The Effect of Deposition Time on Textured Magnesium Diboride Thick Films Fabricated by Electrophoretic Deposition

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ABSTRACT

MgB_2 powders suspended in ethanol were electrophoretically deposited on high-purity molybdenum substrates having dimensions of 1 x 0.3 x 0.01 cm. The said substrate was set as the cathode and was placed 0.5 cm away from a graphite rod anode. A current density of ~0.02 mA/cm^2 and a voltage of 600 V were applied. The effect of deposition time was studied by varying it as follows: 15 s, 30 s, 1 min, and 2 min. Heat treatment at 950 ^{o}C for 3 h was done after deposition. MgB_2 thick films were successfully fabricated for the deposition carried out for 2 min. Deposition times less than 2 min resulted in insufficient deposited powder; hence formation of MgB_2 was not facilitated. Films deposited at 15 and 30 s have good surface characteristics, wherein no microcracks were present. X-ray diffraction and surface image analysis reveal that the deposited films have a preferred orientation along the (10l) direction.

INTRODUCTION

The discovery of superconductivity with T_C at 39 K in magnesium diboride (MgB_2) was announced in the early part of 2001 by Akimitsu et al. (Takano et al., 2001). This stimulated an interest in MgB_2 as a new family of high-temperature superconductors because it introduced a new, simple (three atoms per unit cell) binary intermetallic superconductor with a record high (by almost a factor of 2) superconducting transition temperature for a non-oxide compound (Bodoardo et al., 2004).

MgB_2 has the hexagonal aluminum diboride (AlB_2) type crystal structure wherein hexagonal close-packed layers of Mg atoms separate graphite-like sheets of boron atoms (Kortus et al., 2001). The low anisotropy, low-cost potential, large coherence lengths, and transparency of grain boundaries to current flow in comparison to cuprates are reasons for great interest in this material (Buzea & Yamashita, 2001). MgB_2 has been synthesized in many forms: thin films, wires, tapes, bulk, and single crystal.

One method of synthesizing MgB_2 film is by electrophoresis. Electrophoretic deposition (EPD) is a colloidal processing technique in which ceramic particles suspended in a liquid medium migrate in an electric field and deposit on an electrode. Solvents usually used are polar aqueous dispersing liquids such as ethanol, acetone, and methanol. Binding agents may also be incorporated to enhance mechanical binding of particles (Gani, 1994).

EPD allows the shaping of freestanding objects and also allows deposition of thin films and coatings on substrates. This technique is being developed for the shaping of thin films and coatings, laminates, and graded and textured materials (Windes et al., 2002).

Resulting films have high density and uniformity and conforms to the shape of the substrate used. The

thickness of the deposited film can be easily controlled and microlamination is also possible (Sarkar et al., 1994). Due to the use of an electric field, EPD is suited for the formation of uniform films on substrates of complicated shapes, deposition on selected areas, and impregnation of porous substrates (Sarkar & Nicholson, 1996). Sausaging and bubbling which are common in casting techniques do not occur during EPD (Huang & Huges, 1999). Rigid control of the deposition rate is also possible (Zhitomirsky, 1998).

One problem encountered during fabrication of superconducting films using EPD is crack formation in the films. This can be remedied by reducing the particle size of the starting material (Sato et al., 2001).

The investigation of the EPD technique as a means of fabricating MgB_2 thick films was recently done by Bodoardo et al. (2004). Their study, which involved a two-step preparation method, showed that it is possible to produce thick films suitable for practical applications with the use of EPD.

Here is presented the investigation of the effect of deposition temperature on the fabrication of MgB_2 thick films by EPD. The starting powders were deposited on molybdenum (Mo) substrates. Previous studies by the group showed that deposition of MgB_2 on silver substrates results in microcracks on the film as a result of the difference in coefficient of thermal expansion of the substrate and film.

METHODOLOGY

X-ray diffraction (XRD) patterns of commercially available MgB_2 powder revealed that it was of high purity, hence it was selected as the starting material for this study. Fabrication of the films was done using a two-step method: (1) electrophoretic deposition on Mo substrates and (2) sintering of the as-deposited films. Characterization of the film was then done by XRD and scanning electron microscopy (SEM).

MgB_2 powder was ground using a mortar and pestle for 1 h, after which 0.15 g of powder was then mixed in 30 ml ethanol to obtain a well-dispersed suspension in a nonoxidizing medium. Proper dispersion of the powder in suspension is ensured by ultrasonicating the suspension for 10 min. A Mo substrate having dimensions of 1 x 0.3 x 0.01 cm was used as the cathodic terminal, while a high-purity graphite rod was the anode. The electrodes were spaced 0.5 cm apart. Deposition was done under a current density of ~0.02 mA/cm^2 and a voltage of 600 V, with deposition time varied as follows: 15 s, 30 s, 1 min, and 2 min.

The as-deposited films were then heat treated in order to densify and attain effective homogeneity of the film. A sintering temperature of 950 ^oC and soak time of 3 h was done, after which the films were furnace cooled to room temperature.

The surface morphology of the produced film was studied using SEM. Material composition of the sample was analyzed using XRD.

RESULTS AND DISCUSSION

The use of Mo substrates allowed the fabrication of a good quality film. Previous experimental runs using silver substrates resulted in cracked films, even in films having very thin deposits of MgB_2. The cracking of the film is attributed to the difference in coefficient of thermal expansion (CTE) of the Ag substrates and MgB_2 deposit. Ag has a CTE value of $2.0x10^{-5}$ mm/mm/°C and is mismatched with the CTE value of the MgB_2 film which is assumed to have a very low CTE value as other ceramic materials ($0.5x10^{-5}$ mm/mm/°C and below) (Lucas-Milhaupt, Inc.).

The SEM image in Fig. 1 shows that cracks observed in MgB_2 film deposited on Ag substrate is obvious. Due to cracking, the film peeled off from the substrate leaving a thin layer. Upon analysis of the SEM images of the thick MgB_2 layer and the remnant (left after peeling), it was found out that both regions have the same structure. From the result of the SEM analysis, it concludes that the setup is capable of depositing MgB_2, however, the film peeled off due to cracks induced by the difference in CTEs.

In order to minimize cracking, which is theoretically induced by a large difference in CTE values between

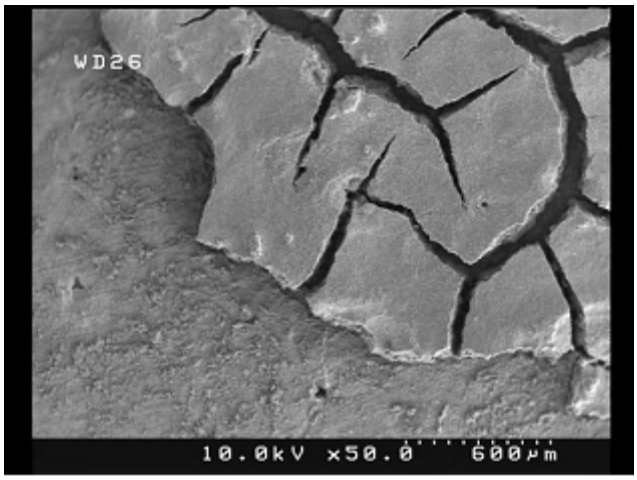

Fig. 1. MgB_2 film deposited on silver substrate.

Ag substrate and MgB_2 films, Mo, which has a lower CTE than Ag, was selected. Mo has a CTE value of $0.6x10^{-5}$ mm/mm/°C (Lucas-Milhaupt, Inc.), which is three times lower than that of Ag and closer to the CTE of ceramic materials ($0.5x10^{-5}$ mm/mm/°C and below) (Lucas-Milhaupt, Inc.). Upon using Mo substrates, cracking was successfully reduced. Though cracks are unlikely to be observed in thinner film deposits, microcracks begin to emerge as the thickness of the film is increased.

SEM images of samples deposited at different periods of time as shown in Fig. 2 shows that after 1 min microcracks started to appear and are more apparent in the film deposited for 2 min, as observed at 400x magnification. It is evident that thinner films deposited for about less than 1 min have good surface characteristics; wherein the surface was evenly covered and shows no signs of cracks.

The x-ray diffraction patterns of the MgB_2 films deposited on Mo substrates by electrophoresis at various times are shown in Fig. 3.

Analysis of the XRD patterns of the MgB_2 films revealed that only peaks having an index of (10*l*) were present. This indicates that the grains have a preferred orientation along the (10*l*) direction as shown in Fig. 4.

It can be seen that the peak intensities of the films deposited for 15 and 30 s are quite low compared with

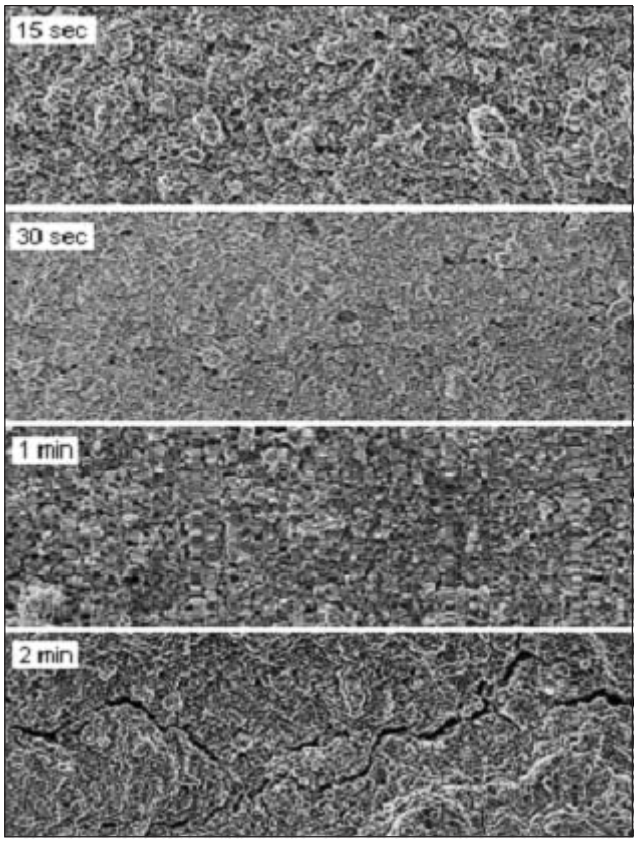

Fig. 2. Deposition surface of MgB_2 films (400x).

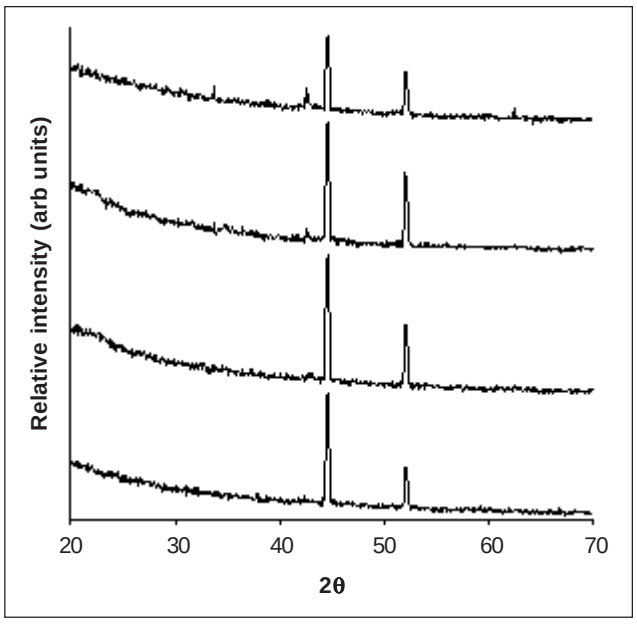

Fig. 3. XRD patterns of MgB_2 deposited on Mo by EPD.

films deposited for 1 and 2 min. It must be noted that the only peaks present in the XRD pattern of the film

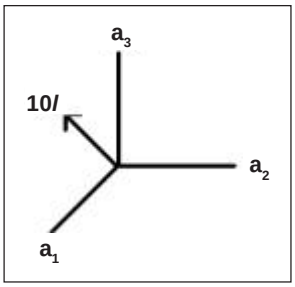

Fig. 4. (10*l*) direction.

deposited for 15 s are those of Mo. Based on the absence of MgB_2 peaks it can be said that trace amounts of the said material was formed. The peak intensities of MgB_2 increase at longer deposition times, wherein they are depicted clearly in the XRD pattern of the film deposited for 2 min.

According to Blum & Hogaboom (1949) the mass of deposits is given by the equation

$$m_{deposit} = \frac{(MW \times I \times t)}{nF}, \qquad (1)$$

where *m* is the expected weight in grams (g), *I* is the total current flowing from the anode to the cathode in amperes (A), *n* is the valency of the atom involved, *F* is Faraday's constant, and *t* is the deposition time in seconds. Notice that in the equation the mass deposited is directly proportional to the deposition time. Hence the difference in peak intensities for the various deposition times can be attributed to the varying mass of MgB_2 powder deposited, wherein depositions carried out at longer durations resulted in greater mass deposited.

Looking at the SEM images depicted in Fig. 5 we can see that spherical-like aggregates are formed at deposition times of 15 s, 30 s, and 1 min. Figure 6 shows the SEM image of the film deposited for 2 min at a greater magnification.

It can clearly be seen that triangular aggregates are formed at this deposition time and that textured MgB_2 is clearly present. The microstructure shown in Fig. 6 is clearly not that of untextured MgB_2, which is hexagonal. The angular structure is evidence of the preferred orientation of the grains along the (10*l*) direction. The layer of powder deposited on the

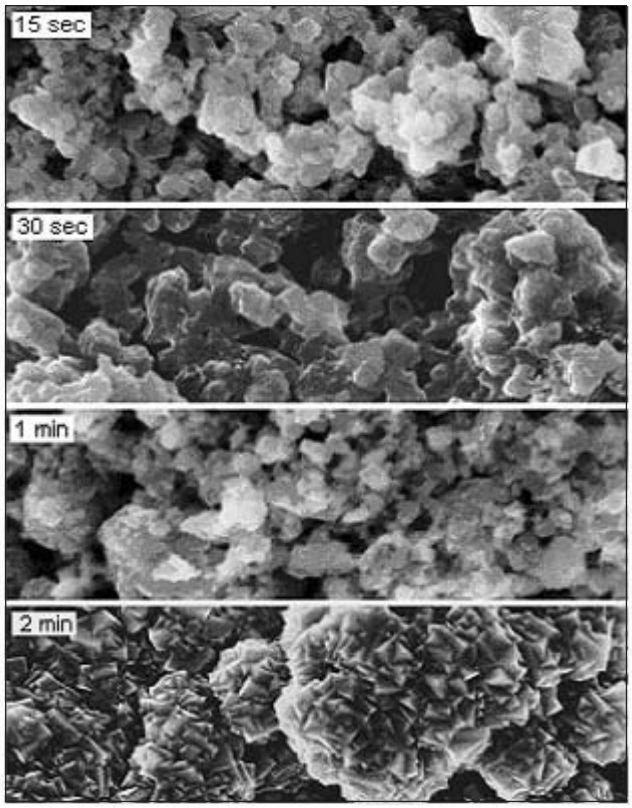

Fig. 5. SEM images of MgB_2 films at 8000x.

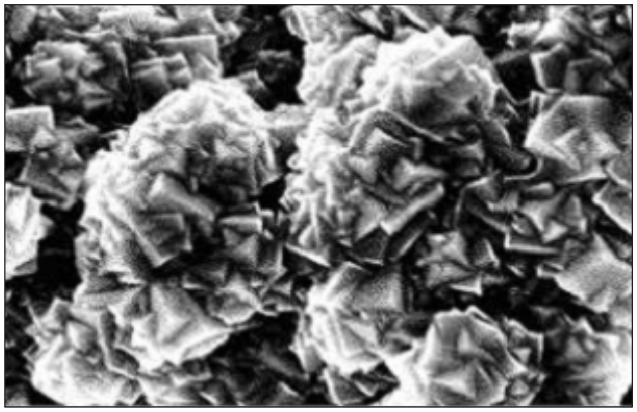

Fig. 6. Enlarged SEM image of MgB_2 film deposited for 2 min.

substrate at times less than 2 min is insufficient to facilitate the formation of MgB_2 films upon heat treatment resulting in low or absence of peaks in the XRD spectra.

CONCLUSION

Textured MgB_2 thick films were successfully fabricated using the electrophoretic deposition method

for a deposition time of 2 min. Deposition times of less than 2 min resulted in insufficient deposited powder, hence formation of MgB_2 was not facilitated. Films deposited at 15 and 30 s have good surface characteristics, wherein no microcracks were present. X-ray diffraction and surface image analysis reveal that the deposited films have a preferred orientation along the (10*l*) direction.

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