

# The effects of substrate materials and powder type on the properties of plasma sprayed ferrite

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The effect of the method of powder production and substrate materials on the physical and magnetic properties of plasma sprayed nickel ferrite films is discussed, including the production of films by spraying an oxalate powder and a solution of nitrates in methanol. Films deposited onto substrates having a larger thermal expansion coefficient than ferrite were found to exhibit better magnetic properties, including squarer hysteresis loops. An optimum choice is proposed for good surface finish, porosity and magnetic properties, consisting of spraying fully fired ferrite powder, of particle size 10 to 30  $\mu\text{m}$ , onto fosterite substrates. The magnetic properties were then comparable with bulk nickel ferrite. If surface finish is not a prime consideration satisfactory results could be obtained from the oxalate powder and the method could be used to produce non-stoichiometric ferrites, possibly with improved properties. Films sprayed with the nitrate solution exhibited very favourable grain structures after annealing and it is probable that the method could be useful once problems associated with atomizing the liquid are overcome. Attempts to spray mixed oxides led to films with extreme roughness, due, in part, to a tendency of the powder to agglomerate. The films, as sprayed, were strongly magnetic demonstrating that solid state reaction had occurred, probably on the surface of the hot substrate.

## 1. Introduction

The use of bulk ferrite components in the communications field has been established for many years, but the recent rapid rise in monolithic integrated circuit technology and the resultant reduction in the size of most systems have rendered magnetic components somewhat impractical on account of their size.

The use of thick film techniques (e.g. silk screen printing) for producing hybrid circuits, often incorporating integrated circuits in chip form, on ceramic substrates has become increasingly popular. The deposition of thick films of ferrite onto suitable ceramic substrates by the arc plasma spraying (APS) process is a possible technique for producing magnetic components compatible with conventional thick film circuitry, both as cores for inductors or, at microwave frequencies, as strip line isolators and circulators. In addition, the plasma spraying of ferrite, combined with suitable masking techniques, could

be of interest for the fabrication of thick film magnetic recording heads.

The first published mention of the deposition of thick films of ferrite by APS was given by Harris *et al.* [1] and by Harris and Janowiecki [2]. Although these authors gave few details of the techniques used, they claimed considerable success, both with spinnel and garnet materials, and mentioned that the resulting films have a small grain size ( $<0.1 \mu\text{m}$ ) and that substrates with a thermal expansion less than  $8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  were unsuitable.

Since this paper a number of other reports have appeared [3-9]. For example, Babbit reports on the deposition of nickel zinc ferrite using a number of different powder types and concludes that powder particles in the size range 1 to 10  $\mu\text{m}$  should be used. His work also demonstrates the importance of a substrate preheat on reducing substrate cracking and promoting a good film-to-substrate bond.

Some interesting results were reported by Sugimoto [5] using a plasma torch of a novel design that allowed the use of 90% oxygen in the arc gas by sheathing the electrodes with an auxiliary argon flow. When argon alone was used for the arc gas, the resulting films were found to be porous containing a large amount of Wustite (FeO) but the use of an oxidizing arc gas produced dense films containing little precipitate. This conflicts with the present authors [6] who have always used argon as the arc gas and have never observed Wustite precipitates in the sprayed films, although the low electrical resistivities of some films suggests that some reduction has occurred in the torch flame. Sugimoto also noted the presence of columnar grains in the films deposited under conditions where a temperature gradient is created across the film during deposition. The present authors have also observed this effect [8] and have discussed conditions most likely to produce columnar growth [9].

Work by Braguier *et al.* [10] on the deposition of alumina and copper films by APS has demonstrated the importance of high nozzle velocities in reducing the surface roughness of the films. This work led to the present authors redesigning their plasma torch to operate with a 4.75 mm (3/16 in.) diameter nozzle instead of the previously used

6.35 mm ( $\frac{1}{4}$  in.) diameter nozzle. This change combined with an increase in the argon flow augmented the flame velocity from  $600 \text{ m sec}^{-1}$  to  $1400 \text{ m sec}^{-1}$  [11]. That this change was efficacious can be seen by comparing the surface finish of the films sprayed with the fully fired powder mentioned in Table I with previous results given for a similar powder mentioned in [8] (i.e.  $3.6 \mu\text{m CLA}$ ).

The present publication has concentrated on the differences observed by spraying a number of possible powder types onto a number of commercially available substrate materials with a view of establishing an optimum choice. All the powder types produced were manufactured by conventional powder routes that can be easily performed in the average materials laboratory, thus representing a cheap source of starting material. Nickel ferrite was chosen for the present work on account of its ease of production and good stability. In addition, the low permeability of the resultant films eases the problems encountered with magnetic measurements on non-toroidal specimens. The results, however, should be applicable to other ferrites providing the extra difficulties of these materials (e.g. zinc oxide loss from Ni-Zn ferrites and variable valency of Mn in Mn ferrites) can be overcome.

TABLE I The physical and magnetic properties of plasma sprayed nickel ferrite

Substrate	Powder type	Ni-Fe	CLA	$M_S$ (e.m.u. $\text{g}^{-1}$ )		$H_C$ (Oe)		$\mu$	
				As sprayed	Annealed	As sprayed	Annealed	As sprayed	Annealed
UL300	Fully fired	0.448	2.6	44.2	44.6	130	33	4.23	7.17
D16	Fully fired	0.4488	2.3	—	—	108	31	4.08	7.18
DS6	Fully fired	0.448	—	—	—	110	27	3.9	11.18
D38	Fully fired	0.448	—	—	—	111	26	—	—
UL300	Co-prec.	0.347	2.95	42.0	53	80	20	3.41	10.37
UL300	Co-prec.	0.43	2.3	48.8	47.7	83	36.5	—	—
DS6	Co-prec.	0.43	2.3	42.9	49.3	96.5	36.5	—	—
UL300	Co-prec.	0.52	2.6	41.5	46.2	93	23.1	—	—
UL300	Freeze dried	0.52	4.6	40.5	44.4	135	26	3.46	8.31
UL300	Pre-fired	0.41	4.5	44.2	30.7	90	29	3.77	8.72
UL300	Mixed oxide	—	>10	37.2	40.4	62	17	—	—
UL300	Liquid feed	0.42	5.4	40.8	23.7	—	27	—	—
UL300	Haematite	—	—	7	7	—	38	—	—

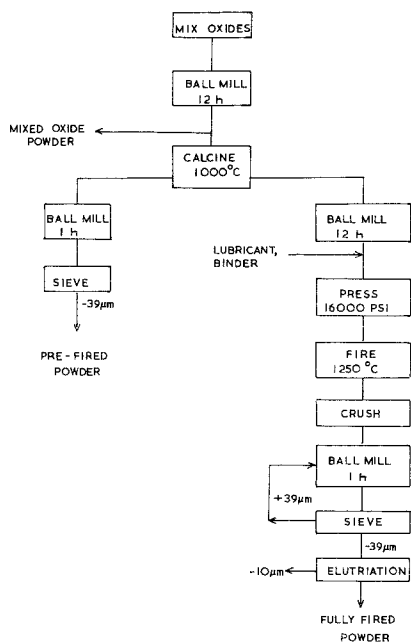


Figure 1 Flow chart showing method of preparing ferrite powders for plasma spraying.

## 2. Experimental procedure

### 2.1. Powder preparation

Five powder types were evaluated in the present work, these being a fully fired ferrite powder, a calcined (prefired) powder, a mixed oxide powder, a co-precipitated oxalate powder, and a spherical powder. In addition, a liquid feed system was attempted. The spherical powder (donated by Dr M. Ertl, Sussex University) was thought to be

produced by a freeze dry technique whilst the other types were manufactured by the methods outlined below.

#### 2.1.1. Ball-milled powders

The fully fired, prefired and mixed oxide powders were prepared by conventional powder techniques as depicted in the flow chart (Fig. 1). The mixed oxide powder was sprayed as ball milled, but the prefired powder was crushed and screened through a  $39\ \mu\text{m}$  sieve. The fully fired powder was sieved to  $-39\ \mu\text{m}$  and was then cleared of fine particles ( $<10\ \mu\text{m}$ ) by a process of elutriation.

#### 2.1.2. Co-precipitated powder

Mixed nickel/iron oxalate was co-precipitated by the addition of saturated ammonium oxalate solution to a solution of nickel nitrate and ferrous ammonium sulphate at  $60^\circ\text{C}$ , containing the cations in the required proportions. After stirring for an hour the precipitate was filtered off, washed with acetone and dried. The resulting oxalate powder was sprayed without prior decomposition.

#### 2.1.3. Liquid feed system

This system was an adaption of the flame spray technique [12] developed for the production of fine ferrite powders and consisted of feeding into the plasma flame an atomized spray of nickel nitrate and ferric nitrate dissolved in a 40% water 60% methanol mixture.

The major difficulty encountered was the

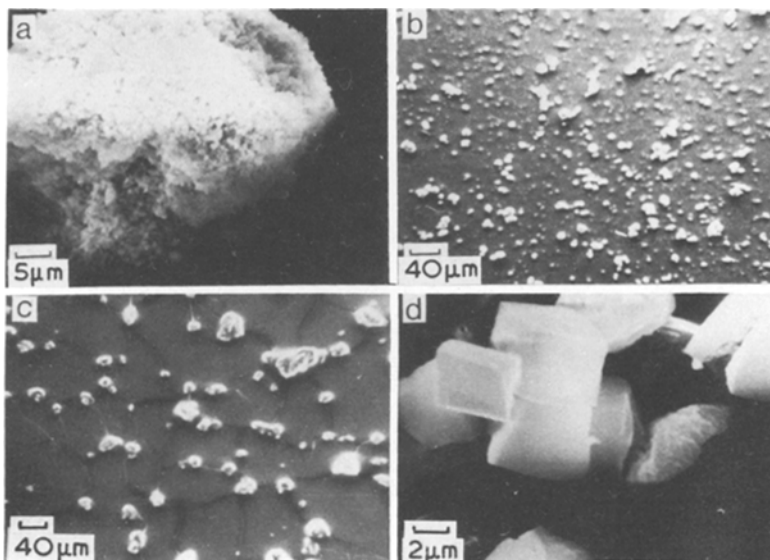


Figure 2 Scanning electron micrographs of the various powders used. (a) Mixed oxide powder, (b) freeze dried powder, (c) fully fired ferrite powder, (d) co-precipitated oxalate powder.

tendency of the atomizer to produce large drops which failed to become entrained into the plasma flame. The use of a slow feed rate, combined with dilute solutions mitigated the problems somewhat and enabled some results to be obtained.

## 2.2. Powder characteristics

Examination of the powders was conducted by utilizing the powder feed hopper system to deposit a thin layer of the powder onto a microscope slide coated with adhesive. The resulting slide was then examined in a scanning electron microscope (SEM), typical results being shown in Fig. 2. It can be seen (Fig. 2a) that the mixed oxides suffered serious agglomeration.

All the powders and sprayed films were analysed with an atomic absorption spectrophotometer and the various nickel to iron atomic ratios are shown in Table I. No detectable change in the nickel to iron ratio was found during spraying.

## 2.3. Plasma spraying conditions

The plasma spraying was carried out at 500 A, 28 V with an argon gas flow of 43 litre min<sup>-1</sup>. A torch to substrate separation of 47.5 mm was maintained, this allowed the substrate temperature to rise to 1000 to 1100° C during spraying, thus enhancing the film to substrate bond. Difficulties were encountered with the poor thermal shock resistance of some of the substrate materials. To alleviate this, the substrate sizes were kept to a minimum (10 mm × 10 mm or 10 mm × 20 mm) and the specimens were preheated by traversing them through the plasma flame whilst slowly increasing the arc current from 200 A to 500 A.

## 2.4. Physical examination

Surface roughness was assessed quantitatively by means of a Rank Taylor Talysurf and the morphology was examined in an SEM. Films were prepared by Syton polishing the surfaces prior to

metallographic examination both unetched and after etching with hot orthophosphoric acid.

## 2.5. Magnetic measurements

Initial permeabilities were measured at 1000 Hz in a field of 1 Oe using an a.c. technique, whilst saturation moments were determined with the aid of a vibrating sample magnetometer [13]. The same magnetometer was adopted for the determination of sample *M-H* loops by sweeping the electromagnetic field and displaying the magnetometer output and a signal proportional to the field, obtained from a Hall effect probe, simultaneously on an *X-Y* recorder [14].

## 3. Results and discussion

The results of the physical and magnetic measurements are summarized in Table I, whilst Table II shows the data, obtained from the manufacturers, pertinent to the substrate materials used. Little success was achieved with the barium titanate (D38) as the material tended to peel during deposition. Small pieces of film on this material were used to check the coercive force. The mixed oxide films and some of those sprayed with the co-precipitated powder tended to peel off from the substrate during annealing, probably as a result of film shrinkage arising from decomposition and sintering effects.

### 3.1. Surface morphology

The best surface finishes were obtained with the fully fired and co-precipitated powders (Figs. 3 and 4). The poorer surface finishes of the films sprayed with the prefired material are attributed to the very fine particle size of this material (>1 μm). In results concerning the deposition of nickel powder, Smyth [15] demonstrated that there was an optimum particle size to produce good finishes and decreasing the powder size below this limit caused deterioration of the surface finish.

TABLE II Properties of substrate materials

Substrate	Manufacturer	Manufacturers designation	Thermal expansion (° C <sup>-1</sup> )	Thermal conductivity (cal cm <sup>-2</sup> sec <sup>-1</sup> ° C <sup>-1</sup> )
Alumina	Wade	UL300	6.9 × 10 <sup>-6</sup> (25–200° C)	0.064
Magnesium titanate	Trans-Tech Inc.	D16	7.5 × 10 <sup>-6</sup>	0.01
Fosterite	Trans-Tech Inc.	DS6	10 × 10 <sup>-6</sup>	0.009
Barium titanate	Trans-Tech Inc.	D38	9.4 × 10 <sup>-6</sup>	—

The roughness of the films sprayed with the mixed oxide powder and the liquid feed system is attributed to agglomeration of the fine powder in the first instance (Fig. 2a) and the poor atomization in the latter (Fig. 4c).

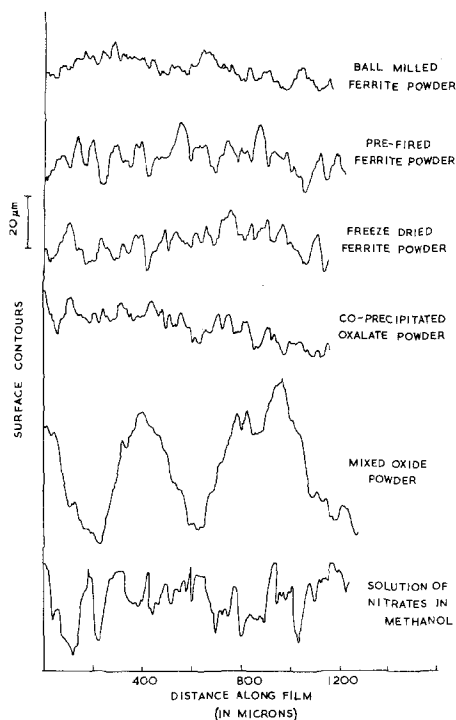


Figure 3 Diagram showing surface finish of films sprayed with different powder types.

### 3.2. Microstructure

Films deposited onto alumina substrates exhibit cracks, as previously reported [8], whilst those sprayed onto the other substrates were found to be crack free, due to the better match between their thermal expansions and that of the ferrite. The porosity was found to be least for the fully fired material. The extremely porous nature of the films sprayed with the liquid feed system (Fig. 5c) suggests this to be a direct result of the columnar nature of the surface (Fig. 4c), voids resulting when a particular valley is grown over.

After etching the films displayed a typical confused structure of variable grain size (Fig. 5), the grain size being extremely fine in the co-precipitated and liquid feed films.

Annealing at 1200°C for 1 h resulted in considerable grain growth resulting in a fairly regular grain size in the films sprayed with the spherical powder and liquid feed system (Fig. 5c and d). In the films sprayed with the fully fired powder a uniform grain size was not achieved, possibly as a result of the uneven particle size of the starting material.

### 3.3. Magnetic measurements

#### 3.3.1. Initial permeabilities and coercivities

The permeabilities and coercivities of the films sprayed onto different substrate materials (Table I) show no appreciable variations, suggesting that effects arising from the different substrate

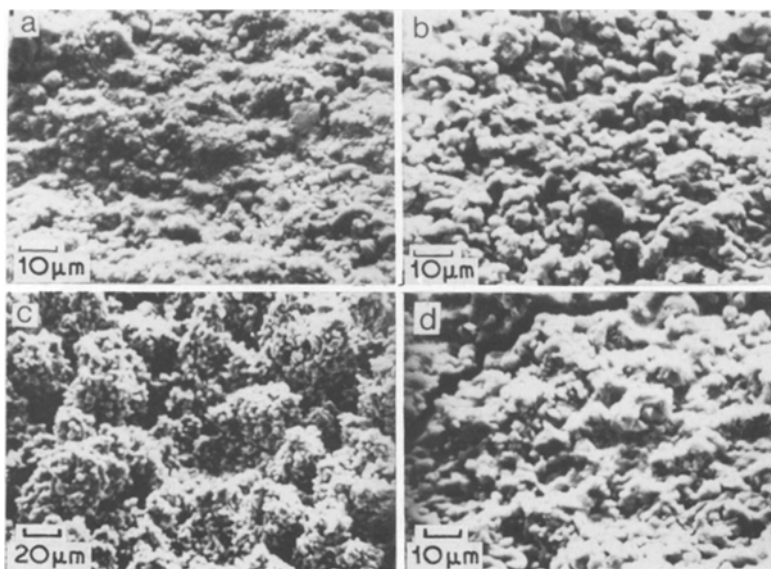


Figure 4 Scanning electron micrographs showing surface morphology of the various films. (a) Fully fired powder, (b) co-precipitated oxalate powder, (c) solution of nitrates in methanol, (d) freeze dried powder.

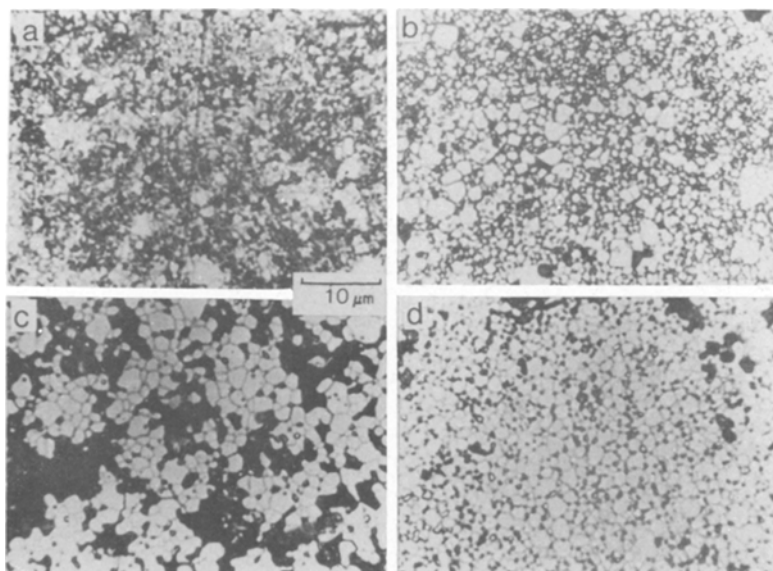


Figure 5 Etched microstructures of the ferrite films. (a) Fully fired powder, as sprayed, (b) fully fired powder, annealed, (c) nitrate solution, annealed, (d) freeze dried powder, annealed.

materials are masked by dominant effects due to quenching stresses and irregular grain size. Clearly, the demagnetizing effects associated with the cracks, present in the films deposited onto alumina, have little effect on the magnetic behaviour of the material in the as-sprayed condition.

Annealing the films in air at 1200°C enhances the permeabilities by a factor of two or three and reveals differences in the behaviour of films sprayed onto the various substrate materials. Films sprayed onto magnetisium titanate and alumina exhibit similar permeabilities and coercivities, whilst those sprayed onto fosterite and barium titanate have much improved properties.

This observation is consistent with the sense of the stresses induced in the films due to thermal expansion mismatch with the substrate material. The films sprayed onto alumina and magnesium titanate both with expansion less than that of nickel ferrite ( $\alpha \approx 8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  [16]) are held in tension after cooling from the temperature of deposition to ambient, whilst the films deposited onto fosterite and barium titanate are in compression.

As the saturation magnetostriction of polycrystalline nickel ferrite ( $\approx -26 \times 10^{-6}$ ) is negative, the strain energy due to magnetostriction will be a minimum for the case of tensile stress when the direction of magnetization is normal to the film, whilst the plane of the film is favoured when

compressive stresses exist. At constant field strength one would expect the induction to be decreased by a tensile stress and increased for a compressive stress, for a sample magnetized parallel to the substrate. This would give rise to squarer hysteresis loops in the case of compressive stresses whilst for the tensile stresses the permeabilities should be lower, as was observed. Typical  $M-H$  loops are shown in Fig. 6, where it can be seen that there is a noticeable increase in squareness in the films sprayed onto fosterite.

### 3.3.2. Saturation moment

Some changes in the saturation moment were observed during annealing particularly in the films sprayed with the liquid feed system. It is thought that the large reduction in moment encountered in these films is due to the diffusion of alumina from the substrate during annealing, this effect being greatest in these films on account of their very small thickness.

In the majority of powders both the nickel to iron ratio and the saturation magnetization were below the value for stoichiometric nickel ferrite ( $M_S = 50 \text{ e.m.u. g}^{-1}$ ), suggesting that the excess iron exists as non-magnetic haemetite. A mixture of haemetite and nickel ferrite having the same nickel to iron ratio as the fully fired powder was calculated to have a moment of  $47.3 \text{ e.m.u. g}^{-1}$  compared with the experimentally observed value of  $45 \text{ e.m.u. g}^{-1}$ .

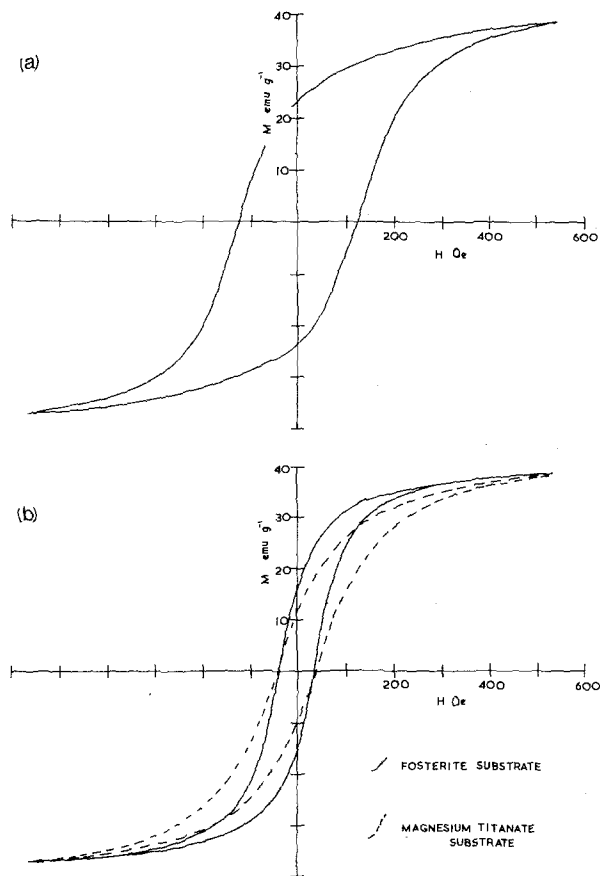


Figure 6 Hysteresis loops derived from ferrite films. (a) As-sprayed, (b) annealed at 1200° C.

Reduction during spraying has previously been suggested to explain the low electrical resistivities of the films before annealing. To assess the likely magnitude of this, films of haemetite were sprayed and their magnetic moments were found to be  $\approx 7 \text{ e.m.u. g}^{-1}$ , indicating the formation of approximately 6% magnetite during spraying. Excess haemetite in the starting material should not, therefore, be greatly reduced during spraying.

Reconciliation must be made between the apparently single phase nature of the films and the small width of the spinel field at the deposition temperature. It is, therefore, suggested that either the haemetite is present as a sub-microscopic precipitate, probably at grain boundaries, or the excess iron remains in the spinel as a super-saturated solution. This latter behaviour has been observed in magnesium ferrite due to the slow kinetics of the precipitation [16].

Moderate variations in saturation moments were observed between different samples sprayed with the same co-precipitated powder. Decom-

position of the oxalates probably occurs on the surface of the substrate and these variations could be due to incomplete decomposition. Ferrous oxalate decomposes to magnetite, thus excess iron could lead to an increase in the saturation moment above that of nickel ferrite in the co-precipitated films.

#### 4. Conclusions

The best results with respect to film density, surface finish, and magnetic properties were obtained by the deposition of fully fired powder onto fosterite substrates. Some evidence exists to suggest that the particle size of this powder ( $\approx 20 \mu\text{m}$ ) is close to the optimum with regard to surface finish.

Co-precipitated powders gave reasonable results, the material apparently being decomposed successfully during spraying and the technique could be used to produce non-stoichiometric films, possibly with improved properties.

Films sprayed with the liquid feed technique

exhibited very favourable microstructures after annealing, but the surface finish and porosity were poor. It is likely that improvements in atomization technique would greatly improve the situation.

Attempts to spray the mixed oxides led to films with extreme roughness due, in part, to a tendency of the powder to agglomerate. The films, as sprayed, were strongly magnetic demonstrating that solid state reaction has occurred, presumably on the surface of the hot substrate.

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