JOURNAL OF MATERIALS SCIENCE 8 (1973) 964–967

Plasma spraying of ferrites

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The production of thick films (> 20 μm) of polycrystalline ferrite by the arc plasma deposition process is described. Operating conditions of a plasma torch of the authors' own design are quoted. "As-sprayed" films have high electrical conductivity and low magnetic permeability, but these parameters are restored close to the bulk values by annealing. The surface finish of the films is coarse and unaffected by the particle size of the powder sprayed.

1. Introduction

The successful plasma spraying of ferrites was reported by Harris *et al* [1] in 1970, where it was reported that thick films of ferrite displaying properties similar to the bulk can be produced by this technique. No details of the spraying parameters, other than choice of substrate, were given. The commercial plasma arc sets used are capable of a wide range in input power, gas flow rates and choice of arc gas. The effect of varying particle size was not disclosed. Work reported below is concerned with the spraying of thick films of polycrystalline ferrite using a plasma spraying set of our own design and construction.

2. The plasma spraying process

The plasma spraying process is a development of the earlier technique of flame spraying. Here, powder of the material to be sprayed, is injected into a hot flame and heated to its melting point. The powder is swept along by the velocity of the gases in the flame, and allowed to impinge against a suitable substrate placed a small distance from the flame, where a film of the material is built up. In the plasma spraying technique, the necessary flame is produced by means of an electric arc. The electrically produced flame has a higher velocity and temperature than those produced by conventional oxy-gas torches and the use of plasma spraying equipment has led to a renewed interest in the spraying of ceramic materials.

The heart of the plasma spraying apparatus is the plasma torch, illustrated in Fig. 1. An electric arc is struck between the tungsten cathode and the water cooled copper nozzle that also serves as the anode for the discharge. Argon, fed into the torch, blows the arc into the nozzle, and from this nozzle emerges an extremely hot jet of gas, a plasma flame. The torch can be powered by standard arc welding power supplies.

A current of about 400 A was found to be suitable for the spraying of ferrites, and at this current the arc burnt at a voltage of 26 to 28 V and required an argon flow of 8.6×10^{-4} kg sec^{-1} for stable operation. Measurements of the temperature rise in the cooling water showed that about 40% of the energy delivered was dissipated in the water, the rest of course remaining as energy in the emerging argon. Consideration of the enthalpy of the emerging gas and the mass flow to the torch suggests that the argon emerges from the torch at an average velocity of about 600 m sec^{-1} and temperature of 10000°C [2]. The hot jet emerging from the gun rapidly entrains the surrounding atmosphere leading to a rapid cooling of the flame. Measurements of temperature at about 5 cm from the gun shows that the temperature here has fallen to about 1000°C.

We see, therefore, that the torch produces a hot fast flame, but the length of the flame is only small, meaning that although initially particles injected into the flame will experience rapid heating and acceleration, their dwell time in the region of extreme temperature will be small. Outside this region the particles will only cool and decelerate. The substrates were therefore placed as close to the gun as possible, compatible with protection of the substrate and mounts – a distance of 5 to 6 cm. Increasing this distance merely leads to reduced deposit efficiencies due to divergence of the beam.

The ferrite powder was conveyed to the torch

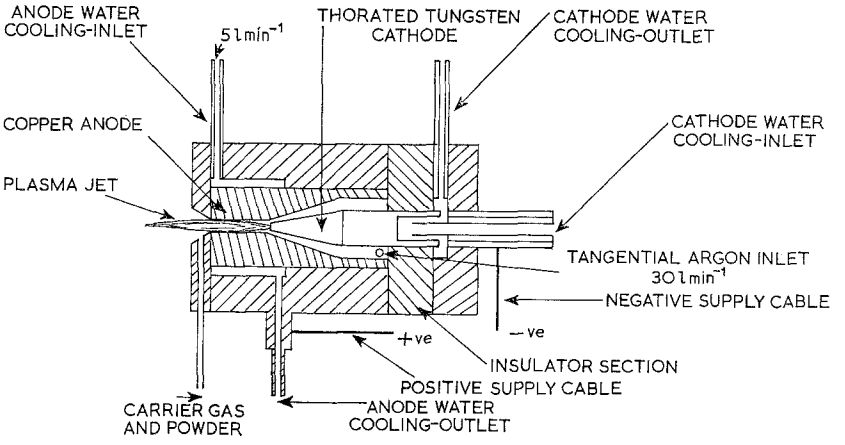

Figure 1 Plasma spraying torch.

by means of an auxiliary gas stream and injected into the plasma flame by means of the powder feed port, as shown in Fig. 1. The powder was introduced into the auxiliary gas stream by means of an aspirator fed by the vibratory hopper, as illustrated in Fig. 2. A flow of about 7 l min^{-1} is required for powder injection resulting in transport of about 3 g of powder per min. The hopper system was able to maintain this constant to within $\pm$ 10% The actual deposition rate was only about 0.1 g per min. This does not, however, represent a meaningful deposition efficiency since with the small specimens prepared most of the powder adhered to the mask and surround.

2.1. Substrates

All the work reported here is concerned with films deposited on alumina substrates. The material was supplied as plates 0.5 mm thick and with a surface finish having a C.L.A. of approximately 1 μm. No preparation of the substrate, other than cutting into suitable sizes, was found necessary and the films were deposited on to substrate material as supplied.

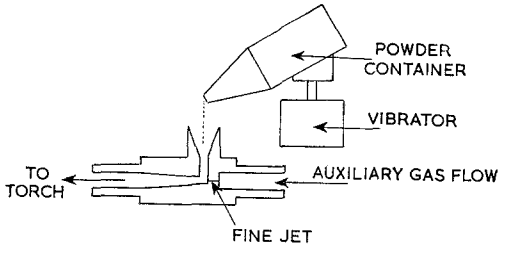

Figure 2 Powder feed system. Powder is shaken from the powder container by the vibrator, and falls by gravity into the cone on the aspirator where it is entrained into the auxiliary gas flow.

To obtain a uniform deposit over any reasonable area, it is necessary to scan the substrate through the flame. To effect this, the substrates were traversed to pass the torch at a rate of 3 cm min^{-1} and simultaneously moved up and down about once a second.

No heating or cooling of the substrate during spraying was found necessary, the substrate being allowed to adopt whatever temperature is appropriate to the torch substrate separation used. Substrates attained a temperature of about 600 to 700°C during spraying.

2.2. Powder

Powder for the plasma spraying was obtained by either grinding up fully fired bulk material or by preparation directly from the component oxides. In the former process the material was ground to produce a fine powder with particle sizes of about 1 to 2 μm or a coarse powder with particle size 39 to 54 μm. In the latter technique the component oxides were mixed by wet ball milling, and fired at 1200°C to promote reaction. The resultant magnetic material was broken up and reduced to micron size by a dry ball milling. Experiments were conducted either employing nickel ferrite or a nickel zinc ferrite ($Ni_{0.6}Zn_{0.4}Fe_2O_4$).

3. Examination of the sprayed films

X-ray powder diffraction photographs were taken for the case of the reacted oxides of the starting material, the sprayed material and the sprayed material after annealing at 1200°C in an oxygen atmosphere. These photographs were

sufficiently similar to suggest that no other phases than the ferrrite were present in the material at either of the three stages mentioned. Table I shows the measured values of d for three sets of planes in the material at the three stages.

TABLE I Values of d-spacings for ferrite at various stages of plasma spraying process.

hkl	Sintered powders	After spraying	Sprayed material after annealing
551	1.589 Å	1.592 Å	1.588 Å
440	1.462 Å	1.463 Å	1.462 Å
533	1.260 Å	1.259 Å	1.260 Å

The surface finish of the sprayed films was investigated using the Rank Instruments Talysurf. The C.L.A. of the film (~ 12 μm) shows that a rough finish was obtained. A typical surface profile is shown in Fig. 3. and profiles similar to this were obtained both with the fine and coarse powder used as spraying material.

Measurements were made of the electrical conductivity of the films at low frequencies (less than 1 KHz) and these showed that the conductivities were considerably higher than those usually encountered with nickel ferrites. Resistivities in the range 10 to 50 Ωcm were typical. Heating the films to about 1000°C restored the conductivities to the usual low values encountered with bulk nickel ferrite.

A limitation in the thickness of the deposited films was encountered. If films greater than about 70 to 80 μm were produced these cracked and broke from the substrate. The magnetic measurements referred to later were made on films with deposit thicknesses in the range 20 to 50 μm and these films seemed to be bonded firmly to the substrate as tested by lapping with emery cloth.

3.1. Magnetic measurements

The films for magnetic measurements were produced as strips of 4 cm × 1 cm with a typical thickness in the range 20 to 50 μm. The demagnetizing factor in the longitudinal direction is sufficiently small that permeabilities could be measured using the simple apparatus shown in Fig. 4. where the magnetizing field is supplied by a long solenoid and the induced moment in the specimen measured by observation of the voltage produced by the pick up coil around the specimen. A similar pick up coil connected in antiphase to the first is also placed in the solenoid to back off the output due to the air flux in the coils. To obtain the magnetization of the specimen at higher fields, the output from the pick up coil was electrically integrated and the peak height of the resulting signal measured.

The initial permeability of the nickel ferrite films was found to be in the range 2.5 to 3, whilst that of the nickel zinc films was of the order 8 to 9, similar values being obtained when both fine and coarse powders were sprayed. Small variations in the substrate torch separation (from 5 to 7 cm) and in the power fed to the gun (from 300 to 400 A) did not alter the permeabilities of the films significantly.

Improvements could be made by annealing the films in an atmosphere of oxygen, for after annealing the nickel zinc ferrite films at 1000°C the initial permeabilities of the films were increased to about 16, and after annealing at 1200°C increased to 33. Similarly annealing the nickel ferrite films at 1200°C augmented their

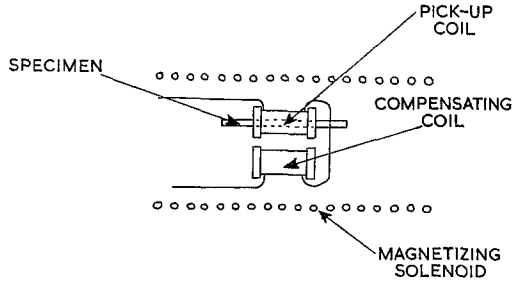

Figure 4 Apparatus for measuring initial permeability.

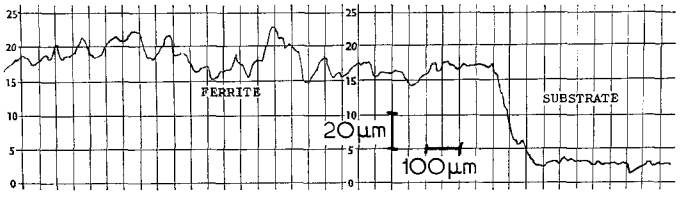

Figure 3 Talysurf trace of ferrite on alumina substrate.

permeabilities to about 7. The magnetization curve of a nickel ferrite film, before and after annealing, is shown in Fig. 5.

Measurements made on material that had become detached from the substrate during spraying showed that the initial permeability of this free standing material was 75 after annealing at 1200°C.

4. Discussion

The as-sprayed films although substantially ferrite display only poor properties, but these can be improved by annealing. The measured initial permeabilities of the annealed films was always considerably below those encountered with the bulk material. The permeability of the nickel zinc ferrite used for the powder preparation was measured to be about 120, whilst the same material now sprayed on to substrates had a permeability of only 30. (The bulk ferrite was fired at about the same temperature at which the films were annealed.)

The tendency of the thicker films to peel from the substrate is due to the mis-match between the thermal expansion of the substrate material and the film resulting in the film substrate bond rupturing on cooling. (Thermal expansion of nickel ferrite is 11×10^{-6} whilst for alumina is about 7×10^{-6}°C.) The strain locked into the films due to this cause may also explain the difference in permeability between the films and the free standing sprayed material. Taking typical values of Young's modulus (1×10^{11} N m^{-2}), saturation magnetostriction (-6×10^{-6}) gives a strain-induced anisotropy value of 2.5×10^3 J m^{-3} resulting from cooling from 700°C. The anisotropy constant, K_1, of the Ni-Zn ferrite used is about 3×10^3 J m^{-3}.

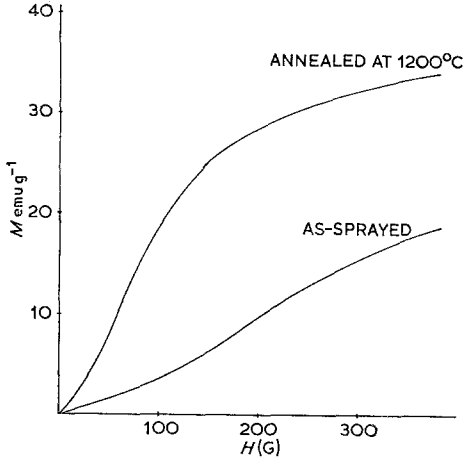

Figure 5 Effect of annealing on plasma sprayed film of nickel ferrite.

The low resistivity of the as-sprayed films is probably due to oxygen deficiency caused by the melting of the ferrite in the hot flame. Clearly the use of argon as the arc gas aggravates this disadvantage and the use of oxygen or an oxygen rich mixture in the emergent arc would be advantageous. The use of oxygen or oxygen rich mixtures in a plasma torch is prohibited as this would lead to the extremely rapid erosion of the white hot tungsten cathode.

The different powders used show that the physical nature of the film is independent of the form of the starting material, the process in general appeared to be somewhat insensitive to changes in spraying parameter. The use of powders formed directly from the oxides suggest the use of the plasma spraying process as a method of small scale ferrite manufacture, the spraying operation replacing the pressing and grinding stages of the conventional process.

Acknowledgements

The authors wish to thank Professor J. E. Thompson, Head of the Wolfson Centre for the Technology of Soft Magnetic Materials, where the work was carried out. They are also grateful to the Data Recording Instrument Co Ltd, Staines, Middlesex, for the provision of a research grant and financial support for C.W.D. Andrews, and to Dr B. Delf of University College, Cardiff, for carrying out the X-ray studies.

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Received 6 September 1972 and accepted 21 January 1973.