HUNGARIAN JOURNAL
OF INDUSTRY AND CHEMISTRY
VESZPRÉM
Vol. 42(1) pp. 39–42 (2014)

INVESTIGATION THE PROPERTIES OF Y-BA-Cu-OXIDE SUPERCONDUCTORS PREPARED BY HYDRAULIC PRESSING AND MOLDING

ANNA MALOVECZKY,✉ MARGIT ENISZ-BÓDOGH, AND TAMÁS KULCSÁR

Institute of Materials Engineering, University of Pannonia, Egyetem str. 10., Veszprém, 8200, HUNGARY
✉E-mail: anna.maloveczky@gmail.com

Levitation applications of superconductors require the fabrication of bulk ceramic superconductors with special shapes. The conventional hydraulic pressing is not suitable for the production of superconductors with complicated forms, so we have applied slip casting to shape bulk superconductors. Superconducting powders with different $YBa_2Cu_3O_y$ (123) and Y_2BaCuO_5 (211) phase content and different (Pt, Pb, Ce) additives were prepared by solid-state reactions. The non-superconducting (211) particles can be considered as flux pinning centres; thus the magnetic properties can be influenced by their amount and particle sizes. The addition of a few weight percent of dopant in the nominal composition can modify the particle size and distribution of the (211) grains. We have investigated and compared the phase compositions, morphologies and magnetic levitation forces of bulk superconductors formed by hydraulic pressing and moulding. The shielding abilities of a moulded superconductor were simulated with the COMSOL Multiphysics 4.4 software.

Keywords: YBCO superconductor, moulding, shielding, modelling

Introduction

The use of superconductivity is promoted by the need for stable high magnetic fields. The high-temperature superconductors are attractive for engineering applications, such as contactless superconducting bearings, trapped field magnets, levitation trains, fusion reactors, and NMR spectrometers. An important application of superconducting magnets is the Magnetic Resonant Imaging (MRI). Superconducting magnetic shielding can be used simultaneously to protect the personnel and other medical equipment from the strong magnetic fields produced by an MRI system.

The relative magnetic permeability of Type I superconductor is theoretically zero, which means when we use it for shielding, it expels the magnetic fluxes from itself. The high-Tc superconductors can also be used for shielding sensitive electronic devices from external electromagnetic fields. Due to the MEISSNER effect [1,2], it is sufficient to surround the volume to be protected by a thin film. For quasi-monocrystalline films of YBaCuO thickness of 1 μm would be sufficient for virtually perfect shielding. A granular ceramic layer would require a larger thickness, but in all cases the thickness and weight of the superconducting shields would be much less than those of magnetic materials providing a comparable effect. For these applications of high-Tc superconductors outstanding magnetic properties and special shapes are required.

The scientific literature suggests two main ways for improving the magnetic properties of superconductors that are structure damaging or doping [3–9]. Both methods work the same way, such as by increasing the amount of pinning centres (such as 211 phase) in the superconducting (123) material and decreasing the size of these centres by addition of different dopants. The damaging method could be done by ion or neutron radiation to destruct the bulk of the material and generate faults.

Preparation of high-Tc superconductors with special, complicated forms is a particular challenge due to their brittle nature. Slip casting, namely pouring low viscosity water-containing slurry into moulds is the oldest ceramic forming method for production of special shapes. For superconductors slip casting of shapes is also possible although the use of water as liquid phase is not optimal due to hydrolysis and other reactions. Another preparation method for ceramic superconductors is tape casting of viscous slurry containing ceramic particles in organic solvent [10].

Materials and Methods

In this work, Y-Ba-Cu-oxid-based superconductive powders were prepared with different 123/211 phase content and different (Pt, Pb, Ce) additives. Shaped bulk superconductors were produced from these powders with hydraulic pressing and moulding. The effects of these parameters were investigated on the phase compositions, morphologies and magnetic levitation forces of the sintered bulk superconductors.

For modelling the superconductor as a shield in different geometries, COMSOL Multiphysics 4.4 software was used that provides a simulating and

Table 1: The peak intensity of the crystalline phases

	Samples		Peak intensity, counts				
	Binder	Solvent	123	211	011		
					$BaCuO_2$	CuO	$BaCO_3$
			d=2.72 Å	d=2.99 Å	d=3.05 Å	d=2.52 Å	d=3.72 Å
1.	polyvinyl formal	dioxane	4460	1122	562	956	-
2.	metylan	dest. water	2952	919	737	725	-
3.	metylan	ethanol	1477	765	679	459	-

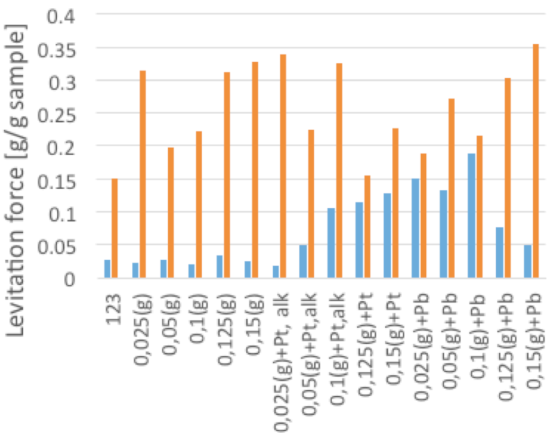

Figure 1: Levitation forces of the heat treated samples

modelling environment using the finite element method. Instead of the original AC-DC module of COMSOL, a module by ROBERTO BAMBILLA was used, which was developed for modelling YBCO superconductors.

Results and Discussions

Samples Made by Hydraulic Pressing

The superconducting samples were prepared by using Y_2O_3, $Ba(OH)_2{\cdot}8H_2O$ and CuO. The latter was obtained by the calcinations of $Cu(OH)_2{\cdot}CuCO_3{\cdot}nH_2O$ with a specific surface area of 18.4 m^2 g^{-1}, $PtCl_4$, PbO and $Ce(NO_3)_3{\cdot}6H_2O$ starting materials. The 123:211 molecular ratio of the nominal compositions was changed in the range of 1.00:0.15. Samples were prepared without additives as well as with 2.0 wt% Ce + 0.5 wt% Pt, and 2.0 wt% Ce + 0.5 wt% Pb dopants.

For sample preparations, barium-hydroxide was ground in agate mortar, but in some cases the pulverization and grinding was made in the presence of alcohol. The mixture of raw materials was homogenized by thoroughly mixing with alcohol in an agate mortar and compacted into disks of 25 mm × 3mm by hydraulic pressing at 70 MPa. Firstly, the samples were pre-reacted at 960 °C for 4 hours to obtain the desired (123+211) phases by solid-state reaction. The heat-treated samples were ground and the powders were pressed into pellets by hydraulic pressing using a pressure of 70 MPa. The relatively dense structure was obtained by liquid state sintering at 1010 °C peak temperature for 6 hours in oxygen atmosphere [11].

The levitation force of the samples after the heat treatments is shown in *Fig.1*. As described in the literature, we also found that the levitation force shows an increasing trend with increasing amount of 211 phases. In the case of Ce+Pt and Ce+Pb dopant containing samples higher levitation forces can be obtained after the first heat treatment at 960 °C. It is notable that the samples prepared from barium hydroxide ground in the presence of alcohol showed improved magnetic properties.

Samples Made by Moulding

Part of the pre-reacted at 960°C ground samples were used for shaping superconductors by moulding. Previously, superconductive slurries were prepared with different organic liquid additives and those were burnt out during the annealing. From these materials only a few were good enough for further studies. Samples providing a proper cohesion and appearing to be homogeneous were selected for future analysis. After heat treatment, X-ray diffraction analysis was used to study the phase composition changes caused by addition of organic materials for deciding if any of the dopants has a negative influence on the superconductor properties.

As shown in *Table 1*, the metylan reduces the amount of the superconducting phase (123) and this leads to the tetragonal, non-superconducting structure. Polyvinyl formal did not have a negative influence on the formation of 123 phase. Thus, the polyvinyl formal binder was chosen with dioxane for further experiments. With respect of ideal concentrations, it was found that 1 wt% of polyvinyl formal/dioxane must be added to the superconducting powders to obtain a slurry with a density of 2.4 g cm^{-3}, which was dense enough, but still can be poured. The second step was to find the appropriate mould form.

Different types of materials were investigated, such as stainless steel, glass, plastic, gypsum, and silicone rubber. The prepared slurries stuck to most of these materials rendering them useless for moulding with the exception of silicone rubber as sample could be removed perfectly. Using this type of moulds we can make superconductors with complex geometry.

The moulded samples were heat treated at the same program as used for hydraulic pressed samples. The moulding technique applies no pressing thus provides a porous structure. However, the pores can lead to poor superconductor properties. To decrease the porosity melt-producing dopants were applied. Ag and Pb with Ce proved to be good in the case of hydraulic pressed samples.

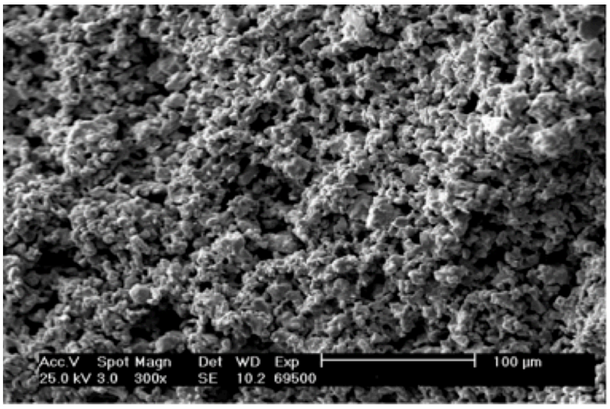

Figure 2: SEM micrograph of the moulded sample ground conventionally

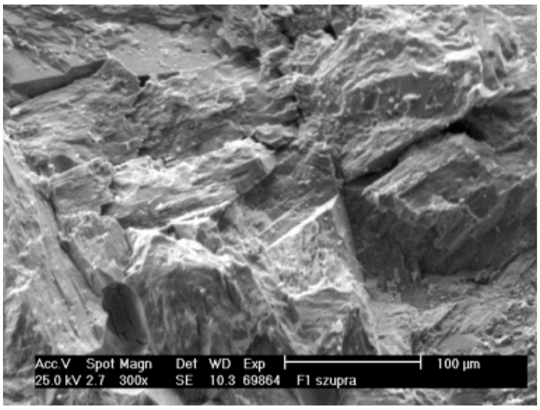

Figure 3: SEM micrograph of the molded sample ground in alcohol

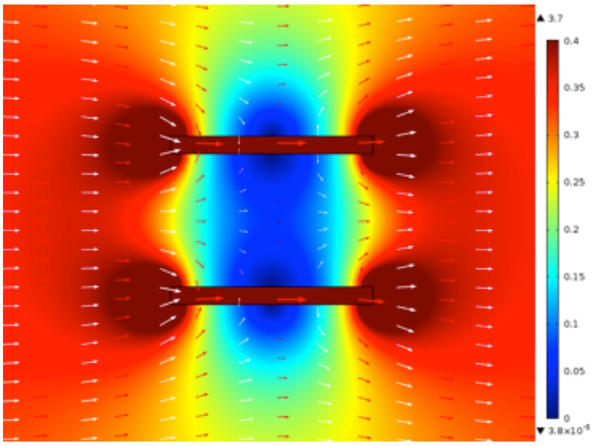

Figure 4: Simulation of iron shield

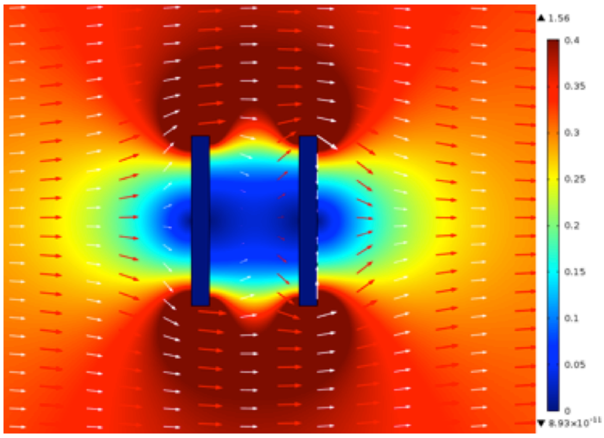

Figure 5: Simulation of superconductor shield

It was found that only in the moulded samples prepared from barium hydroxide ground in alcohol provide enough melt for efficiently fill the pores. The use of dopants alone toward this goal was not sufficient. Furthermore, with this grinding technique, the peritectic temperature of the superconducting phase (123) decreased, which allowed for a more economical heat treatment. It can be proposed that this grinding resulted in particle size reduction of barium hydroxide and the higher specific surface area leading to higher reactivity. In this case bulk superconductor with higher density can be obtained, which has an oriented, large plate-like 123-crystalls containing structure *(Figs.2* and *3)*.

Modelling YBCO as Magnetic Shield

YBCO can shield from magnetic fluxes due to the MEISSNER effect. It works the opposite way than the commonly used ferromagnetic materials, which means that superconductor expels the magnetic fluxes from itself, while iron collects them. Using the COMSOL Multiphysics 4.4 package, the shields of iron and superconductor were compared in *Figs.4* and *5.*

The shielding ability of the superconductor is comparable with iron, and even better. It has the advantage that in alternating magnetic field it does not get heated. The ferromagnetic materials shield poorly in too small and too big fields because they have saturation flux density. Superconductors are being used as shields in various devices [12–16].

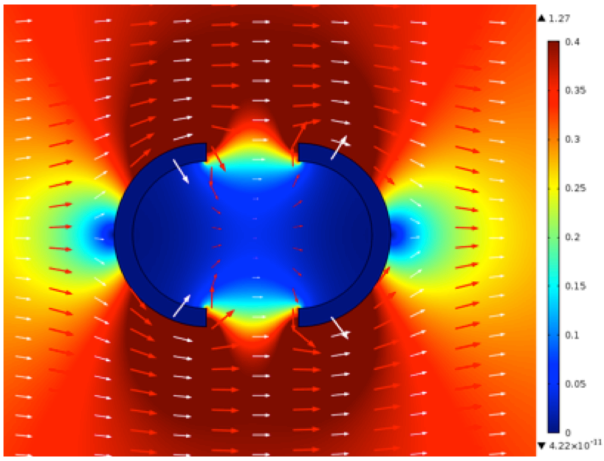

Figure 6: Simulation of shielding for sphell geometry

With a geometry shown in *Fig.6*, very sensitive magnetic devices could be fully shielded and *vice versa* the environment could be protected from a device, which induces strong magnetic field. With the shape in *Fig.7*, for example a skull could be protected in the MRI in case of presence of metal implants in the head.

Theoretically moulding could be used to prepare these shields. It would be cheaper and thin layers could be made, thus more economical wall could be produced by a few thin layers.

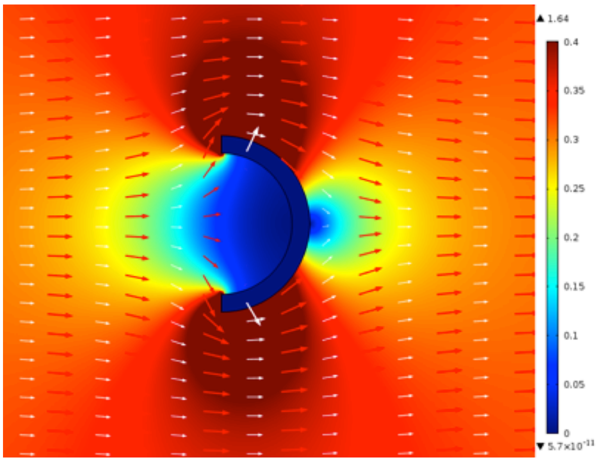

Figure 7: Simulaton of shielding using a semi-sphell geometry

Conclusion

In the case of the hydraulic pressed pellets, the results confirmed those from the literatures. Improved magnetic properties were noticed with the increasing of the 211 phase content. This was further enhanced by the presence dopants. It was found that Pb performs as good as Pt or even a little bit better, which is preferred due to the price of Pt. The grinding of barium-hydroxide in the presence of alcohol provided a denser structure and more melt phase leading to better superconducting properties. Furthermore, it seems that this method decreases the peritectic temperature of the superconducting 123 phase. The homogenization needs to take place after grinding in alcohol to be effective.

The adequate liquid-to-material ratio to make a slurry with 1 wt% polyvinyl formal in dioxane and the ideal moulding form of silicone rubber were determined. This allowed for making complex shaped superconductors. The melt-producing dopants cannot reduce the porosity enough to sufficiently improve the levitation force. Alternative heat treatment programs with slow annealing up to 500 °C, while all of the organic materials burn out, can avoid the cracks in the structure. Application of vacuum during the moulding can also be useful, since it can eliminate trapped air bubbles from the mass.

Simulations carried out using Comsol Multiphysics 4.4 software indicated YBCO being a good shielding material. Utilization of complex geometries, sensitive devices can be protected, such as skull protection during MRI measurements.

REFERENCES

[1] TAKASH M., TOMIOKA Y., MIYAUCHI T., SATO S., MURAI A., IDO T., WAKITA K., TERADA H., OHKIDO S., MATSUBARA M.: Characterization of a large-scale non-doped $YBa_2Cu_3O_7$-x superconductor prepared by plastic forming without high-pressure molding, J. Amer. Ceram. Soc. *2007*, 90(7), 2032–2037

[2] EVETTS J.: Concise Encyclopaedia of Magnetic and Superconducting Materials, Pergamum Press, Oxford, *1992*, pp. 532–533

[3] MONOT I., LEBLOND C., MARINEL S.M., DESGARDIN G.: Precursor and microstructure control for melt texturing of high-Tc superconductive YBCO ceramics, Development of high-temperature superconducting alternators combining rotating and levitating principles, Russian Academy of Science, Saint-Petersburg, *2002*, pp. 27–45

[4] SHLYK L., NENKOV K., KRABBES G., FUCHS G.: Melt-processed YBCO with Pt or Ce additions: comparison of pinning behaviour, Physica C *2005*, 423, 22–28

[5] RICHES J.D., ALARCO J.A., BARRY J.C.: Effects of PtO_2 and CeO_2 additives on the microstructures of the quenched melts of Y–Ba–Cu–O materials Physica C Superconductivity, *2000*, 336, 43–56

[6] LEBLOND C., MONOT I., PROVOST J., DESGARDIN G.: Optimization of the texture formation and characterization of large size top-seeded-melt-grown YBCO pellets, Physica C, *1999*, 311, 211–222

[7] HARDY V., SIMON C., PROVOST J., GROULT D.: Pinning forces in Bi-2212 single crystals irradiated by 6 GeV Pb ions, Physica C, *1993*, 206, 220–226

[8] WESCHE R.: Magnetic relaxation and flux pinning in $YBa_2Cu_3O_7$ a high-Tc oxide irradiated by 5.3 GeV Pb ions, Physica North-Holland C *1992*, 190, 289–298

[9] HORVAT J., WANG X.L., DOU S.X.: Vortex pinning in heavily Pb-doped Bi2212 crystals Physica C *1999*, 324, 211–219

[10] GRADER G.S., JOHSON D.W.: Forming methods for high Tc superconductors, Thermochimica Acta, *1991*, 174, 239–251

[11] KOMLAI K.: Investigation of the the properties of the incongruent melting reaction of YBa_2Cu_3O-y superconductor phase, M.Sc. Thesis, University of Pannonia, *2013* (in Hungarian)

[12] TAVERNIER S.P.K., VAN DEN BOGAERT F., VAN LANCKER L.: The design of a magnetic shielding for an array of photomultipliers in a strong external field, Nucl. Instrum. Methods, *1979*, 167, 391–398

[13] BITTER T., EISERT F., EL-MUZEINI P., KESSLER M., KINKEL U., MEMT E., LIPPERT W., MEIENBURG W., WERNER R.: A large volume magnetic shielding system for the ILL neutron-antineutron oscillation experiment, Nucl. Instrum. Methods Phys. Res., *1991*, A309, 521–529

[14] TRIPATHI A., VEDAVATHY T.S.: Electromagnetic shielding using superconductors, Pergamon Press Ltd, Oxford,Vol. 2, No. I, *1994*, pp. l–5

[15] SPILLANTINI P.: Active shielding for long duration interplanetary manned missions, Adv. Space Res., *2010*, 45, 900–916

[16] YUSUF S.M., OSGOOD III R.M., JIANG J.S., SOWERS C.H., BADER S.D., FULLERTON E.E., FELCHER G.P.: Magnetic profile in Nb/Si superconducting multilayers, J. Magnet. Magnetic Mat., *1999*, 198–199, 564–566