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Textured $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ Tiles Manufactured from Sintered and Plasma-Sprayed Precursors for Magnetic Shielding

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Superconducting magnetic shields have potential weight advantages over conventional materials as efficient, light, shielding materials. Shielding properties in high fields depend on many material features, including alignment, critical current densities, and flux pinning. Diffusion texturing can produce grain alignment with the *c*-axis parallel to the sheet plane. In this article, the superconducting tile is made by bonding the ceramic precursor, $SrCaCu_2$, to a metal substrate before texture growth with Pb-Bi-O. The bonding can be produced by sintering or by plasma spraying. After diffusion texture growth, a tile with a superconducting transition temperature of 110 K and a critical current density greater than 2500 A/cm^2 has been manufactured and characterized.

1. Introduction

THE following materials are used in various configurations for alternating current (ac) or direct current (dc) magnetic shielding in applications such as magnetically levitated vehicles (MAGLEV), magnetic resonance imaging, encephalography, etc. In the first of these systems, weight is an important design consideration,[1] because the cabin is built like an airplane. Commonly used shielding techniques are summarized below.

Ferromagnetic shields or yokes (with some ac shielding) are provided by high-permeability materials[2] (*e.g.*, Mumetal). Shields have a low magnetic reluctance in dc fields, but the reluctance increases in ac fields with increasing frequency. The required shield thickness is determined by the saturation field, B_s. The thickness, D, of shield needed to screen a field extended over height, h, with average strength B is given by:

$$D = Bh/B_s \quad [1]$$

Calculations show that 2-cm-thick high-silicon sheet steel with $B_s = 1.2\ T$ (12,000 gauss) will shield dc fields of 200 gauss to fields below 2 mT (20 gauss) in the vehicle cabin.[3] The weight of such shielding is 160 kg/m^2. This weight is considerably greater than what is possible using high T_c materials as discussed below.

Eddy current shields are available for ac, typically manufactured of aluminum.[3] Shielding occurs within a skin depth:

$$\delta = (\pi\sigma f\mu\mu_0)^{-1/2} \quad [2]$$

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at frequency f, where σ and $\mu\mu_0$ are the conductivity and permeability of the aluminum, for which $\delta \sim 8.4 f^{-1/2}$ cm. The amplitude of electromagnetic waves decays with depth, x, inside the metal as $\exp(-x/\delta)$. Thus, a field intensity with frequency 500 Hz is reduced by 100 in a thickness of 8 mm weighing 24 kg/m^2.

Active coils to counteract external fields are available that are controlled by sensors.[3] Conventional superconducting shields, operating close to the temperature of liquid helium, *e.g.*, at $T < 15$ K for Nb_3Sn are also available.[3] The thickness of material needed for perfect shielding depends on the penetration depth, $\lambda(T)$, which is proportional to temperature[4] as $[1 - (T/T_c)^4]^{-1/2}$. The shields can be made as thin as 25 by 10^{-6} m, provided they are sufficiently homogeneous and that mechanical strength is provided by a substrate. The shields are effecient at screening both dc and ac fields. The chief weight factor involved in the use of conventional low-temperature superconductor shielding lies in the cryogenic engineering.

High-T_c systems have comparatively simple cryogenic insulation and offer much greater design flexibility than is possible for conventional superconductors. This is particularly true if the shields have a duel use as the outer temperature shield of the superconducting magnets. The critical transition temperatures of $YBa_2Cu_3O_{7-x}$ [123], $Bi_2Sr_2Ca_2Cu_3O_{10}$ [2223], and $Tl_2Ba_2Ca_2Cu_3O_{10}$ [T2223] are 93, 110, and 125 K, respectively. The high shielding factors observed[5,6] at frequencies of $0.1 < f < 1000$ in an external field of $B < 0.1$ mT and specimen temperature of 77 K correspond with measured materials properties including the critical fields, $H_{c1}c$[7] (fields of 10 mT are shielded at 40 K) and H_{c2},[8] and critical current density, J_c[9]. Shielding occurs even when the applied field is greater than H_{c1}, because there is a region of zero field inside the superconductor if the applied field:

$$B^* < \mu_0 J_c D/2 \quad [3]$$

where μ_0 is the permeability of free space, J_c is the critical current density of the specimen, and d is its thickness (see Fig. 1).

The applicability of this model depends on sufficient flux pinning forces. In this article, the novel techniques for fabrication of large area, high T_c shielding tiles with a textured microstructure is discussed.

2. Fabrication of High-T_c Tiles

"Alignment" refers to preferred microstructural orientation such as that required in superconducting shields to (1) gain optimal shielding from anisotropic material against directional applied magnetic fields, (2) shield, without excess weight, high magnetic field strengths requiring high critical current density in the superconducting material, and (3) maximize flux pinning through orientation effects.

The authors have previously reported a diffusion texture technique in the Bi-Sr-Ca-Cu-O system.[10] This texture technique involves liquid phase sintering of Bi-Pb-O, compound from $3(Bi_2O_3) \cdot PbO$, and $SrCaCu_2O_x$ [0112], which has been previously bonded to a metal substrate. The zero in the [0112] nomenclature signifies that the compound contains no Bi, which is subsequently added to form the superconducting product.

A feasibility study of tile fabrication was first carried out by the "brush-on" method as described below. In a second experiment, plasma spray deposition was used to produce the [0112] precursor. The term "precursor" indicates that this initial layer of superconducting material is used as the foundation for subsequent ceramic coatings. Thus, the precursor coatings act in the same way as a bond coat for metal/ceramic systems.

Plasma spray processing is widely used to deposit both metallic and ceramic materials. Among the latter, high-temperature superconductors have been produced by air plasma spraying (APS), though the product is multi-phased[11-13]. Furthermore, as described here, large areas of homogeneous [0112] can be rapidly deposited by APS with a judicious choice of deposition parameters.

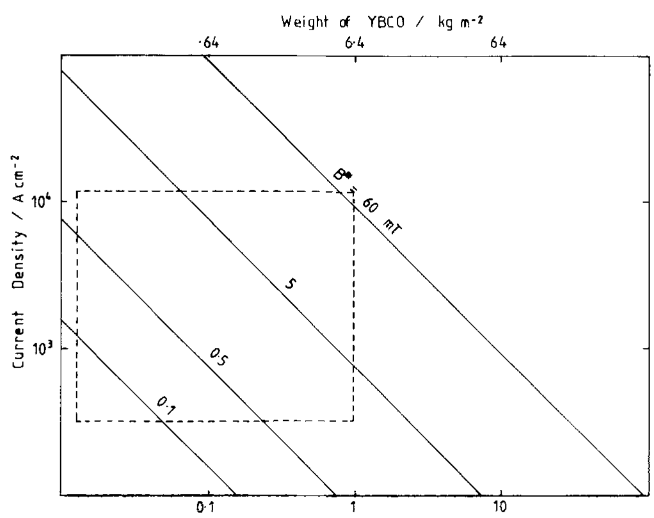

Figure 1 Relationship between current density, shield thickness, and applied field, B^*, derived in Eq 3. Also shown is the weight per square meter of a shield made of $YBa_2Cu_3O_{7-x}$, dependent on thickness and density. The other superconductors described have similar densities. The dashed line encloses the region of practical application with the present material.

3. Experimental Procedures

3.1 *Brush-On Method*

[0112] powder was pressed (at 20 MPa) onto a Ni (99.99% pure) sheet (~10 μm thick, 5 by 5 cm^2). The specimen was then sintered at 985 °C for 12 hr to form a bond between the metal substrate and the ceramic precursor. The specimen was naturally cooled by switching off the furnace. Finally, a layer of Bi-Pb-O slurry mixed with methanol was brushed onto the substrate before sintering at 845 °C for 100 hr to promote the formation of [2223] phase.[14]

3.2 *Plasma Spray Method*

The substrate was grit-blasted and ultrasonically cleaned. A hand-held Metco 3MB plasma spray gun was used to deposit the [0112] powder onto Co-Fe alloy substrates (1 mm thick, 1 by 5 cm^2). The spray parameters were 62 V and 500 A, with Ar and H_2 plasma gases at flow rates in Metco console graduations of 80 and 15, respectively. The Ar carrier gas (at 40) fed the powder into the flame with a flow rate of about 10 g/min, and the spray distance was about 75 mm. A layer of Bi-Pb-O mixture was brushed onto the sprayed [0112] coating, and finally the coating system was sintered at 845 °C for 72 hr.

4. Results and Discussion

The microstructure of the deposited layer was studied on an ISI 30X scanning electron microscope (SEM) equipped with a PGT energy dispersive spectrometer (EDS). The superconduct-

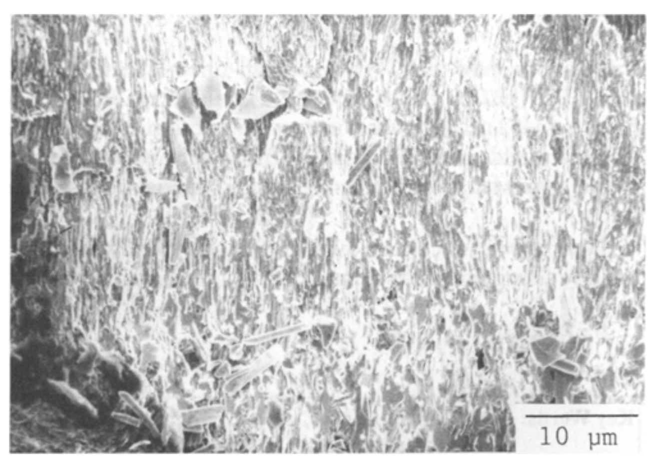

Figure 2 Secondary electron image showing aligned microstructure on cross section of fractured $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ tile made by the brush-on method.

ing transition temperature (T_c) and critical current density (J_c) of the specimens were measured resistively by the standard four-probe method. In this method, two contacts are used to pass current, while between them, two other contacts are used to detect the voltage drop across a part of the specimen. The small current passing between the latter two contacts minimizes the voltage drop due to contact resistance.

4.1 *Brush-On Method*

Strong bonding was found with no visible cracks in the [0112] after the solid-state reaction between [0112] and Ni sheet. The aligned Bi-Sr-Ca-Cu-O (BSCCO) superconducting grains, where the *a-b* planes are parallel to the sheet normal, were observed in a secondary electron image (SEI) micrograph (Fig. 2). The reaction of Bi-Pb-O with [0112] forms a superconducting BSCCO phase with $T_c \cong 110$ K. The value of J_c, measured at 77 K, is greater than 2500 A/cm^2, the measurement being limited by Joule heating at the resistive contacts.

4.2 *Plasma-Sprayed [0112] Precursor*

Feedstock [0112] powder was prepared by repeated pressing, sintering, and grinding. Several considerations determine optimum particle size. First, if the particle size is below 10 μm, then the fine particles within the powder clog the carrier feeding tube so that inadequate amounts of powder are supplied to the flame and the flow rate becomes irregular. Second, fine particles lack sufficient momentum to enter the center of the plasma, where maximum heat transfer can be obtained. Instead, the fine particles travel through the outer turbulent regions of the plasma. Third, oxide particles generally have relatively low thermal conductivities. The outer surfaces of larger particles can vaporize before heat is conducted to the inner core. Total melting does not then occur. On the other hand, finer particles may totally vaporize within the plasma flame. All of these considerations affect the deposition rate.

Thus, a careful balance between powder size, composition, and plasma parameters must be established to produce dense coatings with the molten particles. The optimum [0112] particle size was between 44 and 80 μm to produce a 0.5-mm-thick coating. The deposition rate was about 0.3 g/min. Energy dispersive spectrometer analysis revealed stoichiometric, homogeneous composition, and a typical splat-formed surface was observed (Fig. 3).

After the coated [0112] layer was reacted with the Pb-Bi-O compound, crystal alignment was observed (Fig. 4). The metal substrate, in this case a Co-Fe alloy, oxidized during the sintering reaction in air. By comparison with earlier results from the brush-on method, it was found that Ni metal is the superior substrate for this application. The T_c of the superconducting product is 105 K. The J_c of this material is expected to be similar to that measured earlier in the brushed-on film, because it has a similar microstructure.

Both of the superconducting films adhered well to the metal substrate, with no signs of spallation when viewed in the hand. However, polished surfaces, observed by SEM, showed interfacial microcracks in the brushed-on coating at the metal surface. These microcracks were not evident in the plasma-sprayed film, which are therefore presumed to have stronger adherence. A metal substrate, such as Ni, can improve mechanical strength of the film and can provide additional magnetic shielding if it is a soft ferromagnet. If mechanical strength is required, as in applications for MAGLEV, then strong adhesion is essential.

In conclusion, these experiments show that large areas of aligned superconducting sheet can be bonded to metal substrates by either brush-on or plasma-spray techniques through diffusion texture processing. The superconducting sheet is single phase $Bi_2Sr_2Ca_2Cu_5O_{10}$. The shields have great potential, because the

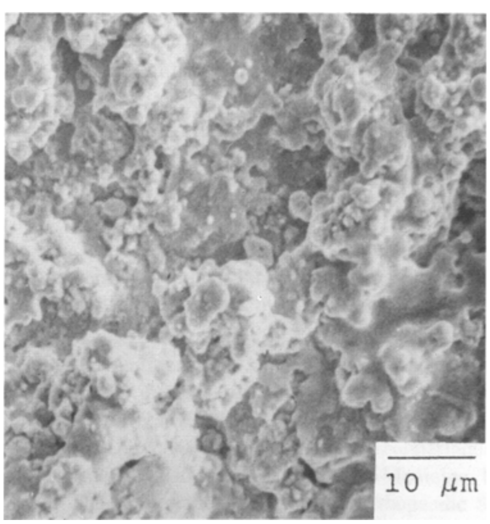

Figure 3 Secondary electron image showing the coated surface of [0112] precursor.

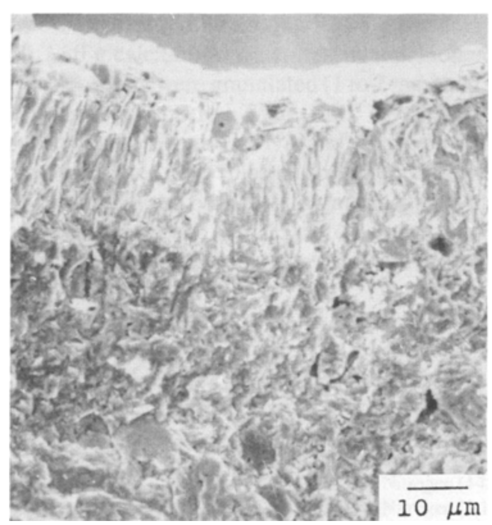

Figure 4 Secondary electron image showing the alignment of superconducting BSCCO, after the coated [0112] precursor reacted with Bi-Pb-O compound.

planes with high J_c lie normal to the sheet plane. This is the orientation, which on the Bean model,[15] gives greatest shielding in high fields. However, further studies of flux pinning in directional magnetic fields are needed to confirm the applicability of the model.

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