$YBa_2Cu_3O_{7-x}$ MELT-TEXTURED THICK FILMS DEPOSITED ON ALUMINA-TOUGHENED ZIRCONIA SUBSTRATE

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Melt textured superconducting YBCO films with an approximate thickness of 50-120 μm and $T_{c(0)}$ values ranging between 86.5 and 88.5 K have been prepared on polycrystalline yttria-stabilized zirconia substrate, toughened by 20 wt.% Al_2O_3. Between the substrate and superconducting film an interface layer was formed. Their AC and DC magnetization characteristics were measured and the values of the magnetic penetration field H_{p1} were estimated. The penetration field H_{p1} of 2.7 kA m^{-1} was obtained for the thinner film deposited with a higher spin coating rate, while for the thicker film deposited with a lower spin coating rate H_{p1} = 4.4 kA m^{-1}. Repeated temperature cycling between room and liquid nitrogen temperatures and corresponding measurement of the magnetization hysteresis curves reveal the significant decrease of the grain superconducting properties caused probably by arising cracks.

INTRODUCTION

High T_C superconductors prepared by a partial melt-processing are known to have superior properties in comparison with those prepared by a sintering method. However, when these materials are prepared in form of thick films, the presence of a liquid requires substrates, which should be very dense and the chemical reactions between the substrate and melt should not affect the properties of the superconductor.

Highly textured $YBa_2Cu_3O_7$ (YBCO) thick films prepared by a controlled peritectic reaction process are highly promising in electronic industry. They show a great potential for a production of large area materials with various shape [1]. However, for fabrication of such materials only a very limited number of substrates can be used [1-3]. The reactivity of the liquid, which is formed above the peritectic melting temperature of YBCO, towards the substrates is very high. In consequence, the superconducting phase is deteriorated. The most of the commonly used substrate materials for thin films are unsuitable for a preparation of thick layers owing to generally higher temperatures required for a processing of thick films [1]. The preferred substrate for a preparation of thick YBCO films is yttria-stabilized zirconia (YSZ) [2]. On the other hand, Al_2O_3 substrates are not suitable for melt-texturing of YBCO, because of their high reactivity towards the Ba-CuO melts. It is well known that the Al_2O_3 addition to yttria stabilized zirconia yields composites with improved strength and toughness [4]. This ceramic material is widely used for construction purposes. However, its application as a substrate for superconducting films has not been reported yet.

In this contribution a series of YBCO films with an approximate thickness of 50-120 μm was prepared by a spin-coating method using the YBCO pasta. Polycrystalline yttrium stabilized zirconia toughened with 20 wt.% Al_2O_3 addition (YSZ/Al_2O_3) was used as a substrate.

EXPERIMENTAL

The 3 % yttria stabilized zirconia toughened with 20 wt.% Al_2O_3 addition (YSZ/Al_2O_3) purchased from TOSOH, which was sintered at 1650°C for 4 h, was used as a substrate. The substrates pressed to pellets were sintered to 90-95 % of theoretical density.

The pasta for the dip-coating deposition of the superconductor was prepared by milling 15 g of commercial YBCO powder (Solvay, medium particle diameter 2.6 μm) together with 6 ml of terpineol (Roth) for 40 min at 60 rpm in zirconia ball mill.

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The deposited films were prepared by means of spin coating of a pasta using spin rates of 400 and 700 rpm. The samples were consecutively dried in air at 200°C. The heat treatment included a heating in air to 1050°C, holding at this temperature for 6 min and cooling to 900°C (with a rate of 300°C/h). At 900°C the furnace atmosphere was changed to oxygen and the samples were cooled down to 550°C (with a rate of 146°C/h). The films were then oxygenated at 550°C for 4 hours and cooled down to room temperature.

The obtained samples were characterized by four point T_C measurements, X-Ray Diffraction patterns, Scanning Electron Microscopy and EDX analysis. The AC and DC magnetization characteristics were measured by means of a second order SQUID gradiometer, employing the compensation method after zero-field cooling at 77 K in magnetic fields ranging from 10^{-1} to 10^5 A/m. For AC magnetization measurements a frequency of 0.1 Hz was used. Also, the effect of the thermal cycling between the room temperature and the boiling point of liquid nitrogen on the magnetization characteristics was investigated.

RESULTS AND DISCUSSION

Superconducting films with $T_{c(on)}$ of 91.5 K and $T_{c(0)}$ values ranging between 86.5 and 88.5 K were prepared on 3 % yttria stabilized zirconia substrate toughened with 20 wt.% Al_2O_3 addition (figure 1). According to the X-ray diffractograms the layers show good texture and a ratio of the intensities of the (*005*)/(*103*) diffractions is strongly increased in comparison with a powder YBCO sample. The samples deposited at lower deposition rate of 400 rpm show a more developed texture in comparison with those deposited at 700 rpm (figure 2).

The scanning electron microphotographs of a cross sections show that the thicker samples, deposited at lower spin rate, show better texture, and have a denser microstructure than the thinner films (figures 3 and 4). According to the EDX analysis of the cross section, between the substrate and the superconducting film an intermediate Cu, Zr and Ba rich layer was formed (exp. 7 wt.% CuO, 54 wt.% BaO, 37 wt.% ZrO_2, theor. for $BaZrO_3$ 55 wt.% BaO, 45 wt.% ZrO_2). In this layer also Y and Al were present, however, in low amounts. It is in accordance with ref. [6], where it has been reported that the reaction between the molten YBCO system with the zirconia substrate leads to a formation of $BaZr_{1-x}Cu_xO_{3-y}$ intermediate layers. From the above results it can be estimated that the effective thickness of the superconducting film in samples deposited with a higher spin coating rate is approximately 50 µm (figure 3), while the films coated at 400 rpm have a thickness of approximately 120 µm (figure 4). The superconducting film layer consists of Y, Ba and Cu (exp. 30 wt.% CuO, 19 wt.% Y_2O_3, 47 wt.% BaO, theor. for YBCO 37 wt.% CuO, 17 wt.% Y_2O_3, 47 wt.% BaO) and further of small admixture of Zr (the molar ratio Cu : Zr = 0.01). The Zr admixture can result from the some abrasion from milling balls during the preparation of pasta. An other explanation would be a diffusion of Zr from the substrate. On the other hand, the EDX analysis did not show any presence of Al in the superconducting film.

The SEM microphotographs of the surface show the microstructure of molten ceramics (figure 5) and also a presence of spherulites [2]. On some microphotographs of a thicker film a presence of cracks is also evidenced (figure 6).

The magnetization hysteresis loops of two samples are compared in figure 7. The obtained superconducting films are without noticeable intergrain weak links. From virgin magnetization measurements considering the

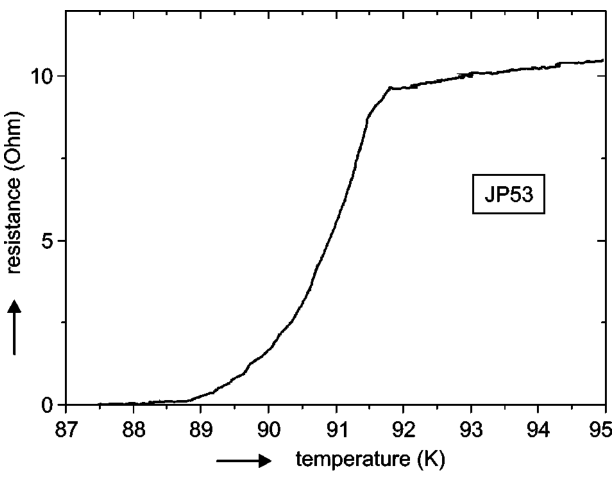

Figure 1. R-T dependence of a film deposited on YSZ/Al_2O_3.

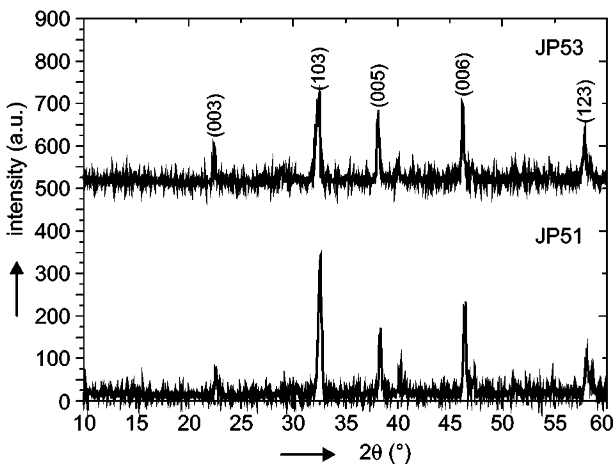

Figure 2. X-Ray diffractograms of films on YSZ/Al_2O_3; upper: deposited at 400 rpm, lower: deposited at 700 rpm.

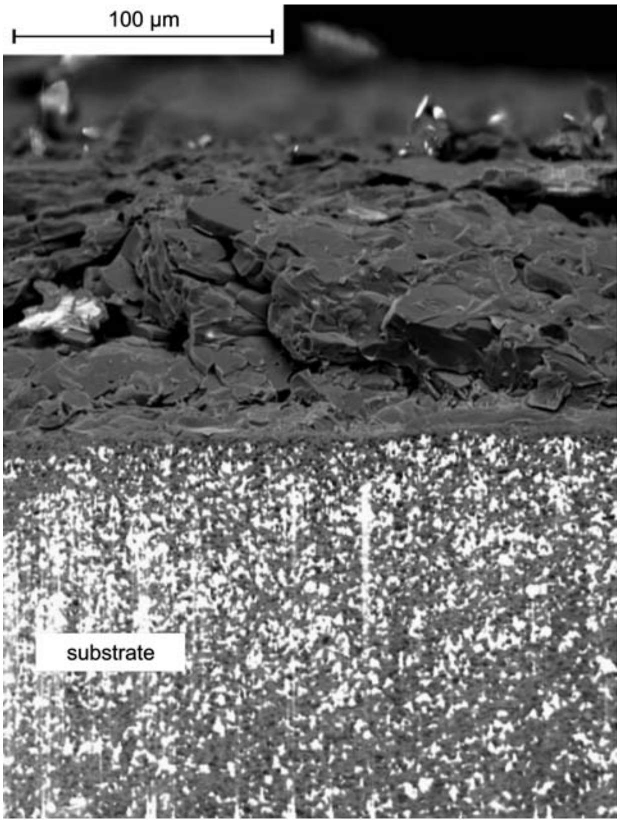

Figure 3. SEM microphotograph of the cross section of the film deposited at 700 rpm (JP51).

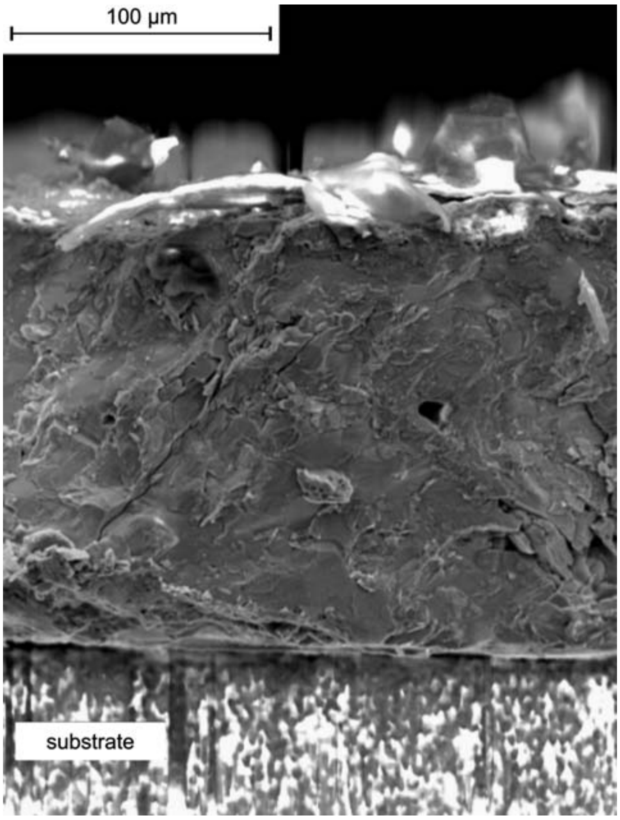

Figure 4. SEM microphotograph of the cross section of the film deposited at 400 rpm (JP53).

demagnetizing factor we estimated the values of the magnetic penetration field H_{p1} at 77 K. They are about 2.7 kA/m for the thinner sample deposited at higher spin velocity and 4.4 kA/m for the thicker samples deposited at lower spin velocity. It can be assumed that in thinner films the relative influence of the intermediate layer on the superconducting properties of the YBCO film is greater. On the other hand, the thinner films show significantly smaller tendency to cracking.

The effect of the thermal cycling between the room temperature and the boiling point of liquid nitrogen on the magnetization hysteresis loops is demonstrated in figure 8. The magnetization measurements reveal significant decrease of the superconducting "grain" properties after five cooling-heating cycles between 293 and 77 K. This fact can be explained probably by decreasing size of the shielding current paths, e.g. due to cracks arising at fast changes of temperature.

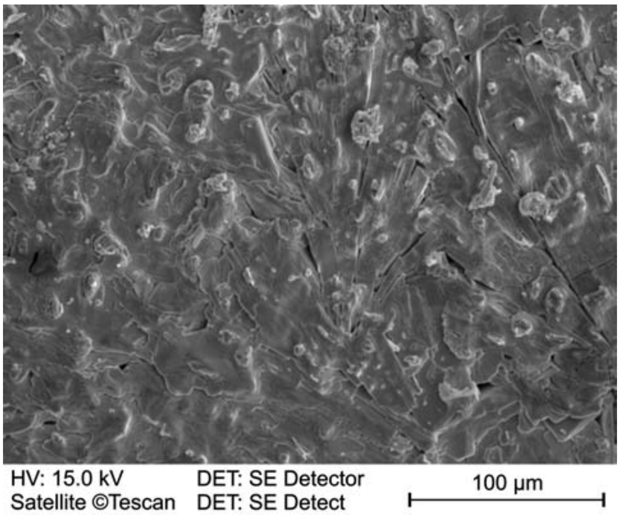

Figure 5. SEM microphotographs of the surface of the deposited YBCO film JP51.

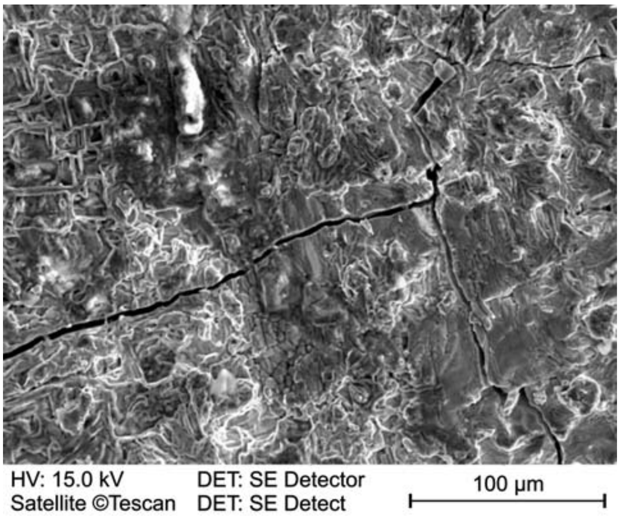

Figure 6. SEM microphotographs of the surface of the deposited YBCO film J53 cracked after thermal cycling.

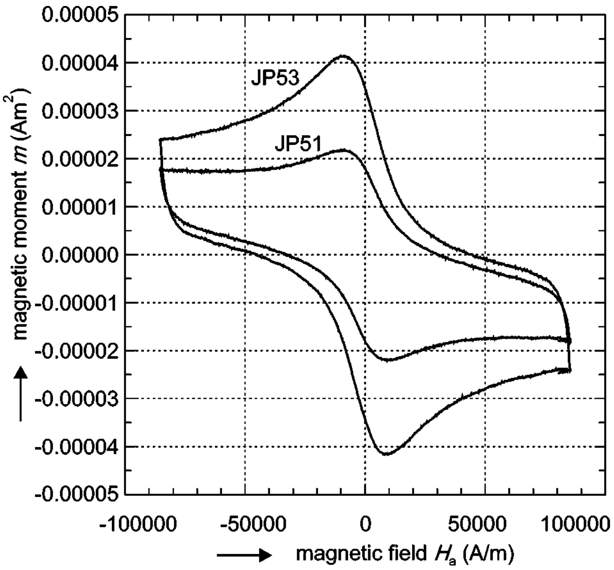

Figure 7. The AC magnetization hysteresis loops of the thicker (JP53) and thinner (JP51) film.

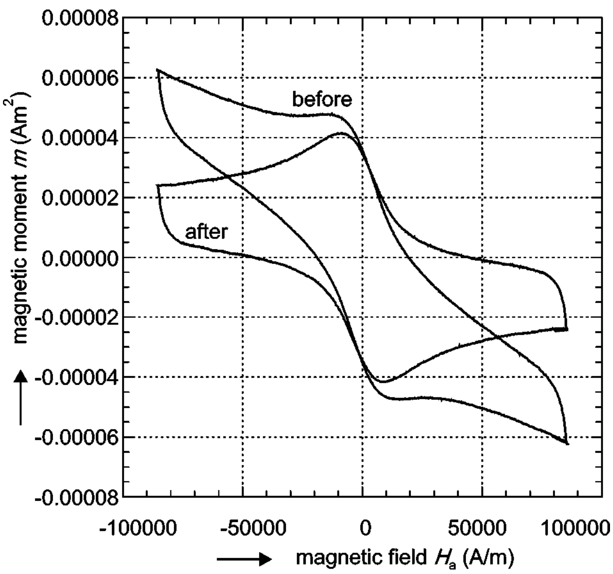

Figure 8. The AC magnetization hysteresis loops of the YBCO film (JP53) before and after five thermal cycles.

CONCLUSIONS

Polycrystalline yttria stabilized zirconia substrate toughened with 20 wt.% Al_2O_3 addition is a suitable substrate for preparation of melt-textured superconducting YBCO thick films with $T_{c(0)}$ values ranging between 86.5 and 88.5 K. Films with an approximate thickness of 50-120 μm have been prepared. Between the YBCO film and the zirconia substrate a Cu, Ba and Zr rich intermediate film is formed. The magnetization measurements show that the values for magnetic penetration fields H_{p1}, which reflect the quality of the superconducting properties, are lower for thinner samples. On the other hand, these samples show significantly smaller tendency to cracking. The optimization of the experimental procedures, which would allow a preparation of YBCO layers with improved superconducting properties, is in progress.

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TLUSTÉ VRSTVY $YBa_2Cu_3O_{7-x}$ TEXTUROVANÉ TAVENÍM NANÁŠENÉ NA SUBSTRÁT OXIDU HLINITÉHO ZHOUŽEVNATĚNÉHO OXIDEM ZIRKONIČITÝM

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Supravodivé vrstvy YBCO texturované tavením o přibližné tloušťce 50-120 μm s $T_{c(0)}$ mezi 86.5 a 88.5 K byly připraveny na polykrystalickém oxidu zirkoničitém zhouževnatělém 20 hmot.% Al_2O_3. Mezi substrátem a supravodivým filmem byla vytvořena mezivrstva. Byla změřena jejich střídavá a stejnosměrná magnetizace a byly odhadnuty velikosti magnetického penetračního pole H_{p1}. Penetračního pole H_{p1} = = 2.7 kA m^{-1} bylo dosaženo s tenčími filmy vytvořenými větší rychlostí pokrytí metodou *spin coating*, zatímco s tlustšími vrstvami vytvořenými pomalejší rychlostí bylo dosaženo H_{p1} = = 4.4 kA m^{-1}. Opakované cyklování teploty mezi pokojovou teplotou a teplotou kapalného dusíku a příslušné měření křivek magnetické hystereze odhalilo podstatný pokles supravodivosti zrn pravděpodobně způsobený vznikem trhlin.