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Fabrication, microstructure and critical current density of pure and Cu doped MgB_2 thick films on Cu, Ni and stainless steel substrates by short-time in-situ reaction

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Abstract

Pure and Cu doped MgB_2 think films have been prepared on Cu, Ni and stainless steel substrates using a short-time sintering method. Results showed that single MgB_2 phase films can be easily formed in a short period of time (3 min) at temperatures above 700 °C. Un-doped MgB_2 films were found to be loosely attached to the Ni and stainless steel substrates. However, the MgB_2 with Cu powders addition adhered well to the substrates without serious degradation of T_c and flux pinning. The J_c increased one order of magnitude and irreversibility field determined from M–H loops also increased when sintering temperature increased from 745 to 900 °C. J_c values in the range of 1–9 $\times 10^5$ A/cm^2 at 15 K have been achieved for both doped and un-doped films sintered at 900 °C for 3 min.

Keywords: A. Film; E. Substrates; Magnesium diboride; Phases; Critical current density

1. Introduction

Since the discovery of the 39 K superconductivity in MgB_2 [1], extensive research has been done on the fabrication of this superconductor in various sample forms, such as polycrystalline bulk samples, single crystals, metal clad tapes, wires, thin and thick films [2–7]. MgB_2 thick films have great potential on applications in magnetic shielding devices and large power antenna. Since thick films are relatively easy to make compared with thin films, single crystals and metal sheathed tapes, it is more convenient to check the chemical compatibilities of Mg and B, or MgB_2 with other metals or oxides in the form of thick films. With respect to phase formation, MgB_2 phase can be produced via an in-situ reaction between elemental Mg and boron over a wide temperature range between 550 and 1000 °C. Several hours of sintering have been widely employed [4,5]. However, Wang et al. [8] have found that by using elemental Mg and amorphous boron powders, the MgB_2 phase can form quickly, even in a matter of several seconds or minutes, at temperatures above the melting point of magnesium (650 °C). This finding means that liquid magnesium can instantly react with amorphous boron to form MgB_2. It has been also observed that the superconducting performances of samples obtained from such a short-time in-sintering are as good as those obtained from the conventional long-time sintering method [8]. Films of MgB_2 have been grown mostly on oxide substrates [7], stainless steel [9], and flexible plastic substrates [10]. However, films were found to have poor adherence to the stainless steel substrate and the critical current densities and irreversibility field are poor compared with tapes/wires, bulk samples and thin films [9]. Recently, Dou et al. [11] have discovered that the nano-SiC addition can significantly improve the flux pinning and irreversibility field in bulk MgB_2 and Fe sheathed wires. As Ni and stainless steel show better deformation properties than Fe [5], they can be alternative choices of sheath material for industrial application. In this paper, we report fabrications and characterisations of MgB_2 thick films on Cu, Ni and stainless steel substrates using a very short-time sintering process.

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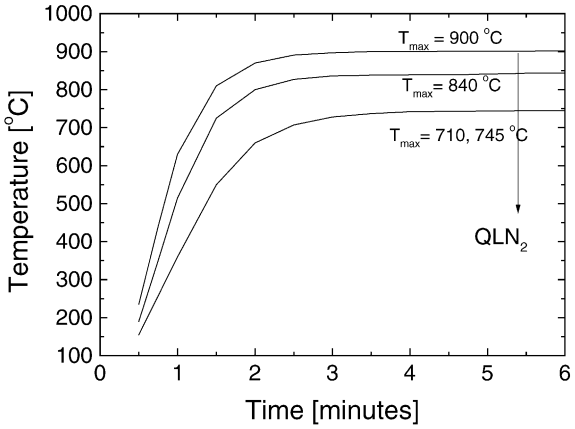

Fig. 1. Temperature profile for samples' sintering.

2. Experimental

Magnesium and amorphous boron powders were mixed in atomic ratio of Mg:B=1:2, the mixed powders then stirred with acetone in an agate mortar thoroughly. Polished substrates of Ni, Cu or stainless steel pieces of approximated sizes of 5 mm × 10 mm × 1 mm were placed in the bottom of the mortar. After the evaporation of the acetone, a layer of mixed powder was formed. This procedure was repeated several times until a desired layer of the mixed powder was formed. Some of these samples were also have 5 wt.% of Cu powder added. A piece of the same size stainless steel was placed on the top of the substrate piece, covering up the mixed powder sample layer, then were pressed under high pressure to increase the density of the deposited films. So, the two metal pieces bonded together tightly so it can also avoid the loss of Mg, and help preventing the oxidation of Mg during sintering at high temperatures. These samples were loaded into a tube furnace having a pre-set temperature T_{max} (710, 745, 840 and 900 °C) and were kept inside for 3 or 6 min accordingly. Through out the whole process of the sintering, a flow of high purity of argon gas was maintained within the tube furnace. Soon as the predefined sintering time was up, samples were quenched into liquid nitrogen directly upon taken out of the furnace. As shown in Fig. 1, it took about 2–3 min for the sample to reach the T_{max} after the sample was put into the furnace. Therefore, samples were only sintered at T_{max} for a period of 3–4 min. Sample phases and morphologies were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Superconductivities such as T_c and J_c versus fields were characterised using a physical property measurement system.

3. Results and discussion

Fig. 2. shows SEM images for three selective samples: (a) $T_{max} = 745\,°C$, time in the furnace for 3 min, on stainless steel substrate; (b) $T_{max} = 840\,°C$, time in the furnace for 6 min, on stainless steel substrate; (c) $T_{max} = 840\,°C$, time in the furnace for 6 min, Cu-added, on Ni substrate. It can be seen that sample (a) showed a looser surface structure compared to (b) and (c). This indicated that higher sintering temperature gave better grain connectivity in MgB_2 thick films. As a result, higher critical current density J_c is expected as we will see later on. It is also obvious that, unlike other samples, sample (c) showed many small sized voids embedded in a highly dense MgB_2 matrix. This is in agreement with that observed in Fe sheathed MgB_2 wires using short-time in-situ reaction [8]. Fig. 3(a) shows a closer look on the cross-sections of the MgB_2 thick films grown on Cu substrate. We can see that the film grown on Cu is well attached to Cu substrate. This good adherence is caused by reaction between Cu and Mg at the interface surface. However, pure MgB_2 films made on stainless steel and Ni did not attach to the substrate and can be easily removed off from

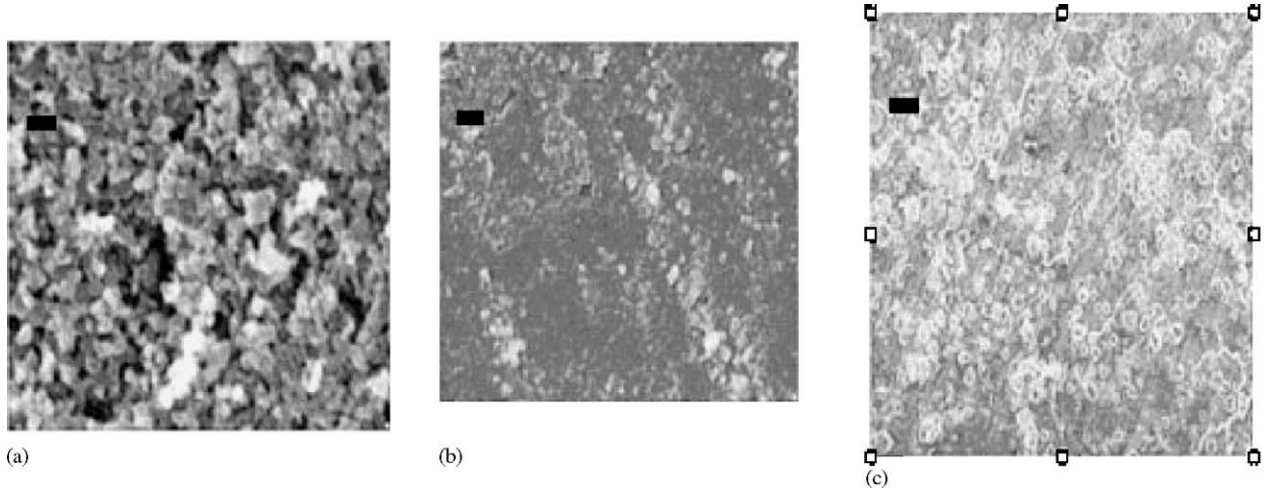

Fig. 2. SEM images for three different samples. Black bars within these images represent 10 nm: (a) $T = 745\,°C$, $t = 3$ min, on stainless steel substrate; (b) $T = 840\,°C$, $t = 6$ min, on stainless steel substrate; (c) $T = 840\,°C$, $t = 6$ min, Cu-added, on Ni substrate.

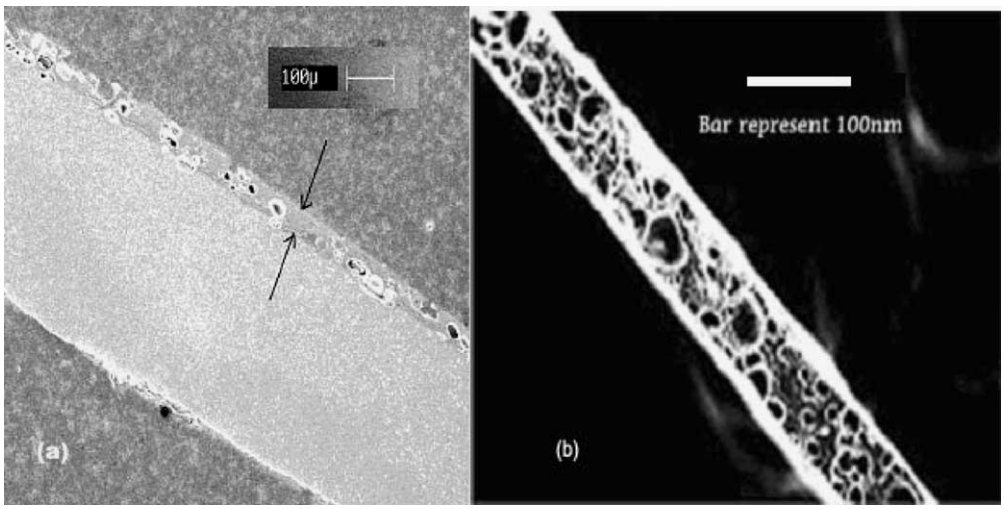

Fig. 3. SEM of cross-section for MgB_2/Cu film (a) and MgB_2 film removed off from the Ni substrate (b).

the substrate. Fig. 3(b) shows a SEM cross-section image for a typical film removed from either the stainless steel or the Ni substrate. It is quite possible that the poor adherence was resulted from the difference on heat-expanding coefficients between Ni or stainless steel substrates and MgB_2. After doping with Cu powders, the films were found to be well adhere to Ni and stainless steel substrates.

All samples from the short-time sintering method showed nearly single MgB_2 phase. For samples doped with Cu, Cu_2Mg were presented as a secondary phase. Fig. 4. shows typical XRD patterns for films with and without Cu addition, sintered at different temperatures for the same short period of time of about 3 min. All the peaks can be indexed using lattice parameters of MgB_2. This is a confirmation that the MgB_2 phase can be formed in such a short period of time. The films made using the short-time sintering method showed a very sharp superconducting transition as

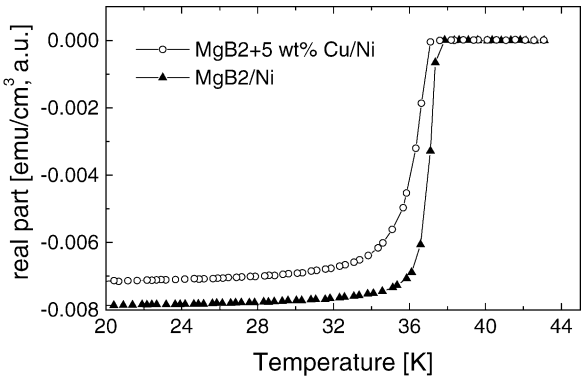

Fig. 5. The ac susceptibility of films of stainless steel substrates.

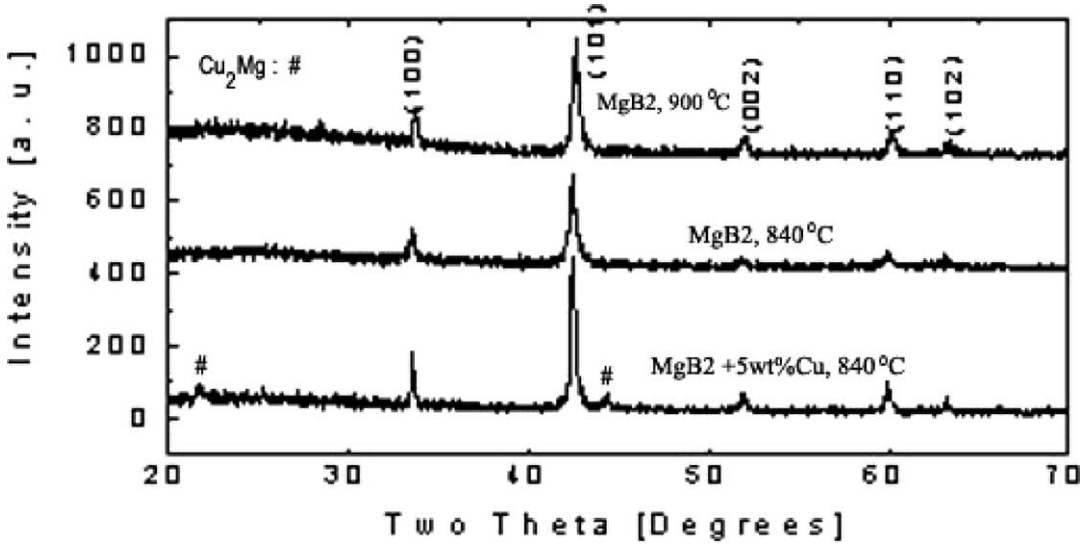

Fig. 4. XRD patterns for films on Ni substrates sintered at different temperature.

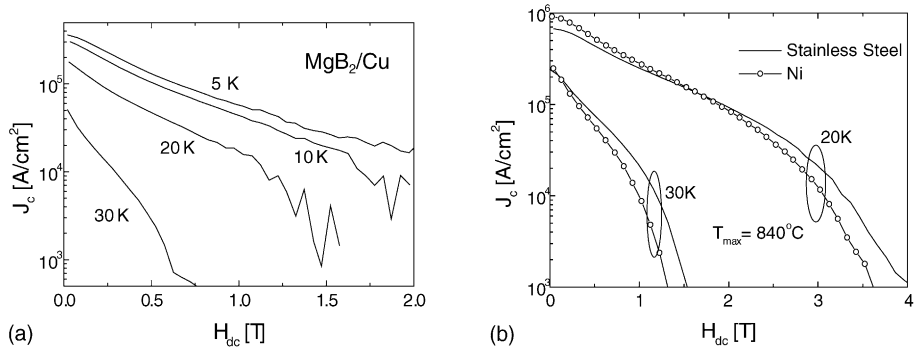

Fig. 6. J_c vs. magnetic field for MgB_2 films grown on Cu: (a) sintered at 710 °C on Ni and stainless steel substrates, (b) sintered at 840 °C.

determined from ac susceptibility with T_c around 37.5 K. The transition is a bit wide for films made on Cu substrates, being caused by strong diamagnetic signal from Cu itself. Fig. 5 shows ac susceptibility measured for MgB_2 grown on Ni with and without 5 wt.% Cu addition. The Cu addition did not cause any obvious degradation of T_c and transition width, only with a slight reduction of superconducting volume.

The critical current density J_c at different temperatures and fields was calculated from magnetic hysteresis loops using the Bean model, $J_c = 20\Delta M/[a(1 - a/3b)]$, where a and b are the sample dimensions. The field dependence of J_c at different temperatures for samples sintered at 710 and 840 °C for Cu and both stainless steel and Ni, respectively, are shown in Fig. 6. It can be seen that films/Cu have J_c of about 4×10^5, 2×10^5 and 6×10^4 A/cm^2 in zero field and at 5, 20 and 30 K, respectively, and it was 2×10^4 A/cm^2 in 2 T and 5 K. These data are the best among all the reported J_c values for MgB_2 with Cu as the supporting material [5]. For films grown on Ni and stainless steel and sintered at 840 °C, they showed almost the same values of J_c of 2.5×10^5 A/cm^2 at 30 K and zero field. J_c values were as high as 7×10^5 and 9×10^5 A/cm^2 in zero field and 20 K. These J_c values are much higher than those J_c values obtained from other thick films, wires and tapes fabricated by both in-situ and ex-situ methods [5] (Fig. 6(b)).

It should be pointed out that our samples were heated treated for only 3–4 min at above 710 °C. This very short period of sintering time would certainly produce smaller MgB_2 grains compare to the conventional long-time sintering methods. Large number of grain boundaries is expected due to the small grains and act as effective pinning centres, hence giving rise to high values of J_c. It is believed that higher J_c values can be achieved as heat treatment conditions improved in the future.

Acknowledgements

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