Platinum in High Temperature Superconductor Technology

LITERATURE SURVEY SUGGESTS POTENTIAL USES

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High temperature superconducting oxides are being subjected to intensive investigation, designed to establish the basic mechanisms governing their superconductivity and to enable their electrical and mechanical properties to be optimised and commercial applications developed. Chemical composition, crystallography, microstructure and the concentration of point defects are all factors that have a crucial bearing on superconductivity. Progress in fabrication and thermal processing would elevate these high temperature superconducting oxides from laboratory curiosities to a position where widespread commercial use could be envisaged. Much has already been published on the use of the platinum group metals with the new superconductors. This article has been compiled from a search of the literature and indicates some of the applications that are, or could be, of commercial significance.

The phenomenon of superconductivity, that is the total absence of electrical resistance in a material when it is maintained below a critical temperature, has found limited commercial application. For example, body scanners used for medical imaging make use of conventional niobium-tin superconductors. However the requirement for liquid helium cryogenic cooling systems, which hold the temperature below the critical temperature, restricts the use of conventional low temperature superconductors.

Applications for superconducting materials would be expected to increase very significantly if their critical temperatures were higher, and therefore easier to achieve. Progress towards this is being made following the discovery and development of so-called high temperature superconductors. These are complex oxide materials that have critical temperatures above the boiling point of liquid nitrogen (77K). The processing of these materials, in order to improve both their mechanical and electrical properties, and hence their performance, is being studied in laboratories all over the world.

Superconductivity is dependent upon many factors including chemical composition, crystallography, microstructure and point defect concentration, and for virtually any application the stability of the superconducting property is crucially important. The superconducting phase in the new materials is thought to be inherently thermodynamically unstable, and thus any thermal treatment will play a vital role, particularly for power applications where the material would be used in bulk form.

The published literature on high critical temperature superconducting oxides amounts to tens of thousands of papers and patents, many referring to the use of platinum group metals. Indeed, over one hundred papers have been published specifically on the use of noble metals with the new superconductors, mostly on aspects of high temperature processing. One critical factor for the successful production of high temperature superconductors is the oxygen defect concentration. This is neither easy to measure nor control. The simple exclusion of oxygen during processing is not sufficient to

Principal Uses of Platinum in Superconductivity	
Containers	crucibles, substrates, coated substrates, pipes
Wires	wire substrates, grids as substrates, barrier layers in fabricating YBCO wires
Ceramic processing	powder as a densifying agent during sintering
Electrochemical	electrodes for characterisation, synthesis and oxygen control
Electrical contacts	usually sputter deposited, also thick film
Composites	barrier layers at interfaces of composite structures:- coatings on YBCO fibres in a matrix, fibres coated with YBCO in a matrix, laminated structures
Thin films/devices	barrier layers allowing use of inexpensive and common substrates, e.g. Si barrier layers for YBCO orientation/ texturing
Chemical studies	compatibility studies with superconductors

control the oxygen defects, which from thermodynamic considerations must exist in the superconducting oxide materials; but a reduction in the number of extraneous perturbing influences on the oxygen content must contribute to improved materials. Thus the use of noble metals as containers, diffusion barriers and electrical contacts, for example, can assist in improving process control.

The driving force behind research and development of these superconducting materials is their potential application in areas such as high power magnets and high speed switches for computers. At this early stage it is not clear which application areas will emerge as the dominant ones, and hence the specific technologies required cannot yet be identified. However by making comparisons with the semiconductor industry it may be possible to make some general predictions on how the technology and application areas will develop, and the roles which platinum will play.

Overview of High Temperature Superconductivity

The advent in 1987 of the new high temperature superconducting materials, such as YBaCuO (YBCO), was hailed as a major step forward in the development of superconductors. Some applications for conventional superconductors—such as high power magnets— were already developed and commercially viable, despite needing liquid helium cooling. Until 1986 the critical temperature had risen by only about 20°C since the first observations of superconductivity were made by Onnes in 1911 (1). Within weeks of the disclosure by Bednorz and Muller of a new class of superconducting material based on copper oxides containing barium and rare earth elements (2), critical temperatures as high as 100 K were being reported. For nearly two years a new high temperature superconducting material or variant was being reported weekly, but relatively little progress was made in understanding the phenomenon. In some respects, the classical superconductivity theory (3) is inadequate to describe the new superconductors, but even now there is no universally accepted replacement. Certain parts of the theory, including Cooper pairs of charge carriers, are retained by most newer theories.

The main drawback arises when attempting to explain the pairing interaction and how it can survive to much higher temperatures than the classical phonon coupling mechanism allows.

Frantic formulation, patenting and publicising of new combinations of materials with superconducting properties at temperatures above 77 K has now been replaced by an alternative approach driven by potential applications. Investigators were initially obsessed with raising the critical temperature ever higher, but it became clear that once critical temperatures substantially above 77 K had been reached, further increases would not be of great significance, unless room temperature could be achieved. Indeed, for most applications the most important parameter is the critical current—the maximum current that can be attained until the self-induced magnetic flux associated with this current causes the system to become unstable and collapse due to interactions between nearby superconducting regions. The low critical currents observed were the major barrier to commercialisation, and to a large extent this is still the case, although progress has been made. The same was true of the classical Type I superconductors, for example niobium, until Type II superconductors such as niobium-tin, were discovered.

The increase in critical current in Type II superconductors depends on the recognition of the phenomenon of flux pinning. Essentially, flux pinning ensures that the magnetic flux associated with localised high current densities of superconducting regions does not interact with the flux due to neighbouring regions in such a way as to exceed the critical magnetic flux density and thereby collapse the superconducting currents. A modern Type II superconductor is an inhomogeneous system by design, with the discontinuities serving to stabilise the system, and effectively prevent instabilities from escalating and destroying the system via a domino effect. Clearly, any region which becomes even momentarily non-superconducting will give rise to a Joule heating effect, which, if the heat is not conducted away rapidly, will result in other regions exceeding the critical temperature, losing their superconductivity, and precipitating further thermal runaway. Thus the thermal design of superconducting systems with, for example, copper sheaths around niobium-tin wire, was the key to establishing the very high critical currents now possible in conventional superconductors.

Successful commercialisation of many new materials has generally depended to a large extent on the recognition of the role of inhomogeneities. In the broadest possible sense we can regard any departure from perfect crystallinity, or a local departure from a single phase amorphous material, as an inhomogeneity. Deliberately introduced inhomogeneities have been used to enhance, and frequently stabilise, the properties of materials. Thus while extremely high purity levels are essential for growing single crystal semiconducting materials, regions deliberately doped with controlled amounts of impurities are used to produce, for example, the pn junctions which are the basis of many electronic devices. The same is true of the mechanical properties: the work hardening of metals leads to the interaction and entanglement of dislocations such that further deformation becomes progressively more difficult. Similarly, the stabilisation of grain boundaries in materials, such as ZGS platinum, gives enhanced properties. Furthermore mechanical damage on the back of silicon wafers is used to "getter" unwanted impurities from the bulk material during quenching after high temperature diffusion processes.

The role of inhomogeneities in the new superconductors is also crucial to their operation, if only because they are Type II superconductors. Different thermal treatments of these materials give rise to widely differing microstructures and electrical properties. Inhomogeneities can be regarded as real and possibly essential parts of superconducting behaviour, rather than as unwanted artefacts. In fact the occurrence of the higher critical temperatures seems to be associated with "dirty" specimens (4).

Comparison of Semiconductor and Superconductor Development

Certain parallels can be drawn between the development of semiconductor materials, as a part of the electronics industry (5), and the new superconductors which may help to predict major applications for the latter, and identify technological goals that will have to be achieved before commercialisation can take place. The new superconductors are generally semiconductors above the critical temperature, and their discovery was also driven by the same requirement for high speed solid state switching.

Another reason for comparing semiconductors and superconductors is that the required performance of the latter is only likely to be attainable, at least for the forseeable future, using techniques which give very close control over material properties, such as crystallinity and chemical composition. Single crystal growth and thin film deposition are currently able to give higher performance characteristics than, for example, ceramic processing, and the former techniques are more likely to be used in the first commercial applications. The semiconductor industry is skilled in such matters and much information is available on the techniques for depositing thin films on single crystal substrates, and so on.

There are likely to be problems in processing superconductors but, except for applications needing bulk materials, the techniques used in the electronics industry are immediately relevant. This is also true of many of the analytical methods, such as secondary ion mass spectroscopy and X-ray scanning auger microanalysis, that are necessary to achieve the required control. Thus, there is not the same learning curve, which compensates for the greater complexity of chemical composition and microstructure of the materials. Fortunately it appears that chemical purity of itself is not as essential as it is with semiconductors.

Growth in Literature on Superconductors

Superconductivity was first reported in 1911 (1). Coincidentally, the first element Onnes investigated was platinum, which does not exhibit superconductivity. Now there are over 46,000 publications on superconductors. Commercial applications for the "old" superconductors are still growing, mostly for applications requiring high power magnets, but there has been a massive upsurge in effort since 1987 when the new high temperature superconductors were discovered.

Platinum in High Temperature Superconductors

At temperatures as low as two millionths of a degree Kelvin and magnetic fields as low as two milli Gauss, no superconductivity was observed in platinum, palladium and rhodium, according to a study in 1978 (6). However, a number of alloys of platinum have been found to be superconducting, such as UPt (7) and MoPt (8), but with one possible exception these have all been low temperature superconductors. The possible exception is CuPt, which a recent patent suggests is superconducting at temperatures as high as 200K (9)! This work has not been confirmed, however, and no other reference to it has been found in the literature.

Over 100 papers and patents have been published specifically mentioning platinum in connection with high temperature superconductivity in either the title or the abstract, and in addition many more papers refer to platinum and its uses in the text. These can be divided into several main groups, in terms of: the final form of the superconducting materials, the techniques used for production and the application areas.

In this way, we can attempt to predict the application areas that may be commercially viable first, the form these superconducting materials will take, the materials processing technologies which will be most relevant and finally what the uses of the platinum are likely to be. It is assumed here that a high level of activity relates to a market need, and that such activity is likely to lead to the first commercial products.

Electrical Contacts

Good electrical contacts for superconductors are of importance, since there is no point in having high critical currents if contact resistance precludes their use because of Joule heating effects. Platinum, gold and silver are the best materials for making contact to the YBCO ceramics (10, 11), since other metallic films interact with the oxide materials to produce alloys with semiconducting behaviour. Such contacts are usually sputter deposited, but can also be formed by pressing (12). Platinum powders and pastes have been successfully used for fabricating terminal electrodes to superconducting ceramics with high critical currents (1000 A/m^2). As with semiconductors, ohmic contacts are not the only ones of use. A platinum-aluminium alloy has been used to produce a tunnel junction on a Josephson junction single crystal YBCO device (13).

Containers

An obvious use of platinum is as a containment vessel during high temperature processing of oxide superconductors. Single crystals of these materials are frequently grown in platinum or iridium crucibles (14, 15, 16), which are also used during the preparation of melts prior to tape casting and wire drawing operations (17). Oxide powders have been sintered on platinum substrates (18) or occasionally in platinum pipes, foils and capsules (19–25), and sometimes the powders are quenched on platinum plates (26). Clearly the high melting points, general chemical stability and non-magnetic qualities of the platinum group metals are ideally suited to thermal processing in oxidising environments. Containers made from materials other than platinum metals are used, frequently with a platinum coating (27).

Ceramic Processing

In addition to containers and substrates, there is another potentially significant use for platinum. A number of reports refer to the use of platinum powder as a densifying agent during sintering, and for improving the mechanical properties of the new superconductors (28–30). Indeed in one case (28), it is claimed that the superconducting properties were enhanced when finely divided platinum was used at a loading below 0.2 per cent. Platinum deposition on the oxide powders during thermal processing is also reported (31). Fired superconducting thick films have been produced from solutions containing noble metals (32). Studies of the chemical reactions of platinum group metals additions during sintering of YBCO have highlighted their importance in high temperature processing of the superconducting oxides, although an additional thermal treatment is needed for optimum properties (33).

Electrochemical Uses

In a number of publications electrochemistry is specifically involved in the preparation or characterisation of superconducting material. Platinum electrodes are extensively used both for the synthesis of material (34, 35) and during its analysis by electrochemical techniques (36, 37). Electrophoretic deposition on a roughened platinum substrate is reported (38) and various superconducting articles have been fabricated by electrodeposition (39).

There have been novel schemes for controlling the oxygen content of the materials, even during active service, using platinum electrodes and solid state electrolytes, which allow transport and control of oxygen ions. For example hot isostatic pressing in a partial pressure of oxygen (with electrically biased electrodes to control oxygen migration) has produced a mechanically strong superconductor (40). A similar process has been reported to produce a thin film superconductor device (41).

Wires

Frequent use is made of platinum wires during the processing of the oxide superconductors, because of their stability at high temperatures and their resistance to oxidation. On passing platinum wires through a melt of oxide materials, superconducting coatings are deposited (42–45); single crystal coatings of superconducting material have also been produced (46). Platinum grids have acted as supports for silicon nitride membranes prior to deposition of YBCO for in-situ studies of thermal processing by electron microscopy (47). Ceramic composites of platinum wires and oxide superconductors have been fabricated (48, 49). Fibres and ribbons of superconducting materials have been produced using the laser heated pedestal technique in combination with platinum wire (50). Platinum has also been used during the fabrication of wires of superconducting material. Platinum and platinum alloy substrates have been employed when powders or oxide layers have been melted by laser beam, and subsequently solidified, so forming wires of superconducting material (51, 52). Superconducting wires have also been fabricated from mixes of oxides and noble metal powders (53) or by lining a metal tube holding oxide powder with silver, gold or platinum powders and then sintering (54). Platinum barriers have been used around superconducting material contained in a copper sheath, when drawing wires (55, 56), and for cladding oxide preforms prior to wire drawing (57). Base metal wire with a platinum diffusion barrier and a magnesium oxide intermediate layer has been a substrate for fabricating superconducting wire (58).

Composites

Superconducting composites comprising oxides, metallic and even glass components of vastly differing shapes and structures have received much attention. The most obvious composite structure, that of a container with the superconducting oxide inside, has already been referred to above. If the container remains in place as a sheath of metal after the contents have been sintered or processed, then the resulting structure is clearly composite, with the inner core being the superconducting component. Apart from the use of platinum barrier layers for the processing of powder compacts (59, 60), such diffusion barrier coatings have been used on the inside of base metal container sheaths (61, 62).

There have been a number of composites based on platinum fibres (48, 63, 64), and dispersed metal phases giving additional mechanical strength (65, 66). Platinum coatings on superconducting oxide fibres in a solder matrix have been proposed (67). Platinum stabilisation layers for wire strips and tapes are reported (68, 69), and there have been examples of laminated structures, both planar (70) and concentric (71) with alternate layers of oxide and metal alloys surrounding a superconducting oxide core. In one instance, the superconducting core was surrounded by a glass envelope with a platinum barrier layer at the interface (72). A laminate structure with glass has also been used in the fabrication of a device (73).

Superconducting Thin Films for Devices

Probably the most commonly cited application of platinum to date has been in connection with thin film electronic devices. Platinum has been used extensively in thin film form as a barrier diffusion layer with three major objectives:

(i) to maintain and control the oxygen stoichiometry

(ii) to prevent chemical impurities diffusing from the substrate and contaminating the superconducting layer

(iii) to orient the oxide film crystallographically. Thus the commonly used substrates for devices, namely silicon, gallium arsenide, sapphire, alumina and zirconia, have all been used to support superconducting oxide films, very often with platinum buffer layers to minimise substrate interactions and provide orientation.

For optimum superconducting properties, the thin oxide film needs to be preferentially aligned with the *c*-axis vertical. Platinum buffer films have been shown to have an orienting effect on the oxide film, even for amorphous substrates such as alumina (74) or zirconia (75, 76). Although there have been many reports of single crystal strontium titanate and magnesium oxide substrates being used, thin films of these materials on amorphous substrates have also been used with platinum buffer layers to give superconducting oxide films with high critical current density (77). Clearly, the practicality of electronic devices using new superconductors will depend to a large extent on the film-substrate compatibility (78).

Conclusions

High temperature superconductors show every promise of being a commercial success despite their technical complexity. Potential application areas, currently unsatisfied, abound. Academic institutions are striving to unravel the complexities of materials and mechanisms and major companies are investing substantially in research and development. Never have so many different technologies and analytical techniques been applied to the understanding and advancement of a class of materials. This is partly the result of the proliferation of the new techniques and analytical instrumentation available, and partly because of the wide range of potential applications.

As with semiconductor materials, thermal processing will be important and there are numerous opportunities here for platinum to assist in the achievement of the desired degree of process control and material stability. The exclusion of ferromagnetic materials during processing is particularly important, as is controlling oxygen migration.

High temperature superconductivity will have an impact on power applications, such as for transportation and energy storage devices (79). However, of the many potential applications for the new superconductors, magnetic and optical detectors, satellite communications, magnetic screening, and magnet/motor technology may be among the first to be commercialised. In terms of volume of platinum, the use for superconducting magnets is likely to be the dominant one, but critical current densities will need to be substantially increased. The use of thin films rather than wire in this application warrants serious study, since in thin films the critical currents can be much larger than in bulk material.

Electronic device applications, using thin films, will probably be commercialised sooner than high temperature superconducting magnets. Specialised detectors (such as antennas) and superconducting interconnects on silicon are emerging as likely applications in the short to medium term. In the long term, the high speed switching application may compete with advances in optical computing for the next generation of electronic devices.

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