

Superconducting and structural properties of plasma sprayed Y-Ba-Cu-O layers deposited on metallic substrates*

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The properties of plasma sprayed Y-Ba-Cu-O coatings deposited on metallic substrates are studied. Stainless steel, nickel steels and pure nickel are used as substrate. Y-Ba-Cu-O deposited on stainless steel and nickel steel reacts with the substrate. This interaction can be suppressed by using an yttria-stabilized zirconia (YsZ) diffusion barrier. However, after heat treatment the Y-Ba-Cu-O layers on YsZ show cracks perpendicular to the surface. As a result the critical current density is very low. The best results are obtained for Y-Ba-Cu-O deposited on pure nickel; here no cracks perpendicular to the surface are observed. The critical current increases with the anneal temperature but annealing for longer than 10 h does not seem to improve the superconducting properties any further.

Keywords: Y-Ba-Cu-O; critical currents; structure

Plasma spraying is a well known technique for the preparation of coatings on ceramics and metals. Because of the large deposition rate plasma spraying enables large areas to be coated. The simplicity of the practical implementation of plasma spraying has led to considerable empirical development of the technique, but with relatively little understanding of the basic processes governing the formation of the coating¹. Recently plasma spraying has also been used for the deposition of ceramic superconductor coatings²⁻¹⁴. For a number of applications a metallic carrier would be very useful. The combination of the complicated properties of bulk ceramic superconductors, the interaction with metallic substrates and the relatively little understanding of the plasma spray process makes the development of high T_c coatings largely an empirical matter.

One of the problems encountered is the decomposition of the material during deposition. Thus a subsequent heat treatment is needed to 'regrow' the superconducting phase. The high temperature required for this leads to additional problems; for instance, a reaction takes place between the substrate and the coating. The use of a diffusion barrier can reduce this interaction problem but cannot prevent it completely, as the most commonly used

barrier materials themselves interact with the coating to some extent. Also, these interactions grow stronger at higher temperatures.

In this paper we will present some structural and superconducting properties of plasma sprayed Y-Ba-Cu-O coatings deposited on metallic substrates, with and without a diffusion barrier.

Experimental techniques

In plasma spraying a powder is fed into a plasma jet. Because of the high temperature in the plasma ($\approx 10^4$ K) the grains melt and are then deposited in the form of molten droplets on a substrate. As Y-Ba-Cu-O has a peritectic melting point the superconducting phase decomposes when it melts. Because the melt is quenched on contact with the substrate there is no time to 'regrow' the superconducting phase. The solid phase in the as-deposited layer is, therefore, a mixture of the oxides that were present in the melt.

If the molten grains stay too long in the plasma the melt becomes so hot that a significant amount of material can evaporate. As the oxides in the melt do not all have the same evaporation rate the composition of the droplets can change. This problem occurs more quickly with smaller grains, as these need less time to warm up. It is, therefore, important to limit the range of the grain size distribution in the spray powder. In order to control the composition of the deposit it is also necessary to optimize the power put into the plasma and the pressure

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and composition of the atmosphere in which it is sprayed. The results presented in this paper are obtained on coatings deposited by the vacuum plasma spraying (VPS) technique where the spraying takes place in a vacuum chamber. Using this chamber a suitable atmosphere can be selected. For our experiments argon was used with pressures varying from 20 mbar to 1 bar. The typical layer thickness of the Y-Ba-Cu-O layers is $\approx 200 \mu\text{m}$.

We used standard construction materials such as stainless steel and nickel-based steels as substrate. For good adherence of the coatings a rough surface is needed. To obtain this the substrates were sand-blasted and a bond layer with similar properties to the substrate was deposited. In some cases the superconducting coating was deposited directly on to the metallic bond layer. In other cases an yttria-stabilized zirconia (YsZ) diffusion barrier was first deposited.

The powder used for spraying was single phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powder obtained from Hoechst AG. The powder has an average diameter of $30 \mu\text{m}$. To make it acceptable for plasma spraying the powder was separated in two fractions: one with grains smaller than and one with grains larger than $10 \mu\text{m}$. The latter fraction was used for spraying.

The sinter treatment used is a two-step process. First, the oven is heated at a rate of 5°C min^{-1} to the sinter temperature and held there for a specific length of time. Then the oven is cooled down at a rate of 1°C min^{-1} to $\approx 500^\circ\text{C}$, where it is held for 10–20 h for reoxygenation. Finally, the oven is cooled to room temperature at a rate of 1°C min^{-1} . The entire treatment takes place in an atmosphere of flowing oxygen. The sinter temperature was varied between 930 and 980°C , with the duration varying from 1 to 50 h.

The structure (morphology) of the sprayed coatings was studied using a Hitachi S800 scanning electron microscope (SEM). The layers were also analysed by X-ray diffraction (XRD) to determine the phase composition and by atomic absorption spectroscopy (AAS) to determine the chemical composition. The superconducting properties measured were the resistive superconducting transition and the temperature and magnetic field dependence of the critical current using a standard four-point method. A voltage criterion of $1 \mu\text{V}$ was used for the determination of the critical currents. With a typical distance of 8 mm between the voltage contacts this gives a criterion of $1.25 \mu\text{V cm}^{-1}$. The contacts were prepared by polishing the surface of the superconductor and depositing silver pads by evaporation. Wires were connected to the silver pads using indium solder.

Results and discussion

The structure of an as-deposited plasma sprayed Y-Ba-Cu-O layer is shown in *Figure 1*. The lamellar structure is typical for plasma sprayed coatings¹. It is formed when a molten particle strikes a flat surface at high velocity. The droplet flattens to form a disc. However, the radially flowing thin sheet of liquid becomes unstable and disintegrates at the edges into small droplets. As the substrate is at a temperature well below the melting point of the droplet and the heat transfer to the substrate is very rapid, the spreading and break up of the droplet are halted by solidification. The



Figure 1 Lamellar structure of an as-deposited plasma sprayed Y-Ba-Cu-O coating

individual lamellae are therefore equivalent to splat quenched material. The composition of the as-sprayed layers was measured using AAS. The spray parameters were optimized so as to give a composition as close as possible to the superconducting phase.

After heat treatment of Y-Ba-Cu-O deposited directly on to stainless steel the superconductor shows strong interaction, very bad adherence and bad superconducting properties. Nickel steels such as inconel, nimonic and hastelloy all contain a substantial amount of chromium (Cr). For improved adherence of the superconducting coatings we used a plasma sprayed $\text{Ni}_{80}\text{Cr}_{20}$ bond layer. Y-Ba-Cu-O deposited on the Ni-Cr bond layer showed a considerable interaction with the Cr. *Figure 2* shows the SEM photograph of part of the



Figure 2 Interaction region of a heat treated plasma sprayed Y-Ba-Cu-O coating on a Ni-Cr bond layer (see text for details)

interacted region of an Y-Ba-Cu-O layer deposited on a Ni-Cr bond layer. Phase separation is clearly visible. EDX analysis of the different phases shows that the grey area at the bottom contains Y, Ba, Cu and O, roughly in the same amounts as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. As this area also exhibits a crystalline structure, it probably consists of the superconducting phase. The grey areas in the middle and the top of the photograph only indicate the presence of Cu and O. The white dendrites that are found in the middle section of the photograph contain Y, Ba, Cu and O, with an increased Y intensity and a decreased Cu intensity compared to the superconducting phase area at the bottom of the photograph. This suggests that the dendrites consist of Y_2BaCuO_5 . The grey matrix surrounding the dendrites contains only Ba, Cr and O, suggesting the presence of barium chromate. Cr is found more than $20\ \mu\text{m}$ deep in the Y-Ba-Cu-O layer after a heat treatment of only 2 h at 930°C . This interaction has been studied in some depth and the details have been published elsewhere^{15,16}.

To suppress interaction with the substrate, YsZ diffusion barriers were used. For stainless steel substrates this produced little improvement in the mechanical and superconducting properties of the coatings. However, a YsZ layer on nickel steel prevented the interaction of Y-Ba-Cu-O with Cr. Here another problem arose. After heat treatment Y-Ba-Cu-O layers deposited on YsZ diffusion barriers showed considerable cracking perpendicular to the surface. Figure 3 shows the SEM photograph of a cross-section of an Y-Ba-Cu-O layer deposited on YsZ after heat treatment. A large crack perpendicular to the surface is visible running straight through the YsZ layer. At present it is not clear if the cracks are caused by thermal stresses induced by the difference in thermal expansion between Y-Ba-Cu-O and YsZ or if the cause is already present before heat treatment.

The best results obtained to date are those with Y-Ba-Cu-O deposited on a pure nickel substrate with a nickel bond layer. Figure 4 shows the SEM photograph of a cross-section of an Y-Ba-Cu-O layer on nickel.

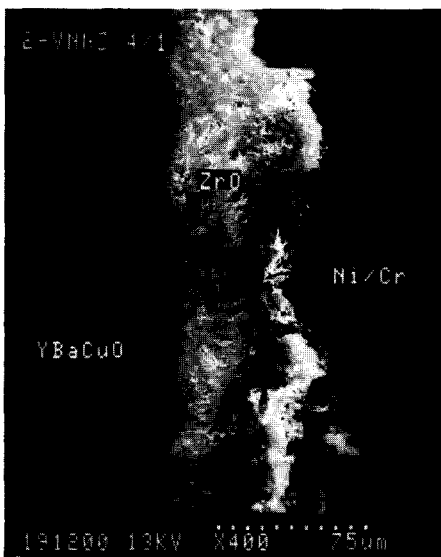


Figure 3 Heat treated Y-Ba-Cu-O on an YsZ diffusion barrier on a nickel-rich substrate (see text for details)

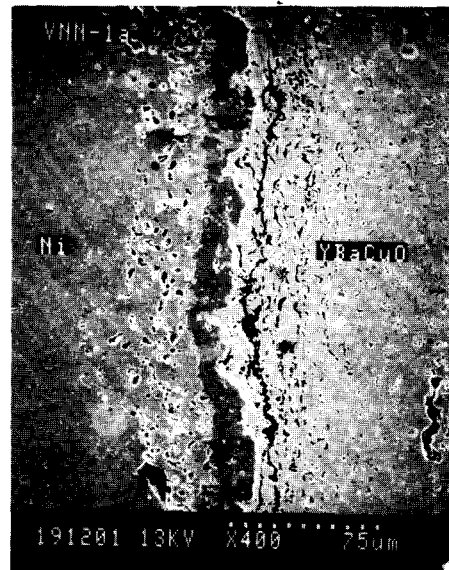


Figure 4 Heat treated Y-Ba-Cu-O on a pure nickel substrate with a nickel bond layer (see text for details)

Apart from some cracking parallel to the interface, which could have occurred during the preparation of the cross-section, no large cracks perpendicular to the surface are found. The dark region found at the interface between Y-Ba-Cu-O and the bond layer is due to the presence of nickel oxide. The nickel oxide diffuses

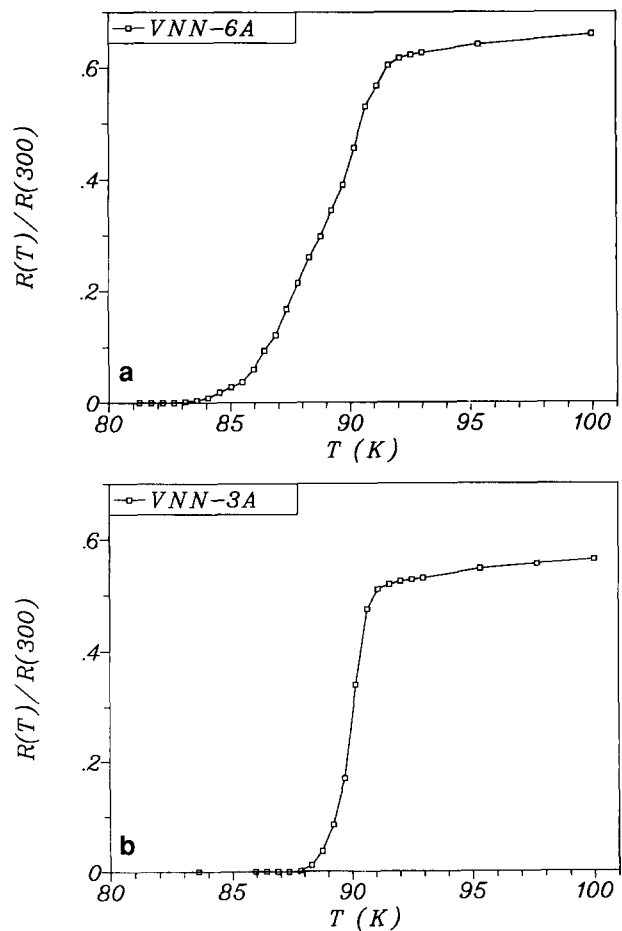


Figure 5 Scaled resistive transitions of two Y-Ba-Cu-O layers deposited on nickel annealed at (a) 950°C and (b) 980°C for 10 h

slowly into the superconductor but does not undergo significant interaction.

The resistive transition of plasma sprayed Y-Ba-Cu-O deposited on an YsZ diffusion barrier can be quite narrow. However, the critical current is always small due to the presence of cracks. The superconducting properties of Y-Ba-Cu-O deposited on Cr containing nickel steels depend strongly on the duration and temperature of the heat treatment. The optimum heat treatment is determined by the balance between the reaction between Y-Ba-Cu-O and Cr and the formation of the superconducting phase. As the interaction with Cr becomes stronger at higher temperatures, it is not possible to improve the critical current by increasing the sinter temperature.

As already mentioned above, the best results obtained in our work to date have been those for Y-Ba-Cu-O deposited directly on a pure nickel substrate with a pure nickel bond layer. In the following text we will discuss the influence of heat treatment on the superconducting properties. Only samples deposited in the same run were used in order to exclude the influence of variations in other preparation parameters on the superconducting properties.

Figure 5 shows typical resistive transitions after annealing for 10 h at 950 and 980°C. There is a clear influence of temperature on the width of the transition. The resistivity of the superconducting layers is difficult

to determine unambiguously because the Y-Ba-Cu-O is deposited directly on to a metallic substrate. If we assume that all current flows through the superconductor, we find values varying between 500 and 5000 $\mu\Omega$ cm. However, these values do not correlate with other properties of the superconductor. Therefore resistivity cannot be used to interpret the properties of the superconductor.

Figure 6 shows the influence of sinter temperature (Figure 6a) and duration (Figure 6b) on the onset temperature ($T_{c,on}$) and zero temperature ($T_{c,zero}$) of the resistive transition. The onset is independent of both the annealing temperature and duration. $T_{c,zero}$ increases with the annealing temperature but is independent of the duration (at least for times longer than 10 h). Figure 7 shows the influence of sinter temperature (Figure 7a) and duration (Figure 7b) on the critical current density, J_c , at 4.2 K. Increasing the annealing time at 980°C does not appear to influence J_c significantly. J_c does increase with the annealing temperature, just like $T_{c,zero}$.

A convenient measure of the quality of the superconductor (as it is easy to measure) is the resistance ratio at 300 and 100 K (R300/R100). Figure 8 shows $T_{c,zero}$ and J_c as a function of R300/R100. Both quantities increase with the resistance ratio.

The temperature dependence of J_c for several samples is shown in Figure 9. The shape of these curves

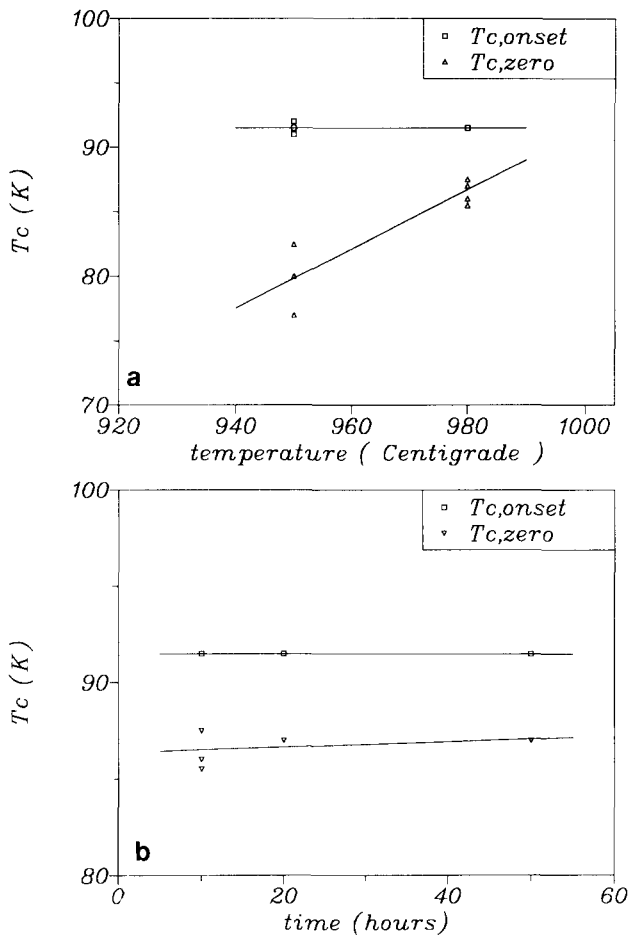


Figure 6 Influence of (a) temperature and (b) duration of heat treatment on the resistive superconducting transition (onset and zero temperature) of plasma sprayed Y-Ba-Cu-O on pure nickel

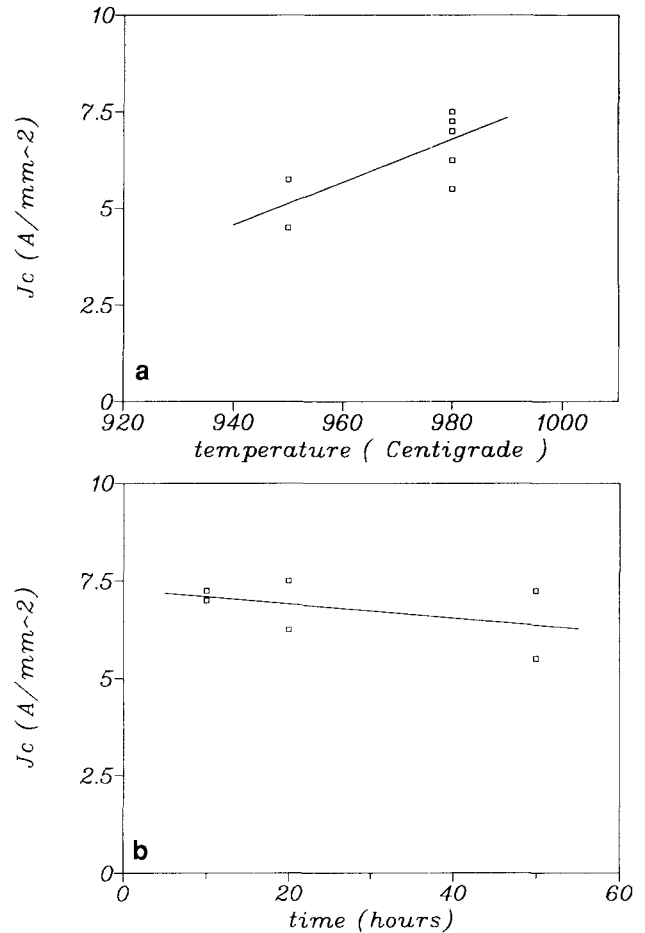


Figure 7 Influence of (a) temperature and (b) duration of heat treatment on the critical current density of plasma sprayed Y-Ba-Cu-O on pure nickel

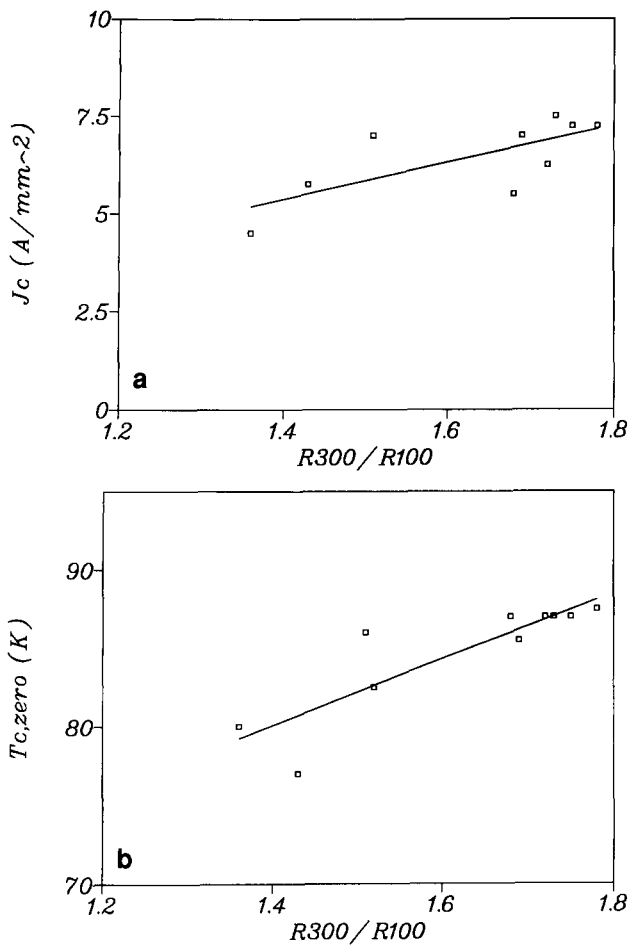


Figure 8 Correlations between the resistance ratio R300/R100 and (a) critical current density and (b) $T_{c,zero}$

can give information about the mechanism that determines the critical current density. One of the limiting mechanisms is flux flow and another is weak links between the grains. Weak link behaviour in granular superconductors is difficult to model because the properties of the weak links are unknown. This situation is better for the flux flow mechanism. According to Tinkham's flux

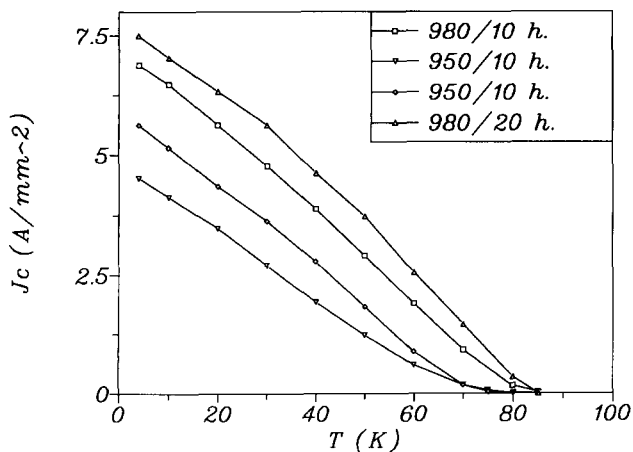


Figure 9 Temperature dependence of critical current density of plasma sprayed Y-Ba-Cu-O on nickel for the temperatures and durations indicated in the figure

flow model the temperature dependence of J_c , for T well below T_c , is given by^{17,18}

$$J_c = J_{c0}(1 - \alpha t - \beta t^2) \tag{1}$$

where $t = T/T_c$, J_{c0} is the critical current density at zero temperature and α and β are more or less constant. According to the model J_{c0} depends on the magnetic field and is proportional to $B^{-1/2}$. If this model is valid a plot of $(1 - J_c/J_{c0})/t$ against t should give a straight line with slope β and cut-off α . Figure 10 shows a typical result for plasma sprayed Y-Ba-Cu-O on nickel. The plot was made using J_{c0} and T_c as fit parameters. The temperature dependence of J_c agrees well with the flux flow model, even close to T_c . A more stringent test of the validity of the model lies in the magnetic field dependence of J_c . Figure 11 shows a double logarithmic plot of the critical current density as a function of the applied magnetic field, measured at 60 K. The result is typical for bulk sintered Y-Ba-Cu-O. From the flux flow model we would expect a slope of $-1/2$. However, the slope of the curve above 3 mT lies in the range -1.5 to -2 , indicating that J_c is limited by weak links. The hysteresis between increasing and decreasing magnetic fields is caused by flux trapped in the grains, which have a larger J_c than the transport current measured.

Conclusions

Plasma sprayed Y-Ba-Cu-O layers on stainless steel and nickel steels undergo strong interaction. A diffusion barrier is needed to prevent such a reaction. YsZ suppresses this interaction but leads to cracks perpendicular to the surface in the Y-Ba-Cu-O layer. The superconductive properties of Y-Ba-Cu-O layers deposited on nickel improve with increasing annealing temperature. On the other hand, an annealing time longer than 10 h does not improve these properties. The temperature dependence of J_c is not sufficient to determine the mechanism that limits the critical current density. The magnetic field dependence also has to be taken into account. The resistance ratio at 300 and 100 K (R300/R100) is a convenient measure of the quality of the superconducting layers as it is easy to measure.

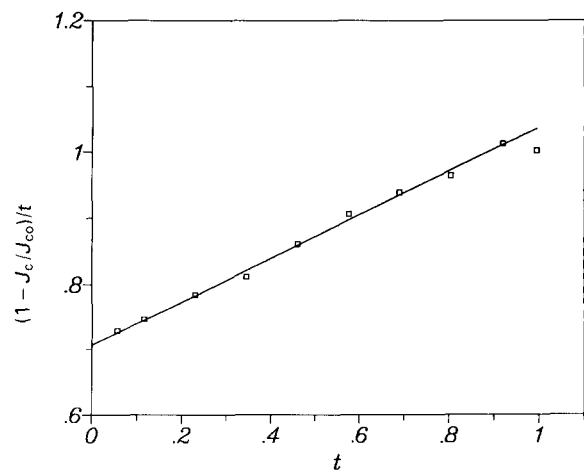


Figure 10 Typical plot of reduced critical current density as a function of reduced temperature for plasma sprayed Y-Ba-Cu-O on nickel. The squares show experimental points and the line is a fit to the data using Tinkham's flux flow model

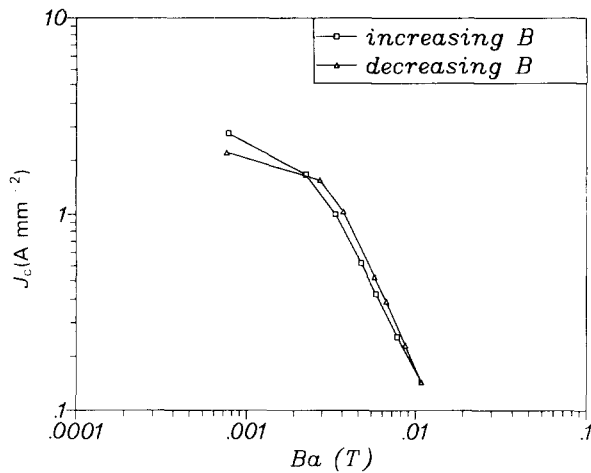


Figure 11 Typical magnetic field dependence of critical current density of plasma sprayed Y-Ba-Cu-O on nickel, measured at 60 K

Acknowledgements

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