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Properties of MgB_2/In composite thick films on ceramic substrates prepared by a screen printing method

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Abstract

In-free and In-added MgB_2 thick films were prepared on ceramic substrates (MgO, YSZ, $SrTiO_3$ and Al_2O_3) using a simple screen printing method. For In-free films, the adhesion between the films and the substrates were very weak; about 10–40% of these films peeled off after firing. We examined the temperature dependence of the resistivity using the non-separated films. These films showed metallic behavior from room temperature to $T_{c(onset)} = 39.7$ K and attained zero resistivity at $T_{c(end\ point)} = 34.0$–37.7 K, depending on the kinds of substrate. For In-added films formed on MgO, almost all films adhere well to the substrates and the transport J_c (4.2 K, 0 T) were also improved remarkably; 70 A cm^{-2} for In-free film and 1.6×10^3 A cm^{-2} for 18 vol.% In film.

Keywords: Superconductors; MgB_2; Microstructure; Thick film; SEM

1. Introduction

Since the discovery of the binary metallic MgB_2 superconductor with T_c of 39 K, many attempt to achieve thin films suitable for technical applications have been made. To date, high-quality MgB_2 thin films have largely been grown by the vacuum deposition techniques such as laser ablation [1], e-beam evaporation [2] and magnetron sputtering [3], while thick film technology for MgB_2 superconductor have received much less attention. This would be due to the processing difficulties associated with the highly volatile and reducing nature of Mg. The thick film technology is particularly important from the view point of practical application for magnetic shielding and substrate wiring. To be useful for thick film electronic device applications, the substrate must have a high resistivity to provide adequate isolation of the circuit elements. Furthermore, in order to obtain excellent superconducting thick films, it will be also necessary to understand the reactions between films and substrates at processing temperature. Few experiments on the MgB_2 thick films formed on ceramic substrates, except for some metallic substrates [4–7], have however been made [8].

In this paper we examine the superconducting properties of screen-printed In-free and In-added MgB_2 thick films on four kinds of ceramic substrates (MgO, YSZ, $SrTiO_3$ and Al_2O_3).

2. Experimental procedures

Following two kinds of powders were prepared: (i) commercially available MgB_2 powder (Alfa Aesar, 98% purity) passed through a 350 mesh sieve and (ii) the MgB_2 powder mixed with the desired volume percent (3.7 and 18 vol.%) of In additive (99%, <45 μm). These powders were mixed thoroughly with an appropriate amount of an organic vehicle (Tanaka-Kikinzoku, TMC-10TB) to form a paste. This paste was printed through 150 mesh stainless screen onto four kinds of rectangular ceramic substrate 3 mm wide and 10 mm long; MgO (1 0 0), YSZ (1 0 0), $SrTiO_3$ (1 0 0) and Al_2O_3 whose surface was chemically etched to a mirror finish. This printing process was repeated twice. The films wrapped in a thin rubber were then hydrostatically pressed under the pressure of 200 kgf cm^{-2} to enhance the connectivity between the grains. The films thus prepared were enveloped by an iron sheet with a small amount of Mg powder to prevent Mg loss and then sealed in an evacuated quartz tube. After that, the films were heated at 830 °C for 3 h.

The thickness of the fired film were about 50–60 μm. The electrical resistivity of the films was measured by a standard DC four-probe method; Ag was deposited on the contact areas using a vacuum method, after which Au lead wires were attached with Au paste.

The magnetization measurements of the films were carried out at 4.2 K for films being cut to a square planar geometry with the side length of 3 mm. The external magnetic field was applied perpendicular to the surface of the films up to 5 T using a SQUID magnetometer (Quantum Design MPMS-XL). The transport J_c measurement in the external magnetic field was also performed

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at 4.2 K using a helium-free 15 T superconducting magnet at the High Field Laboratory for Superconducting Materials, Tohoku University.

The microstructures were studied using the scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy-dispersive X-ray analysis (EDXA).

3. Results and discussion

3.1. In-free MgB_2 thick films

When the fired films were taken out of the quartz tube, some of the films were separated from the substrates; about 10–15% for YSZ and $SrTiO_3$ substrates, and about 40% for MgO and Al_2O_3 substrates. In Fig. 1, we show the photograph of separated film. All other non-separated films were also found to peel off as a result of a peel test using adhesive tape (Scotch 810). This indicates that the connectivity between film and ceramic substrates is very weak, probably due to the low temperature heat-treatment and/or to the weak film-substrate reaction.

He et al. [9] have examined the reactivity of MgB_2 with powdered forms of materials at 800 °C such as MgO, YSZ, $SrTiO_3$ and Al_2O_3, and reported the followings: (i) no reaction occurred for MgO, (ii) MgB_2 and small amount of MgO were produced for YSZ, (iii) MgB_2, MgO, SrB_6 and TiB_2 were produced for $SrTiO_3$ and (iv) Al ion was incorporated in MgB_2 structure and MgO was also produced. Kühberger et al. [10] have also reported that small amount of $MgAl_2O_4$ was produced by a reaction of Mg vapor with Al_2O_3. For the excellent adhesion of the film, it should be necessary that reaction occurs at the interface. We could not however detect the distinct peaks in the XRD patterns, except for the peaks corresponding to MgO phase, of these reaction products from both the film-surface separated from the substrate and substrate itself. This weak reaction between films and substrates would prevent the excellent adhesion.

Fig. 2 shows temperature dependence of the resistivity measured by using the non-separated films. All films show metallic behavior from room temperature to $T_{c(onset)} = 39.7$ K, and attained zero resistivity, depending on the substrates, $T_{c(end\ point)} = 37.7$ K for MgO, 36.9 K for $SrTiO_3$, 35.4 K for YSZ and 33.9 K for Al_2O_3. In these films, MgB_2/Al_2O_3 film show the highest normal-state resistivity and the most broad superconducting transition with $\Delta T_c = 5.8$ K. This would be due to the incorporation of Al into the MgB_2 structure resulting in the decrease in T_c, though the distinct changes in XRD pattern, e.g.

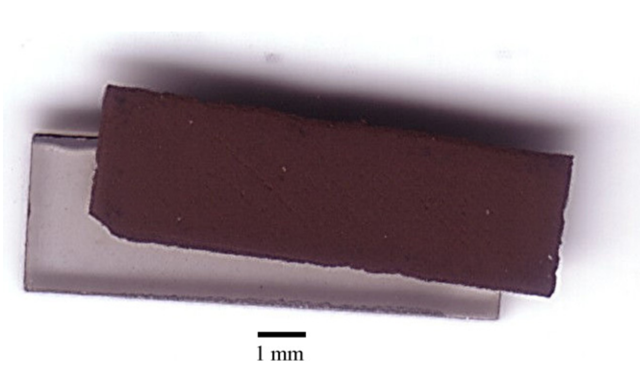

Fig. 1. The photograph of the MgB_2 thick film separated from the MgO substrate.

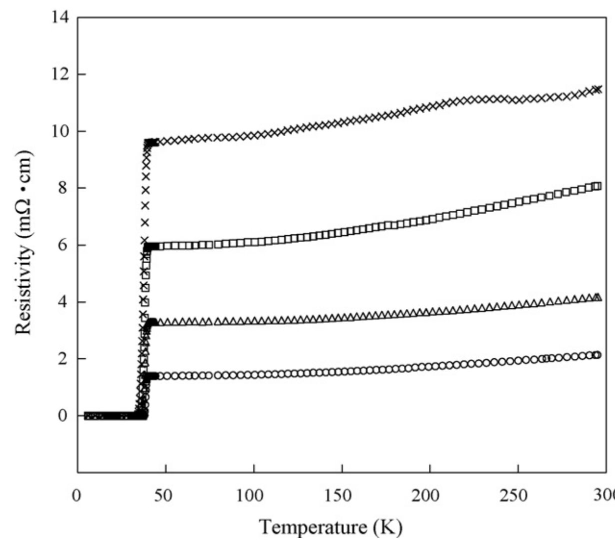

Fig. 2. The temperature dependence of resistivity for MgB_2 thick films formed on the four kinds of substrate: (×) MgB_2/Al_2O_3, (□) MgB_2/YSZ, (△) $MgB_2/SrTiO_3$ and (◯) MgB_2/MgO.

the broadening of (0 0 2) peak and the change in peak intensities [11], could not be detected in the reverse face of our films as mentioned above. This would be probably due to the amount of incorporation being too small to detect.

Fig. 3 presents the XRD pattern and SEM photograph of the surface of the film formed on MgO. The inset on the right in this figure gives field dependence of magnetic J_c at 4.2 K for MgB_2/MgO and MgB_2/Al_2O_3 films. The magnetic J_c values were estimated based on the extended Bean's critical state model according to $J_c = 30\ \Delta M/W$, where ΔM is the difference of magnetization (emu cm^{-3}) measured for ascending and descending applied field and W is the sample width (cm). Several futures are noticeable in this figure. (i) The distinct (2 2 0) peak of MgO near $2\theta = 62.3°$ is observed (the strong intensity of (2 0 0) near

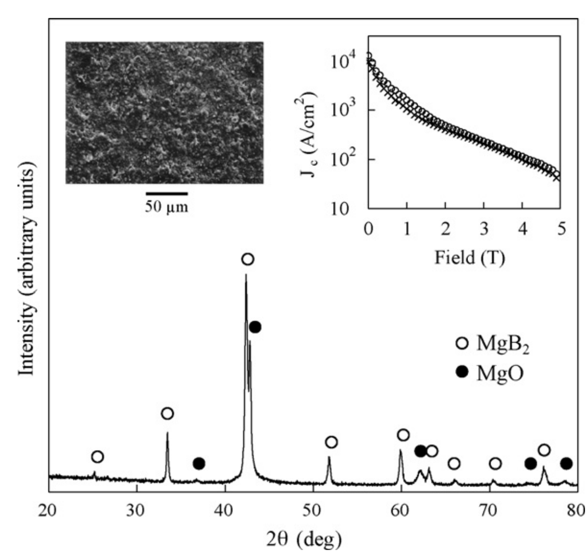

Fig. 3. The X-ray diffraction pattern and surface SEM photograph of MgB_2/MgO film. The inset on the right shows the magnetic J_c as a function of applied field: (×) MgB_2/Al_2O_3 and (◯) MgB_2/MgO.

$2\theta = 42.9^\circ$ is the reflection from the MgO substrate itself). The MgO phase would be produced by the reaction of MgB_2 with the residual O_2 in the quartz tube. (ii) The grains packed densely as can be seen from SEM image. A general surface state of the films formed on other substrates was similar to that shown in this SEM image. (iii) The magnetic J_c value at 0 T for MgB_2/MgO film, whose value was slightly higher than that of the MgB_2/Al_2O_3 film as a whole, was 1.3×10^4 A cm^{-2} and the J_c more than 10^2 A cm^{-2} was maintained up to 4 T. This behavior of the magnetic J_c is similar to that of MgB_2 filament prepared by a suspension spinning method [12].

These results shown in Figs. 2 and 3 indicate that, though the adhesion is weak, the most excellent substrate for MgB_2 thick film would be MgO, which agrees qualitatively with the results reported by He et al.; the only MgO does not produce the reaction products. We examine therefore the effect of In addition on the superconducting properties of MgB_2 thick films by using MgO substrate.

3.2. In-added MgB_2 thick films

The surface of In-added films appeared to be dark brown and the scattered metallic luster visible to the naked eye could be observed on the films. All films taken out of the quartz tube adhered well to the substrates. A peel test using adhesive tape showed the excellent adhesion for 18 vol.% films, though a part of the surface of some 3.7 vol.% films peeled off. The improvement of adhesion would be due to what is called the “anchor effect”, i.e. the In grains segregated along the grain boundaries stick to the surface of the substrate and strengthen the adhesion. For reference, we show the fractured cross sectional SEM photograph and the EDXA mapping of 18 vol.% In film in Fig. 4. It is found from this figure that the In grains marked by arrows stick to the surface and act as anchor.

Fig. 5(a) shows typical surface SEM photograph of 3.7 vol.% In film. The regions A and B marked by arrows were, from the EDXA, Mg- and In-rich regions, respectively. These regions should be identified as MgB_2 and the agglomeration of In grains, since the impurity phases, except for MgO, could not be detected from XRD pattern of this film. The In grains of 2–10 μm in size, not shown in the figure, having the spherical shape and the oblong shape could also be observed on the surface of In-added films. In near In-rich region, the petal-like crystals of a few μm in size could be seen here and there (Fig. 5(b)). These crystals were found to be Mg-rich according to the EDXA, however, it cannot be identified whether these are MgB_2 or MgO.

Fig. 6 presents the temperature dependence of the resistivity for three kinds of film: In-free, 3.7 vol.% In and 18 vol.% In films. The transition temperature T_c and ΔT_c values for these films were almost the same; $T_{c(\mathrm{end\,point})} = 37.3$–$37.7$ K and $\Delta T_c = 2.0$–2.4 K. The normal-state resistivity decreased as the amount of In addition increased due to the improvement of MgB_2 grain linkage [13]. Tachikawa et al. [14] have reported that $T_{c(\mathrm{end\,point})}$ of 10 vol.% In-added MgB_2 tape was improved to be about 35 K as compared to ∼33 K for the In-free tape. We could not however observe the distinct improvement of T_c in our films.

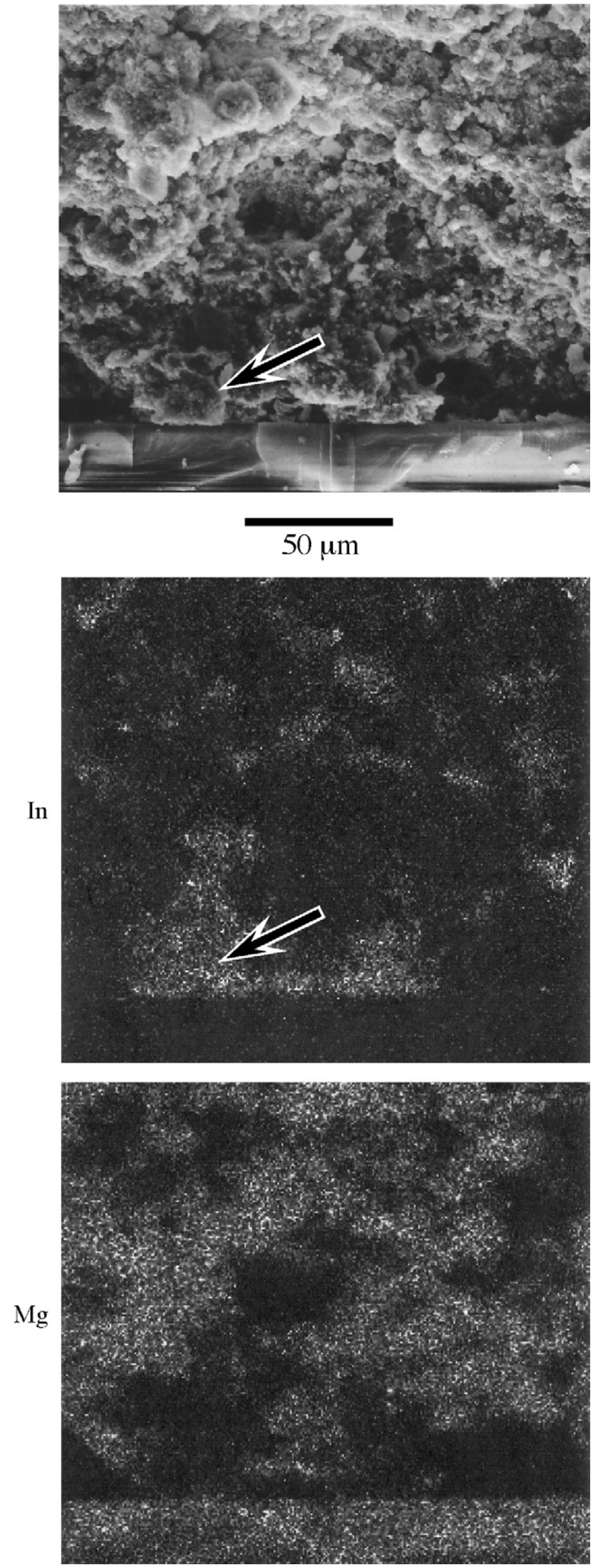

Fig. 4. The fractured cross-sectional SEM image and EDXA mapping of In and Mg for 18 vol.% In-added MgB_2 thick film. The arrows indicate the In grains adhered well to the surface of the MgO substrate.

(a)

(b)

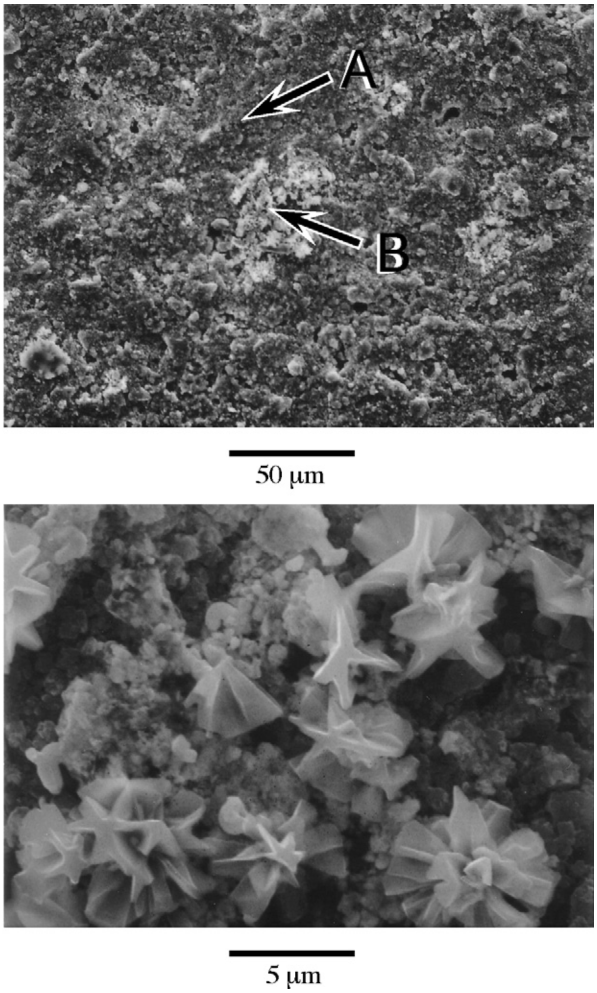

Fig. 5. The surface SEM photographs of 3.7 vol.% In-added MgB_2 thick film: (a) low magnification and (b) high magnification SEM image of the petal-like crystals.

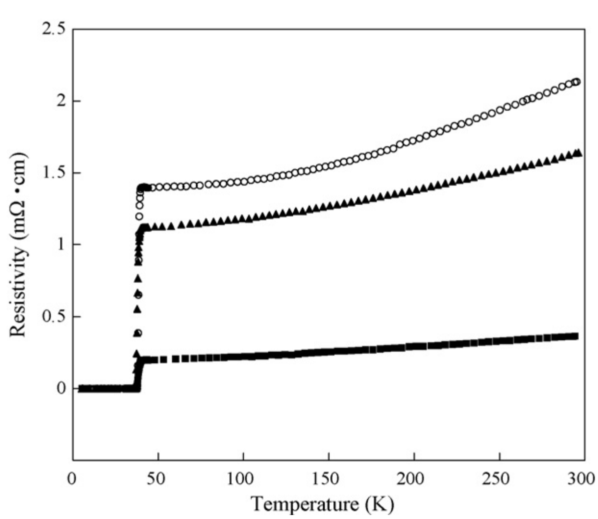

Fig. 6. The temperature dependence of resistivity for In-added MgB_2 thick films formed on MgO substrate: (◯) In-free, (▲) 3.7 vol.% In and (■) 18 vol.% In.

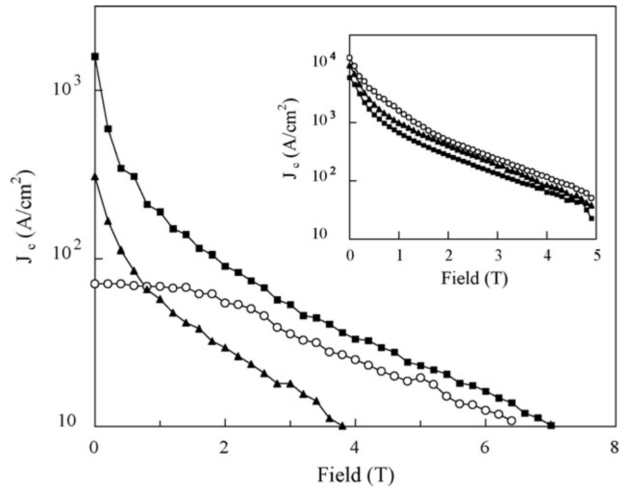

Fig. 7. The transport J_c and the magnetic J_c (inset) as a function of the external magnetic field: (◯) In-free, (▲) 3.7 vol.% In and (■) 18 vol.% In.

Fig. 7 presents the transport J_c and the magnetic J_c (inset) at 4.2 K for the In-free, 3.7 and 18 vol% films. It is found that the transport J_c at 0 T increased remarkably with increasing the amount of In; J_c at 0 T of these films were 70, 3.1×10^2 and 1.6×10^3 A cm^{-2}, respectively. This would be explained as follows: added In disperse among the MgB_2 grains and fill up gaps, which improve the grain linkage leading to the enhancement of transport J_c through the proximity effect [13].

Contrary to the case of transport J_c, the magnetic J_c had a tendency to decrease with increasing the amount of In as can be seen from the inset. Although the detailed mechanism is not clear at the present stage, one possible explanation may be as follows. It has been reported that, in contrast to the case of high-T_c superconductors, the grain boundaries do not limit the supercurrent flow and rather act as one of the most important flux pinning centers [15–18]. The In segregated along the grain boundaries, which is rather thick for serving as effective pinning centers, would prevent the number of well-connected superconducting grains. This would suppress the magnetic J_c, since the magnetization hysteresis should be proportional to the well-connected grain size.

4. Conclusions

In-free and In-added MgB_2 thick films were prepared on MgO, YSZ, $SrTiO_3$ and Al_2O_3 substrates using a screen printing method. The main conclusions of this paper are summarized below:

(i) The adhesion between In-free films and the substrates was weak. A 10–40% of films peeled off after firing.
(ii) Most excellent superconducting properties were obtained for the film formed on MgO substrate.
(iii) The addition of In was very useful for both the improvement of transport J_c and the enhancement of the adhesion of the films.

Acknowledgements

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