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Bi-Sr-Ca-Cu-O superconducting thick films deposited onto metallic substrates by Plasma Spraying

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Abstract

$Bi_2Sr_2Ca_1Cu_2O_x$ thick layers were produced by Vacuum Plasma Spray (VPS) on Ni and stainless steel substrates with Yttria stabilized Zirconia as diffusion barrier and a metallic bond layer.
After spraying the samples were melt-textured in a gradient furnace at temperatures ranging from 890°C to 950°C. The furnace was moved across the samples with velocities that varied from 10 to 3000 mm/h.
X-ray diffraction data show that the thick films are c-axis oriented and contain primarily the 2212 phase. The onset of superconductivity is around 90 K for all the measured samples while zero resistance is achieved over a broad temperature range. The relation between the degree of texturing and the resistance will be discussed.

1 Introduction

One of the potential applications of High Temperature Superconductors will be as materials for shielding enclosures in processes that require minimal magnetic field background noise[1,2,3,4,5]. In this case a high critical current density is not as necessary as the requirement of homogeneity and high density. Plasma Spray is a useful technique, already in use for ceramic materials that offers the capability of coating large areas with a high density and sufficient homogeneity[6,7,8,9,10].
Furthermore, some of the applications of the high temperature superconductors will require a large coating flexible enough, that is a superconducting coating over a metallic substrate.
We have examined the results obtained after spraying BiSrCaCuO superconductor onto Ni and stainless steel substrates.
Nickel is ferromagnetic and it will be difficult to use a superconducting coating deposited onto Ni as a magnetic shielding device. However, the thermal expansion coefficient for Ni is closer to that of BSCCO than any other metal element. Stainless steel also appears as a good candidate and since it can be tailored as to being non-magnetic it looks more promising for certain type of applications.

2 Experimental

Bi-Sr-Ca-Cu-O powders supplied by Hoechst AG had an approximate cation ratio of 3:2:1:2 for Bi:Sr:Ca:Cu. The excess Bi compensates for the loss by evaporation during melting in the plasma.
Three combinations of substrate and bond layer were used:

Nickel substrate + Ni bond layer
Stainless steel substrate + S.S. bond layer
Stainless steel substrate + Ni bond layer

The powder had an average diameter of 15-20 μm and was used without any further processing. Spraying was performed with a A-3000S Plasma Technik equipment at a spray distance of 300 mm. The chamber pressure was 200 mbar of Ar and the plasma gases used were 50SLPM Ar and 40SLPM He. The power was 32 kW. The thickness of the substrate was 0.5 mm, that of the bond layer was around 50-100 μm and the thicknesses of the superconducting coatings range from 50 μm to 200 μm.
Melt texturing was performed in a ten zone gradient furnace with a fixed gradient of 15 K/cm. The maximum temperature was varied between 890°C and 950°C. The moving velocities were changed between 10 mm/h and 3000 mm/h.
Upon completion of the melt texturing process studies of the microstructure and superconducting properties

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were carried out on these films to determine possible correlations between the crystal structure, microstructure and superconducting properties.

The layers were analyzed by x-ray diffraction with a Siemens D-500 diffractometer equipped with a Cu-k_α source. The structure (morphology) of the coatings was examined using a Hitachi S-570 SEM.

A section of the sample 8x2xt mm^3, where t is the thickness of the coating, was cut with a diamond saw to measure the electrical resistivity using the four probe method. The measurements were performed from 4 to 150 K using an ac-current source at 33 Hz with an amplitude of 1 mA. Cu leads were attached to the sample surface by using silver paint.

3 Results and discussion

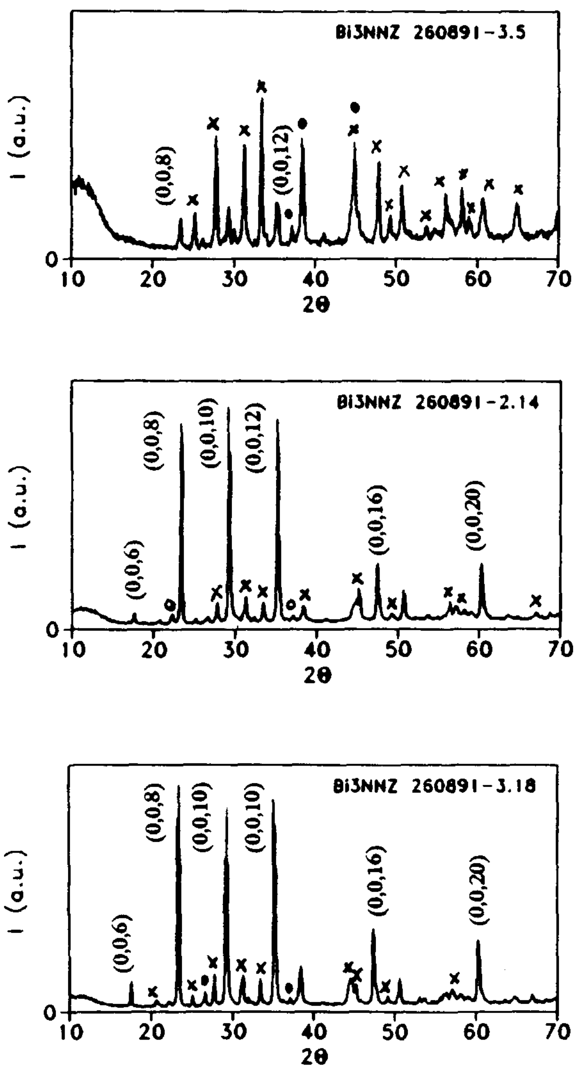

Fig 1 x-ray diffraction patterns for selected Bi coatings. (x) 2212 phase, (▵) 2201 phase, (●) Substrate and (○) Impurities

The sample notation used in this paper is as follows:

- Bi3NNZ BiSrCaCuO coating over a Ni substrate, Ni bond layer and YsZ diffusion barrier
- Bi3SSZ BiSrCaCuO coating over stainless steel substrate and bond layer and YsZ diffusion barrier
- Bi3SNZ BiSrCaCuO coating over stainless steel substrate with Ni bond layer and YsZ diffusion barrier

Fig 1a is the diffraction pattern of a non textured coating deposited onto Ni with a Ni bond layer. The diffraction pattern shows the presence of the 2212 phase plus small amounts of the 2201 phase. The relative peak intensities are in reasonable agreement to the calculated values due to the randomly oriented particles[11].

The diffraction patterns of the textured coatings are shown in Fig 1b and 1c for two typical examples. The strong intensities of the *(0,0,l)* peaks indicate that the c-axis of the material near the surface is preferentially oriented perpendicular to the substrate plane.

Analysis of these data provide an average c-axis length of 30.75 Å for the 2212 phase to be compared with the quoted value of 30.78 Å[11].

It is well known that the x-ray absorption of these high temperature superconductors is very high. A rough calculation suggests that the x-ray prove only a thin layer of the order of 20 μm, therefore it could be interesting to determine how deep the texturing extends into the coating. These measurements are now under study.

Fig 2 shows the degree of texturing versus the pulling speed using the annealing temperature as a third parameter. We have defined the degree of texturing as the ratio between the highest diffraction peak when the sample is textured, i.e. *(0,0,10)* and the peak of highest intensity when the sample is randomly oriented, *(0,2,0)*.

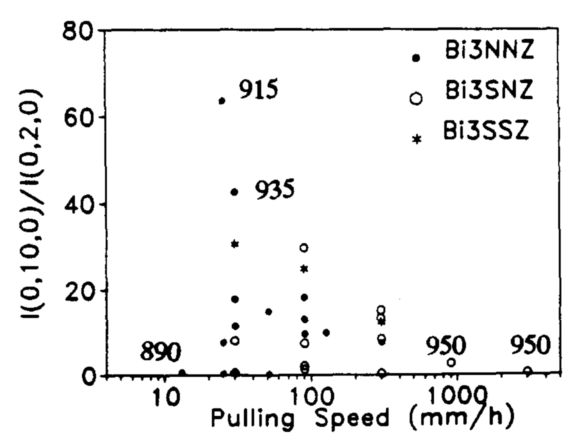

Fig 2 Degree of texturing, I(0,0,10)/I(0,2,0), versus the pulling speed with the temperature as a third parameter

We can observe that texturing is larger in the temperature range between 910°C and 925°C and for pulling speeds between 30 and 300 mm/h.

At the lowest temperatures used for annealing the coatings the layers are not completely molten[12] so that it is easier for the partial melt to recrystallize in the existing seeds situated at random, i.e. at the unmolten particles, than to nucleate new. This might explain the absence of texturing at these low temperature. On the other hand, the samples annealed at the highest temperatures have also been processed at the highest pulling speed. It then seems possible that solidification through the temperature gradient takes place too fast to let the small crystallites orient in the same direction.

Figures 3a and 3b show the resistance normalized to its value at room temperature as a function of temperature for several textured coatings. All the measured samples present a metallic behaviour down to 100 K approximately and a temperature onset for superconductivity around 92-95 K. This temperature is independent of the melt-texturing process parameters or of the substrate material.

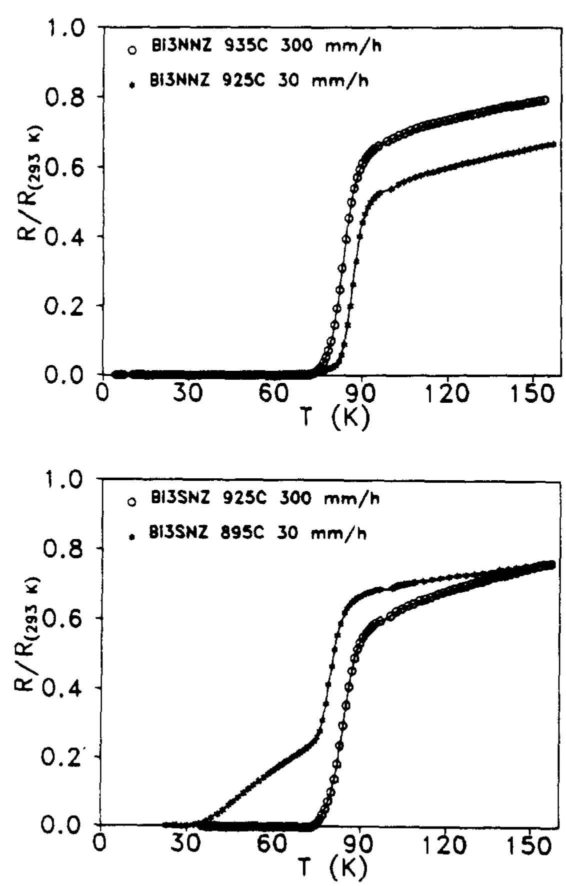

Fig 3 Resistance as a function of temperature for selected BiSrCaCuO coatings

Figure 4 presents the critical temperature, T_{c0}, defined as the temperature at which $R = 10^{-4}\ \Omega$ as a function of the pulling speed. We observe that apart from the coatings obtained at the highest temperatures there seems to be a maximum in the critical temperature when the pulling speed is around 100-300 mm/h.

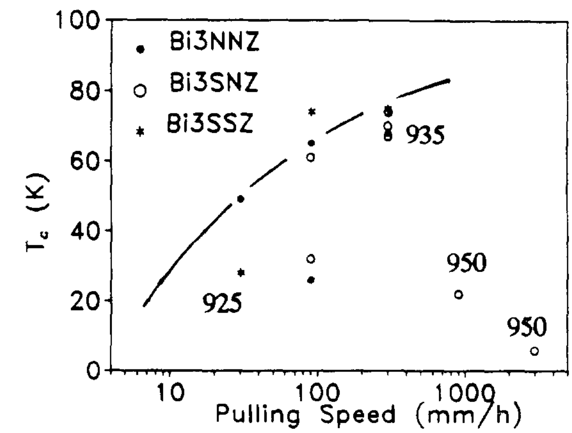

Fig 4 Critical temperature versus the pulling speed

Figure 5 shows the critical temperature versus the resistance ratio R_{300}/R_{100}. This ratio has been experimentally found to be an appropriate empirical parameter to ascertain the quality of the films. We observe that the critical temperature increases with increasing this ratio reaching a maximum value of 80 K for a resistance ratio close to 2.

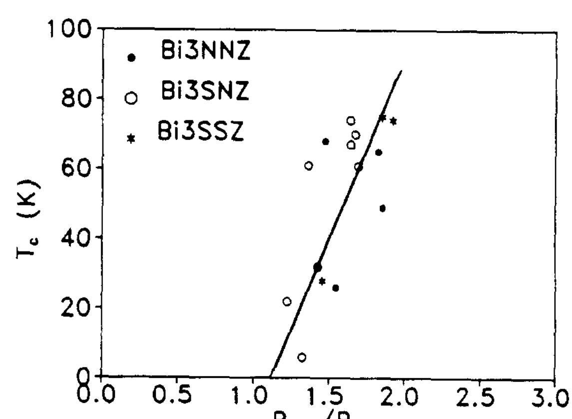

Fig 5 Critical temperature as a function of the resistance ratio R_{300}/R_{100}

Finally, figure 6 shows the critical temperature as a function of the degree of texturing. Again it is observed a tendency towards high critical temperature as the degree of texturing increases.

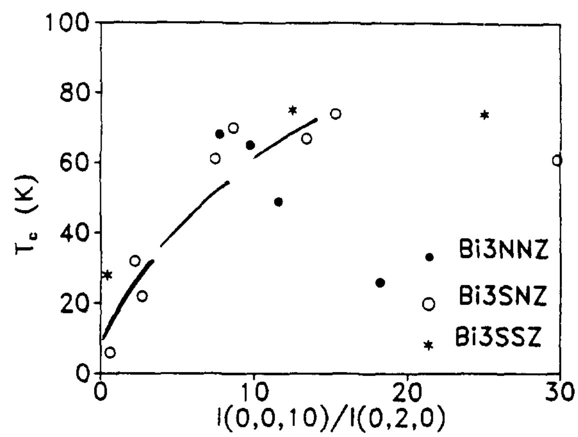

Fig 6 Critical temperature as a function of the degree of texturing

4 Conclusions

BiSrCaCuO plasma sprayed coatings have been produced which show a high degree of superficial texturing after a melt-texturing process.

The highest critical temperature, T_{c0} = 75 K, has been obtained for a coating deposited onto Stainless Steel with a Ni bond layer and a Yttria stabilized Zirconia diffusion barrier melt-textured at a maximum temperature of 925°C and with a pulling speed of 300 mm/h.

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