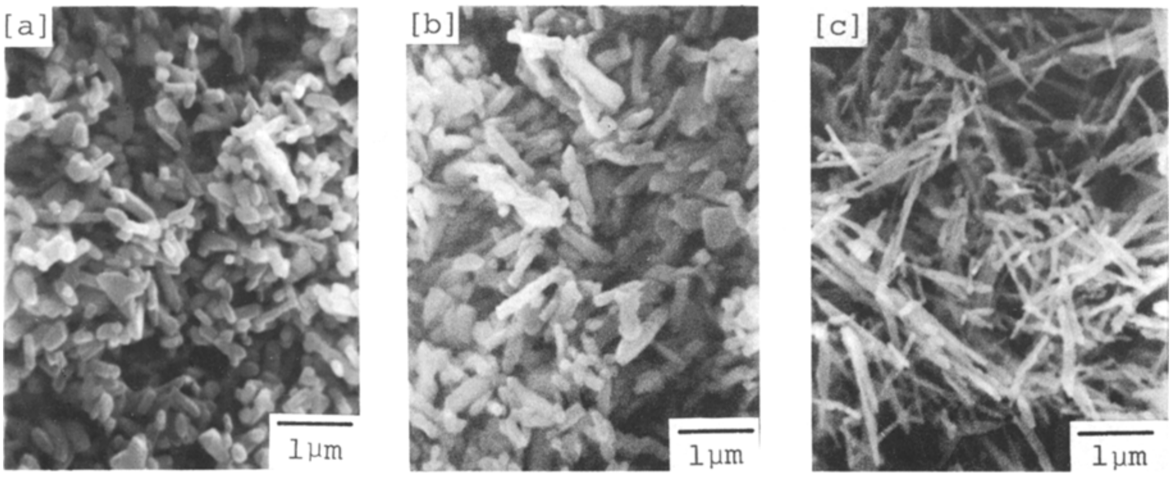

Figure 6 SEMs of zinc-ferrite particles obtained by 1 h heating at 900° C in (a) NaCl, (b) NaCl–KCl and (c) KCl fluxes.

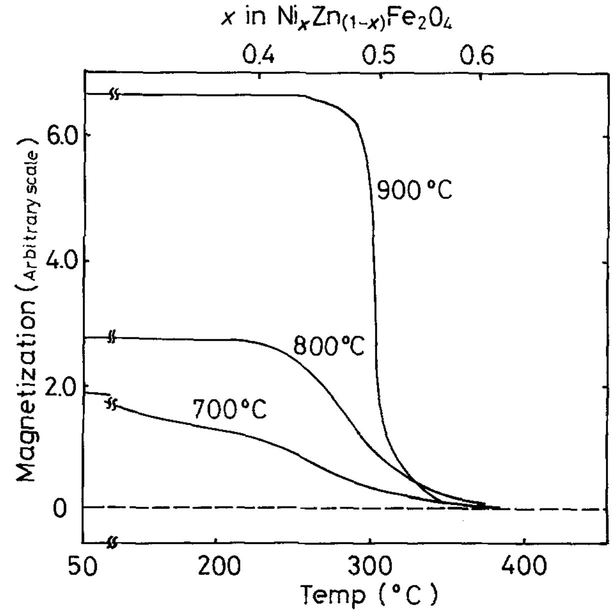

Figure 7 Thermomagnetic curves of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders obtained by 1 h heating in NaCl–KCl flux.

Research Laboratories for supplying a zinc-ferrite single crystal, and Dr T. Hibiya and Dr H. Makino of the Central Research Laboratories, NEC Corporation for supplying a nickel-ferrite single crystal.

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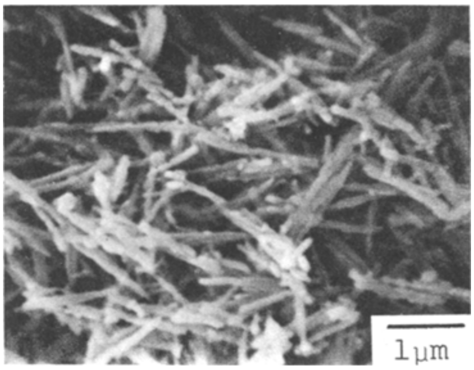

Figure 8 SEM of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder obtained by 1 h heating at 900° C in KCl flux ($W = 4.0$).

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Received 23 May
and accepted 23 October 1985

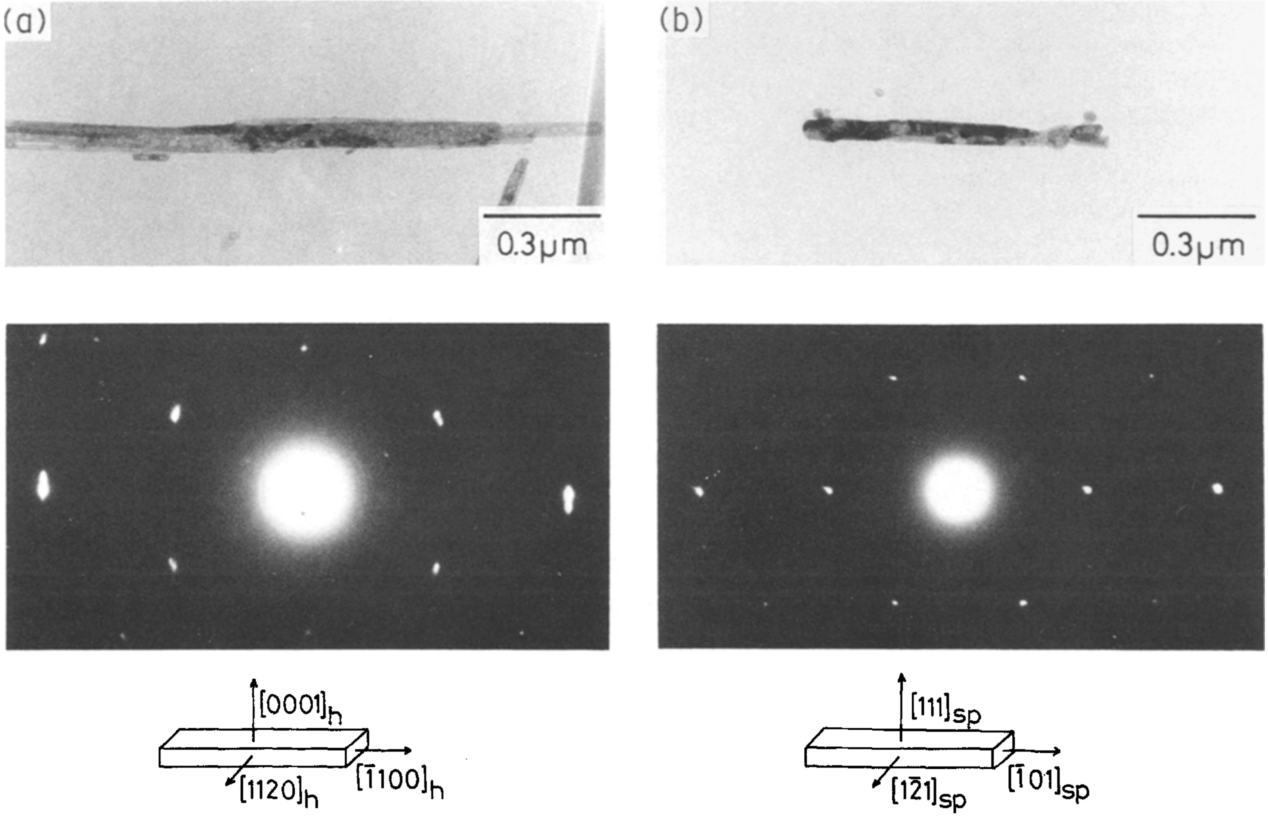

Figure 9 Electron diffraction patterns of (a) acicular Fe_2O_3 and (b) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles obtained by 1 h heating at 900° C in KCl flux ($W = 4.0$).