

Flux Pinning by Platinum and Rhodium in High Temperature Superconductors

PLATINUM ADDITIONS TO YBCO THICK FILMS IMPROVE CRITICAL CURRENT DENSITIES AND SUPERCONDUCTING PROPERTIES

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Screen printed thick film technology is recognised as an inexpensive and effective means for the production of superconductors which have potential applications in the electronics and microwave device industries. Additions of the platinum group metals have been made to superconducting thick films of $YBa_2Cu_3O_{7-x}$, and these have shown significant improvements, relative to melt processed films, in both their superconducting and physical properties, particularly in their critical current densities. A possible mechanism to explain the improvements is discussed.

The field of cryogenic research was begun and greatly advanced in 1908 with the discovery by Hieke Kamerlingh Onnes (1850–1926) of the liquefaction of helium. He used this discovery to investigate the electrical resistance of metallic elements and observed that the resistance of many metals fell dramatically to zero as the temperature was reduced below the critical temperature (T_c) of the material. This was to be the criteria for a new state of matter, the superconducting state. In 1933 another inherent characteristic of the superconducting state was discovered by W. Meissner and R. Ochsenfeld. They found that a material in the superconducting state will act to expel magnetic flux from its bulk.

Major obstacles, such as the cost of liquid helium and the fact that the presence of any external magnetic field destroys superconductivity in a material, however, hindered research in and development of these materials. The dependence of the superconducting state upon temperature, the applied external magnetic field and the ability of the material to carry electrical current is illustrated in Figure 1.

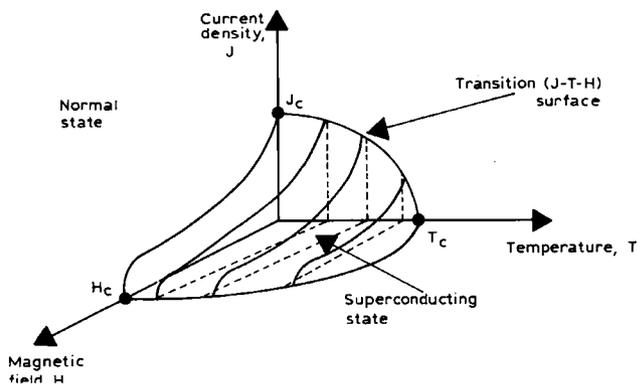
The critical current density (J_c) of a material is an extremely important parameter for electrical applications of superconductors. When a transport current is applied to a supercon-

ducting material, a magnetic field is generated in the superconductor. In Type I superconductors, if this field, coupled with external fields, exceeds the critical field of the material (H_c), then the superconductivity will be destroyed. When a magnetic field is applied to Type II superconductors, such as $YBa_2Cu_3O_{7-x}$ (YBCO) flux quanta penetrate the material as a regular array of vortices. When transport currents are then applied they act to move these vortices, thus destroying the superconductivity. The development of microstructures made of YBCO materials has enabled engineers to increase the J_c within Type II materials by introducing "flux pinning" centres into the material. Many microstructural anomalies, such as oxygen inhomogeneities, twins, stacking faults, cracks, dislocations and second phase particles, have been found to inhibit the possible motion of magnetic flux vortices in these materials.

Platinum Group Metal Additions

Platinum has already been widely exploited in the development of superconductors, even though it exhibits no superconducting properties itself. The principal utilisation of platinum has involved the use of its non-reactive properties for the processing and characterisation of

Fig. 1 The ideal critical surface between the normal and the superconducting states



ceramic superconductors in crucibles, substrates and buffer layers, or as electrodes and electrical contacts.

More recently, it has been found that processing YBCO in the presence of platinum can have a dramatic effect on the microstructure and can improve the superconducting properties of the material produced. It has been observed that platinum additions refine the morphology and distribution of the inherent precipitates of non-superconducting Y_2BaCuO_5 (211) within bulk melt processed YBCO. On refining, the precipitates become greatly reduced in size and are distributed homogeneously throughout the matrix (1). This refinement of the microstructure increases the magnetic hysteresis properties due to flux pinning, and hence increases J_c to values estimated as 2×10^4 A/cm², at 77 K and a magnetic field of 1 T. Rhodium has also been observed to give the same remarkable effect and it was suggested that the platinum group metal addition inhibits the growth of the 211 on processing.

Other work has led to the theory that platinum plays an important part in the heterogeneous nucleation of 211, which is formed by peritectic decomposition of YBCO on melt processing (2, 3). The reactions which occur between platinum and the YBCO system have also been investigated, and it was found that platinum reacts to form many compounds, including $Ba_xCuPt_xO_y$ (0412) which is considered to act as a possible heterogeneous

nucleation site for 211 (4). The synthesis of the 0412 phase and its addition to YBCO have been undertaken and improvements in properties comparable to those caused by platinum were observed (5).

However, other investigators have argued that platinum does not react with the YBCO system on heating, but dissolves into the peritectic liquid phase, thus altering the diffusion rate of yttrium atoms in the system and/or changing the 211/liquid interfacial energy (6–9). The precise mechanism for the microstructural refinement which occurs on addition of platinum is, therefore, still widely debated.

This paper will present results from the systematic doping of YBCO thick films with platinum group metals, discuss the improvements in superconducting properties achieved and suggest the possible mechanism for 211 refinement in the YBCO system.

Developments in Superconducting YBCO Thick Films

The application of bulk ceramic superconductors in the microelectronics and microwave industries is expected to be somewhat limited. However, these industries are already beginning to benefit from the introduction of different forms of these materials which have highly desirable intrinsic properties, such as extremely low resistive loss characteristics. Many research groups and industrial sources have fabricated high quality thin film materials, which have very

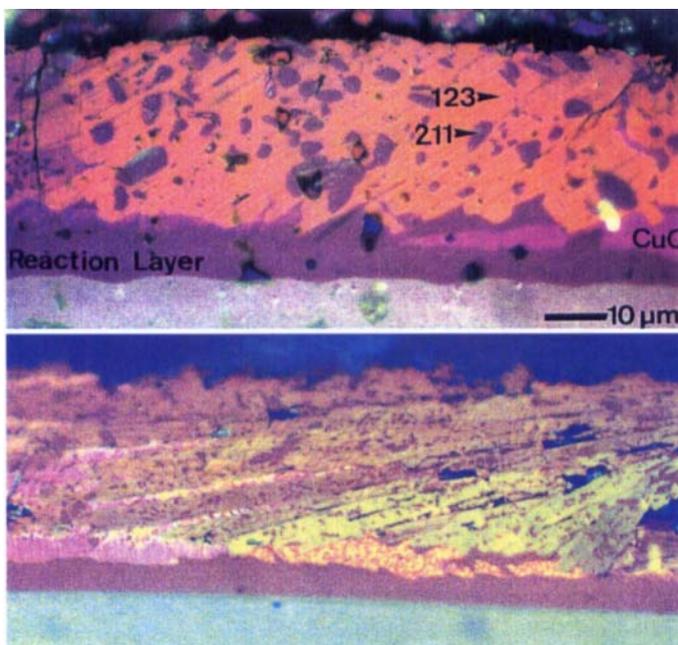


Fig. 2 A polarised light micrograph of a polished cross section of a standard thick film of YBCO showing the textured nature of the film and the irregular dispersion of large 211 precipitates

Fig. 3 Polarised light micrograph of a polished cross section of a platinum doped YBCO film showing the more homogeneous nature of refined 211 particles and the larger amount of detrimental second phases, such as CuO

high current densities and T_c values that are equivalent to those of the bulk material. However, the processing techniques used are expensive and would be very difficult to incorporate into the production of integrated circuits, etc. Thick film technology may offer important advantages in the production of large area coatings on, for example, magnetic shields and/or complex shapes, such as microwave components. These can be produced economically and with relative ease, but until recently their properties (J_c and T_c) were inferior to those of their polycrystalline bulk and thin film equivalents.

While material developments have been made in bulk YBCO by improvements in processing and the implementation of many doping additions, similar improvements in YBCO thick films have not been so dramatic. Previous studies of the superconducting properties of YBCO thick films deposited on a variety of substrates have shown that the film characteristics are highly dependant upon the substrate material, the YBCO precursor material and the processing conditions of the film. YBCO films processed on alumina substrates have yielded poor properties with T_c values around 90 K and

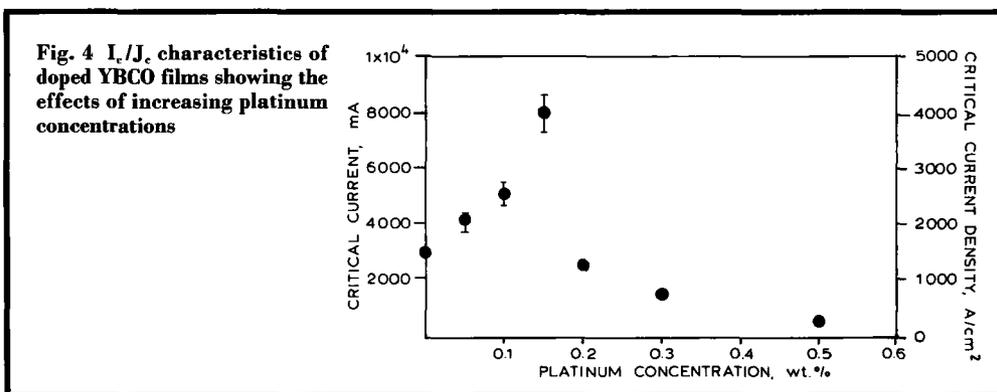
J_c values in the region of 100 A/cm^2 (10).

The properties of YBCO thick films can be significantly enhanced, however, by processing them on yttria-stabilised zirconia (YSZ) substrates, and values of $J_c = 1.5 \times 10^3 \text{ A/cm}^2$ and $T_c = 92 \text{ K}$ are easily achieved (11). Also, certain additives to YBCO films have led to increased flux pinning characteristics; for example BaSnO, additions have increased J_c values up to $2 \times 10^3 \text{ A/cm}^2$, and controlled amounts of Ag₂O have increased J_c values up to $3 \times 10^3 \text{ A/cm}^2$. However, these mechanisms are different to that of platinum group metal additions.

The work reported here was undertaken to gain an increased understanding of the influence of microstructure on the properties of YBCO thick films and the mechanisms by which platinum group metal additions change microstructure, and to improve the power handling capabilities of YBCO thick films by improving the flux pinning characteristics of the material.

Results of Experimental Work

The first series of experiments which were performed involved the addition of platinum sponge (2–250 μm) to YBCO powder prepared



by solid state calcination at 900°C for 24 hours. Previous studies had shown this YBCO precursor material was good for the production of thick films on YSZ substrates (12) and the addition of large particulate platinum sponge was intended as a feasibility study.

The addition of platinum to the YBCO material was found to have a dramatic effect upon the microstructure and the superconducting properties of the processed films. As the concentration of platinum in the system was increased from 0 to 5 weight per cent, the morphology, size and distribution of the inherent non-superconducting 211 precipitates were observed to become refined. Increased volumes of CuO were also seen within the films at 123 YBCO grain boundaries, see Figures 2 and 3.

Quantitative analysis of phases by energy dispersive X-ray analysis (EDX) in the electron microscope has shown that the larger 211 precipitates were composed of yttrium, barium, copper, platinum and oxygen in proportions consistent with the reported supposition that platinum reacts to form a 0412 compound, which then acts as a heterogeneous nucleation site for 211 precipitates (4). Electron microprobe analysis of the same sample section revealed the possible coring of platinum within the largest particles. Coring is the increase in concentration of a particular element towards the centre of a particle.

Additions of rhodium sponge were also observed to increase the superconducting properties by a similar refinement of 211

precipitates, although not to the same extent as with platinum. Maximum improvements in superconducting properties occurred for additions of 0.5 weight per cent: J_c increased from 1.2×10^3 A/cm² to 2.2×10^3 A/cm² for platinum, and from 1.2×10^3 A/cm² to 2.0×10^3 A/cm² for rhodium, both held at 77 K and zero applied field.

Following these initial developments, additions of finer particulate platinum (0.8–1.2 μm) were made to the same YBCO precursor material, in order to refine further the morphology of the 211 precipitates and to increase the superconducting properties. As the concentration of platinum in the system was increased, the texture of the films was observed to diminish considerably and the concentration of non-superconducting second phases increased dramatically. It is thought that the increased surface area of platinum, as platinum is added, and the subsequent increased reaction to form barium-rich $Ba_4CuPt_2O_{10}$, is responsible for the larger quantity of copper-rich phases seen in the films. Transport J_c values measured within these films were not observed to exceed 500 A/cm². The poor superconducting properties are primarily due to the presence of high volumes of these second phases, which inhibit the percolation of supercurrents through the films.

In order to try and prevent the generation of the detrimentally high volumes of copper-rich second phases during processing, a higher purity commercial YBCO precursor material was utilised (Rhône Poulenc 'Superamic Y123').

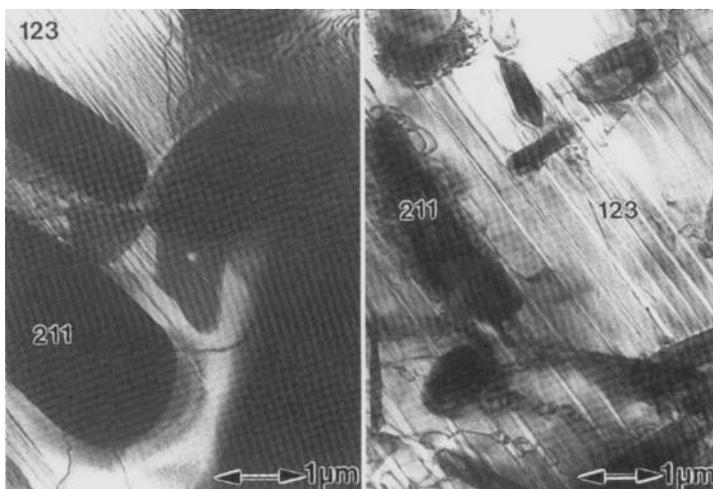


Fig. 5 Far left: TEM micrograph of a standard YBCO film, showing large irregularly shaped 211 particles. The interfaces between the precipitates and the matrix are observed to be relatively defect free

Fig. 6 Left: TEM micrograph of a platinum doped film, showing refined highly anisotropic and sub-micron spherical precipitates. A high volume of dislocations are observed at the interfaces

The superconducting properties of control films made of 'Superamic Y123' were found to be comparable to those of films processed from the YBCO precursor described earlier. Platinum additions of size (0.8–2.5 μm) made to this material were seen to refine dramatically the microstructure of the films – with only limited formation of copper-rich phases – and to improve markedly the J_c characteristics of the material. The variation in transport J_c with platinum concentration is shown in Figure 4.

The optimised doping level of 0.15 weight per cent coincides with a maximised reduction in 211 precipitate size, while maintaining relatively large 123 grains and good c -axis texture.

The addition of platinum having smaller particle sizes (0.5–1.2 μm) was observed to increase the J_c characteristics even further. Transport J_c values up to $6 \times 10^3 \text{ A/cm}^2$ were readily achieved with 0.1 weight per cent platinum. Examination of thin film specimens by transmission electron microscopy showed that the presence of increased dislocation densities was associated with refined 211 precipitates of greater surface curvature, see Figures 5 and 6. This increase in dislocation density is thought to be the main factor contributing to increased flux pinning.

As previous studies have suggested, the refinement of 211 appears to be due to the formation of 0412 nucleation sites (4); the 0412 phase was synthesised by a solid state calcination route and

as an addition to YBCO. Films subsequently processed from the doped material were found to contain highly refined and anisotropic 211 precipitates, as do platinum-doped specimens. Transport critical current densities greater than $7.0 \times 10^3 \text{ A/cm}^2$ were readily achieved with the addition of approximately 0.3 weight per cent of the synthesised 0412 nucleation phase.

Conclusions

The addition of controlled concentrations of platinum and/or $\text{Ba}_4\text{Cu}_{1-x}\text{Pt}_{2-x}\text{O}_{9-z}$ particulates to precursor powders of YBCO, subsequently used for the deposition of thick film superconductors, can effectively improve the critical current characteristics of the processed films. Microstructural observations have shown that the size, morphology and distribution of Y_2BaCuO_5 precipitates within the films become highly refined on doping with platinum and $\text{Ba}_4\text{CuPt}_2\text{O}_9$ (0412). The smaller precipitates in the doped films are observed to be relatively spherical in form, while the larger ones are acicular. An increased number of defects is observed at the 123/211 interface, associated with increased surface curvature of these precipitates. It is proposed that platinum based additions act as nucleation sites for the deposition of refined 211 particles, which in turn act as nucleation sites for dislocation networks and aid flux pinning in the films.

Acknowledgements

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Platinum Electrodes in Choline and Acetylcholine Sensor

Acetylcholine is one of the substances in mammals that is responsible for the transmission of impulses between nerves, especially in the parasympathetic nervous system (which slows down activity in the glands and smooth muscles, but increases digestion) and in the brain. Acetylcholine is released when a nerve cell is stimulated, and this in turn stimulates an adjacent nerve cell which also releases acetylcholine, and so transmits the nerve impulse. Immediately after acetylcholine has finished stimulating an adjacent nerve cell it must be deactivated by hydrolysis, into choline and acetic acid, by the enzyme acetylcholinesterase. Any interference with this deactivation short-circuits the nerve impulse transmissions and rapidly results in paralysis or death.

Choline is a strong base which is present in bile; in the brain it is combined with fatty acids or lecithin, and it regulates fat deposition in the liver. As both choline and acetylcholine are found in the central and peripheral nervous systems, they have an important role in human neuropsychological and neuropsychiatric disorders; therefore a convenient simple detector would assist in the study of diseases such as Alzheimer's, dementia and other neuro disorders.

However, the detection of these substances within the body is not easy as they are not oxidisable and do not have attached groups that can be recognised. The most common method of determination has been via high performance liquid chromatography, followed by a post-column enzymatic reaction with acetylcholinesterase and choline oxidase. Hydrogen peroxide, released by the enzymatic reaction, is detected electrochemically at a platinum electrode, or by chemiluminescence.

Biosensors, which allow the enzymatic con-

version and the electrochemical detection of hydrogen peroxide to occur in the same physical device, offer a suitable alternative. Such devices use choline oxidase/acetylcholinesterase enzymes immobilised on membranes or trapped in some other way. However, most of these sensors are not usable in high performance liquid chromatography as they do not conform to requirements of fast response time or sensitivity, or they are not adaptable to cell geometry.

Now, however, researchers at the Università della Basilicata and the Università degli Studi di Bari, Italy, have reported on an amperometric biosensor, in which the enzymatic conversion and the electrochemical detection of hydrogen peroxide occur together in a stable and highly sensitive device (A. Guerrieri, G. E. De Benedetto, F. Palmisano and P. G. Zamboni, "Amperometric Sensor for Choline and Acetylcholine Based on a Platinum Electrode Modified by a Co-crosslinked Bionzymic System", *Analyst*, 1995, **120**, (11), 2731–2736). In their detector choline oxidase/acetylcholinesterase enzymes are immobilised on a platinum electrode by co-crosslinking with the bovine serum albumin (BSA) and glutaraldehyde. The immobilisation can be adapted to the working electrode and cell geometry typical of electrochemical detectors. The electrochemical cell, of conventional design, has a platinum rod counter electrode, a Ag/AgCl reference electrode and a platinum working electrode made by sealing a platinum disc in a glass body. The co-crosslinkage with BSA produced a very thin enzymatic layer which adhered strongly to the platinum surface and was mechanically highly stable. The sensor had detection limits in the sub-micromolecular range and a response time of around 1 second.