Front. Phys. China (2006) 2: 246–250
DOI 10.1007/s 11467-006-0008-x

RESEARCH ARTICLE

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MgB_2 thick films with remarkable ductility on stainless steel substrate

Abstract We fabricated several superconducting MgB_2 thick films on stainless steel (SS) substrates by using hybrid physical-chemical vapor deposition (HPCVD) technique. The thickness was in the 10 μm to 20 μm range, and the onset critical transition temperature T_c (onset) and the width of the superconducting transition (ΔT) were about 37.8 and 1.2 K. They were dense and textured along (101) direction with high tenacity, despite the existence of a little amount of MgO and Mg. We bent the films at different degrees and studied the ductility and transport properties of these MgB_2 thick films under applied force. The results demonstrated that the superconducting properties of these thick films, prepared by HPCVD, stay almost unaffected even with the films bent to a large degree with a curvature of 0.5 mm. This indicated that the superconducting wires or tapes of MgB_2 with a core of SS had the advantages of avoiding rigidity and brittleness in industrial handling. The technique of HPCVD has, therefore, a high application potential.

Keywords superconducting films, hybrid physical chemical vapor deposition (HPCVD), MgB_2 thick film, stainless steel substrate, ductility

PACS numbers 74.62.Bf,74.70.Ad,74.78.-w

Translated from *Chinese Journal of Low Temperature Physics*, 2005, 27(2) (in Chinese)

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Received December 2, 2006

1 Introduction

MgB_2, a new binary compound superconductor discovered recently, has had considerable impact on the supercon ducting field not only for its remarkable critical transition temperature (T_c) as high as 39 K, large superconducting coherence length (ξ), higher upper critical field (H_{c2}), and critical current density (J_c), but also for its simple crystal structure and economical raw materials [1–4]. It is highly possible to replace the primary low T_c superconducting (LTS) materials over high-field and electronic applications. Compared with LTS, such as NbTi and Nb_3Sn, MgB_2 has a transition temperature within the scope of liquid hydrogen, which can be provided conveniently by a cryocooler instead of using expensive liquid helium equipment. On the other hand, although with a surprising T_c exceeding liquid nitrogen temperature and a high H_{c2}, high T_c superconductors (HTS), such as YBCO, have a shorter coherence length, weak links among the grain boundaries, and,especially, difficulty in formation of tapes or wires due to ceramic intrinsic rigidity and brittleness. With many researches, people find that MgB_2 films or wires can obtain certain ductility by using appropriate synthesis technique over some special substrates or core materials [5].

To date, there are many ways to get MgB_2 tapes or wires,such as powder in tube (PIT) [6], diffusion of Mg vapor into B fiber [5,7]; however, the search for alternative approaches necessary for a more effective and efficient process is still under way. Synthesis of MgB_2 thick films, one of the routine methods, as a prestep toward the largescale production, becomes more attractive and significant.Various synthesis methods of MgB_2 films have been reported so far [8–14]. In general, there are always two favorable programs. One is named “two-step growth,”which can easily obtain a high Mg vapor pressure by sealing amorphous B precursor in an Ar-containing Nb or Ta tube with Mg metal pieces as well as produce good crystalline films with superconducting properties comparable to those of high-quality sintered specimens; however,this technique

can hardly be used to grow Josephson junctions or multilayer films. The other is "*in situ* growth,"which means depositing MgB_2 directly on substrate.Compared with the former technique, MgB_2 films obtained through this method always have a slightly lower T_c(typically 35K), but this approach makes multiplayer deposition feasible. This dilemma has been overcome since the Penn State group has successfully applied hybrid physical-chemical vapor deposition (HPCVD) to growing *in situ* epitaxial film on the SiC and Al_2O_3 substrate [15,16];then, our group first fabricated high-quality MgB_2 thick films on sapphire and textured thick films on stainless steel (SS) substrates by using the same HPCVD technique [17–19].These developments provide additional knowledge and information in the investigation of applied MgB_2 superconducting materials via second-generation tech nique.

In this paper, we reported MgB_2 thick films with improved transportation properties to our former results over the SS substrate resorting to the HPCVD method. These films has high enough tenacity, sufficient bonding strength to the substrate, still considerable transport properties under mechanical deformation, and especially a high deposition rate, which is very significant for industrial production.

2 Materials and method

In the HPCVD process, Mg ingots were vaporized to provide a sufficient Mg supply, and chemical decomposition of B_2H_6 produced boron. This design could easily generate a high Mg vapor pressure around the substrate,which is necessary to maintain the thermodynamic phase stability of MgB_2 at the deposition temperature. The reducing ambient hydrogen suppressed the oxidation of Mg efficiently at the same time. The schematic diagram of the system and the details were described elsewhere [18].

The surface morphology of the MgB_2 thick films with and without deformation was investigated with AMARY 1910FE scanning electron microscopes. The crystal phase and structure were studied by X-ray diffraction by using Philips X'pert diffractometer. A series of R–T measurements was performed by standard four-probe technique on Quantum Design PPMS system with the silver paste as electrical contacts. The two voltage leads were placed across the bending area. The compositional analysis by the energy dispersive X-ray spectroscopy (EDX) of the MgB_2 thick film was described elsewhere [19].

3 Results and discussion

We performed the X-ray diffraction on these MgB_2 thick films, and the details could be investigated in [18]. The XRD pattern indicated that MgB_2 film deposited on the SS substrate was textured along (101) direction and that there was a small quantity of Mg and MgO (impurities) in this film. The existence of Mg was due to the condensation of saturated Mg vapor in the cooling process. Low system vacuum (0.1–0.3 kPa), impure background gas, and trapped oxygen in chamber wall, which will be released at a higher temperature, were responsible for the existence of MgO.

Figure 1 shows a general view over the film surface. The magnifications of Figs. 1(a) – (c) were 100, 6 500, and 50 000, respectively. A smooth surface could be observed in Fig. 1(a). By a higher magnification, we could discover many block-like cracks in Fig. 1(b), which resulted from stress releasing in the cooling process as a consequence of large mismatch of thermal expansion coefficient between the SS substrate and MgB_2 film, especially to the thick one. Figure 1(c), with many highly packed 200–400 nm grains,indicates that the film is dense and solid. SEM image on the cutting cross section, as shown in Fig. 1(d), held that the thickness of MgB_2 film could be estimated about 20 μm, which was much greater than the ordinary value, i.e.,several hundreds of nanometers.

A series of bending tests were undertaken to examine the ductility of film, the bonding strength of the film to the substrate, and most importantly, the effect of the mechanical deformation on the transport properties. As shown in Fig. 2, R–T measurements were performed on the sample progressively at various bending angles: 0°, 40°, 90°, 140°,and 180°. We could obtain T_c(onset)=37.8 K and ΔT_c(10%–90%)=1.2K of these samples without any bending. Note that there was still residual resistance when the superconducting transition was completed, which could be understood with the use of Fig. 1(b). Because the cracking in the film occurred in the cooling process, as mentioned above, the contacting point used in the four-probe measurement inevitably covered the cracking area; therefore,the observed resistance came from the major part of the film and a small segment of SS substrate in the series. This caused the nonzero resistance transition.

Table 1 lists T_c (onset) and ΔT_c (10%–90%) at different bending angles of these samples, which were calculated directly from Fig. 2 with the corresponding curve shown in Fig. 3. T_c and ΔT_c(10%–90%) were 37.84 and 1.2 K with no bending. When it was bent to 180° with a curvature of 0.2 mm, these values became 37.04 and 6.1 K, respectively. T_c went down in the range of 1 K while ΔT broadened by about 5 K. Remarkably, ΔT_c increased slowly when the bending angle was less than 90°, while it rapidly worsened as the bending angle exceeded 90°. That is to say, the superconducting properties would degenerate slightly under deformation; however, a remarkable superconductivity was still manifested.

Figure 4 shows the effect of the tensile strain at various bending angles of these samples. They were bent to 40°, 90°, 140°, and 180° and labeled as a, b, c, and d as

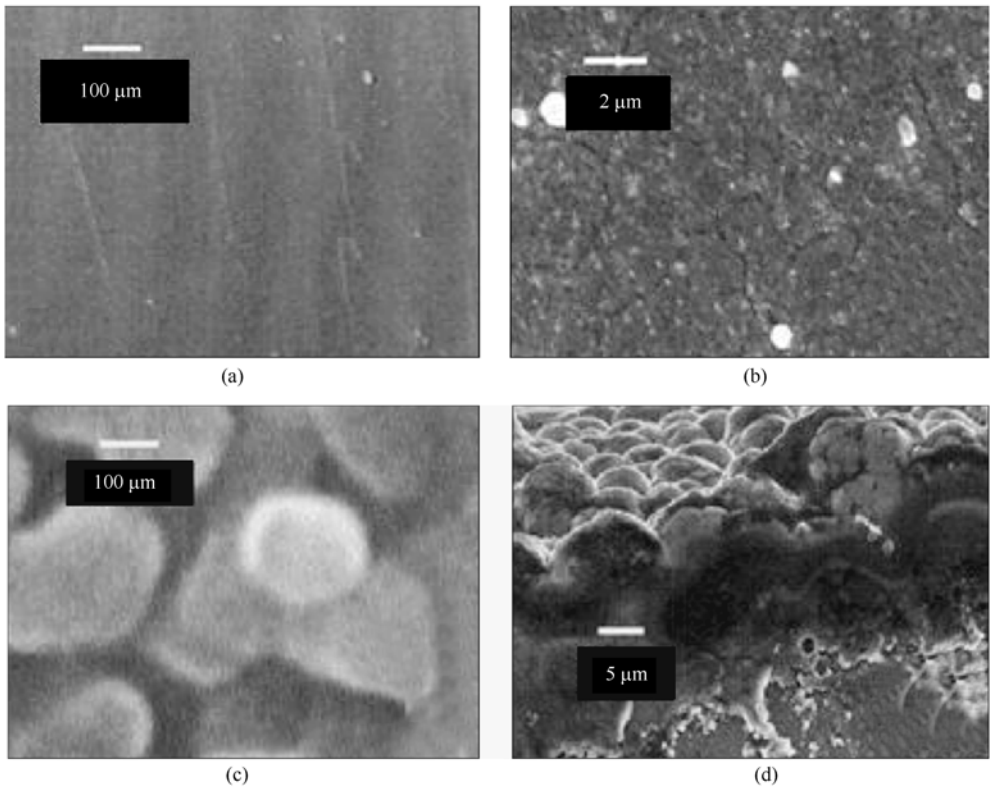

Fig. 1 The SEM images of MgB_2 thick film without any deformation that was magnified ×100 (**a**), ×6 500 (**b**), ×50 000 (**c**), and ×6 150 (**d**) for the cutting cross section of this film

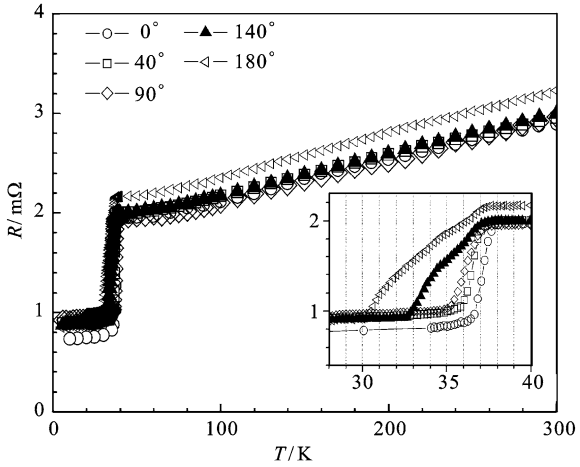

Fig. 2 *R*–*T* curve with different bending angles. The inset shows the details near the transition

shown on the upper four images with magnifications of ×55.6,×52, ×55.8, and ×116, respectively. The next four were the corresponding morphologies of bending area.We could get the following detailed information from these photos:(a) the film remained almost unchanged at a bending angleof 40° ; (b) slightly longitudinal (perpendicular to the bending direction) cracks appeared in the surface under 90° of bending; (c) when bending angle increased further to 140° , it began to clearly show longitudinal cracks with 0.1–0.2 μm widths; (d) as the film was bent to 180° with a curvature

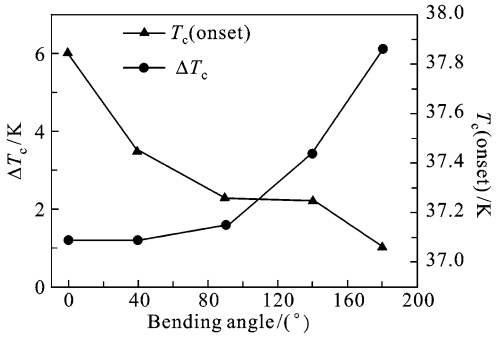

Fig. 3 The bending angle dependence of T_c and ΔT_c of these thick films

Table 1 Tc and ΔT_c of MgB_2 thick film on SS substrate at different bending angles

Bending angle	Transition temperature, T_c (onset) / K	Transition width, ΔT_c (10%–90%) / K
0°	37.84	1.2
40°	37.45	1.2
90°	37.26	1.6
140°	37.25	3.4
180°	37.06	6.1

of about 500 μm , it was lacerated into strips and the width of the cracks became 0.2–0.3 μm . However, the lacerated strips still remained attached to the substrate, and part of

bending area was almost unaffected, demonstrating a strong adhesion to substrate. In general, we found that the film would have clear cracks only under a large bending angle greater than 90° , which will be clearer and wider with bending angle increasing. These results suggested that our MgB_2 superconducting thick films fabricated by HPCVD possessed remarkable ductility and could adhere to the substrate firmly even with a large deformation.

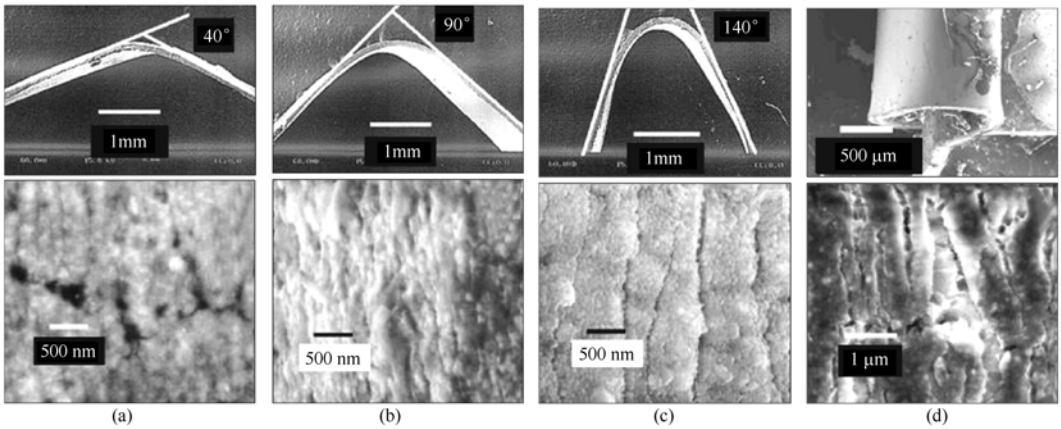

Fig. 4 The SEM photos of different bending angles to MgB_2 thick films on SS

MgB_2 is a kind of material with much rigidity and brittleness [20,21]. Samples with high density will demonstrate rigidity strongly, while brittleness and fragility will be demonstrated at low-density samples. Hence, it was difficult to be pulled into wires directly like NbTi, and thus,we did not consider that overcoming it would be impossible. For instance, brittle alloy Nb_3Sn has already been applied to industry successfully and holds a T_c record among all the applied LTS materials. Hence, we hope that we could produce superconductor wires working in the temperature range of 25–30 K with a higher H_{c2} and J_c in the meanwhile this material was good enough for application.Many exciting approaches have been achieved in this field and the next is aimed at improving the mechanical properties. In this aspect, we once studied the mechanical strength of MgB_2 fiber with boron core at sintering temperatures of 750, 850, and 950℃, respectively [5]. Regarding the completed reaction of B fiber and Mg vapor, upon sintering at 950℃ for 1 h, the resulting MgB_2 fiber superconductors were fragile and easy to break into pieces even with the slightest touch; upon sintering at 750℃ for 2 h, the samples were finally able to obtain a bending capability just because there were still residual boron in the center of MgB_2 wire,as a result of annealing at a lower temperature.

Considering this point of view, we selected SS as substrate in the HPCVD process, which possessed a moderate tenacity by itself, and developed the HPCVD technique for growth of thick films. As we expected, these samples were considerably ductile.

These MgB_2 thick films on SS substrate were different from the thin films on sapphire or SiC substrate by using the same technique reported by Zeng et al. especially on one point. As mentioned above, the rupture happened to our films'surface due to large mismatch of thermal expansion coefficient between the film and the substrate in the cooling process. These fractures reduced the superconducting properties inevitably. To avoid this drawback, we refurnished the first sample with the same conditions. The original MgB_2 film acted as a buffer layer, thereby reducing the mismatch of thermal expansion coefficient; thus, the refurnished one acquired better properties.

Compared with the original one, the refurnished films' T_c and ΔT_c remained unchanged but had a complete R–T transition, as shown in Fig. 5. Figure 6 shows the morphology of destroyed surface of the refurnished sample under a bending angle of 180° . From the fractured part of the film, we could identify the existence of two layers as well as aneven harder rupture to the upper layer. Although there were still cracks in the underlayer, the direction and position of cracks were quite different in the two layers; hence, the

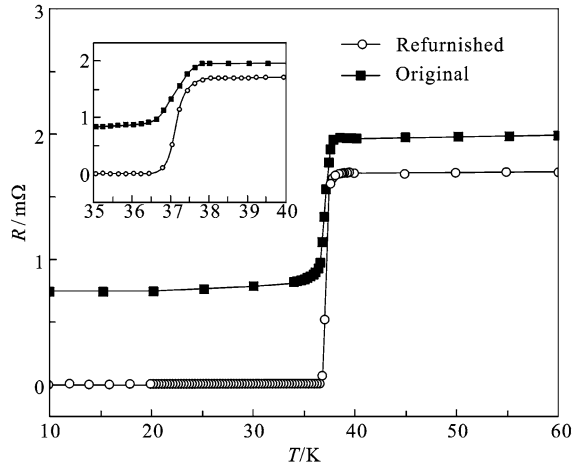

Fig. 5 Comparison of R–T curves between original and refurnished samples

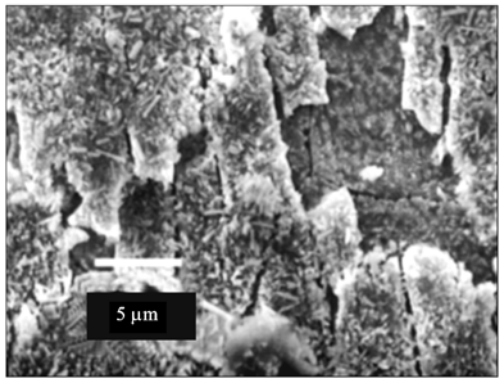

Fig. 6 SEM image of destroyed surface of refurnished sample under a bending force; we could see clearly the bilayer structure with different fractures

cracks could be well connected due to this fact. These refurnished samples demonstrated improved properties in mechanical experiments, which could keep $T_c \approx 37.6$ K and $\Delta T_c \approx 0.8$K almost unaffected at a bending angle of 180° .Considering the applied product line of B fiber, a multiplating technique with a core of tungsten, we believed that the HPCVD technique has great potentials in MgB_2 wire applications.

4 Conclusions

In conclusion, we fabricated MgB_2 thick films on ordinary SS substrate, whose thicknesses range from 10 μm to 20 μm. The film was highly oriented along the (101) direction and composed of packed, microsized crystallites without any porous structures. The deposition rate was about 20 nm/s, which was a rather high value. It indicated that this technique met the need of industrial production. The films adhered to the substrate strongly and were remarkably ductile for the sake of SS substrate. Most importantly, the superconducting properties, such as T_c and ΔT, are highly stable even under the progressively mechanical bending of the samples. This advantage could be well enlarged by a refurnished treatment to the original film. Therefore, this synthesis provides a more effective and efficient method than the PIT and the diffusion of Mg into B fiber in making superconducting tapes or wires.

Acknowledgements This study was supported by the State Key Program of Basic Research of China (No. BKBRSF-G1999064602).

References

1. Nagamatsu J., Nakagawa N., Muranaka T., Zenitani Y. and Akimitsu J., Nature, 2001, 410: 63
2. Jin S., Mavoori H., Bower C. and van Dover R. -B., Nature,2001, 411: 563
3. Bugoslavsky Y., Cohen L. -F., Perkins G. -K., Polichetti M.,Tate T. -J., Gwilliam R. and Caplin A. -D., Nature, 2001, 411:561
4. Canfield P. -C. and Crabtree G. -W., Phys. Today, 2003 (March):34
5. Feng Q. -R., Cao K., Xu J., Guo J. -D., Wang X., Xiong G. -C.,Gao Z. -X., Xu H. -Q., She D. -L., Cai S., Li Z. -Y. and DongY., Chin. J. Low Temp. Phys., 2002, 24(2): 96
6. Glowacki B. -A., Majoros M., Vickers M., Evetts J., Shi Y. and Mcdougall I., Supercond. Sci. Technol., 2002, 14: 193
7. Canfield P. -C., Finnemore D. -K., Bud'ko S. -L., Ostenson J.E., Lapertot G., Cunningham C. -E. and Petrovic C., Phys. Rev.Lett., 2001, (86): 2423
8. Kang W. -N., Kim H.-J., Choi E.-M., Jung C. -U. and Lee S.-L.,Science, 2001, 292: 1521
9. Eom C. -B., Lee M. -K., Choi J. -H., Belenky L. -J., Song X.,Cooley L. -D., Naus M. -T., Patnaik S., Jiang J., Rikel M.,Polyanskii A., Gurvich A., Cai X. -Y., Bu S. -D., Babcock S.-E., Hellstrom E. -E., Larbalestier D. -C., Rogado N., Regan K. -A., Hayward M. -A., He T., Slusky J. -S., Inumaru K., Haas M. -K. and Cava R. -J., Nature, 2001, 411: 558
10. Bu S. -D., Kim D. -M., Choi J. -H., Giencke J., Hellstrom E. -E., Larbalestier D. C., Patnaik S., Cooley L. and Eom C. -B., Appl. Phys. Lett., 2002, 81: 1851
11. Ma P., Liu L. -Y., Zhang S. -Y., Wang X., Xie F. -X., Deng P.,Nie R. -J., Wang S. -Z., Dai Y. -D. and Wang F. -R., Acta Phys.Sin., 2002, 51(2)
12. Ueda K. and Naito M., Appl. Phys. Lett., 2001, 79: 2046
13. Paranthaman M., Cantoni C., Zhai H. -Y., Christen H. -M.,Aytug T., Sathyamurthy S., Specht E. -D., Thompson J. -R.,Lowndes D. -H., Kerchner H. -R. and Christen D. -K., Appl.Phys. Lett., 2001, 78: 3669
14. Wang S. -F., Zhou Y. -L., Zhu Y. -B., Liu Z., Zhang Q., Chen Z.-H., Lu H. -B. and Yang G. -Z., Chin. J. Low Temp. Phys.,2003, 25(Suppl.)
15. Zeng X. -H., Pogrebnyakov A. -V., Kotcharov A., Jones J., Xi X. -X., Lysczek E., Redwing J. -M., Xu S., Li Q., Littieri J.,Schlom D. -G., Tian W., Pan X. and Liu Z. -K., Nat. Mater.,2002, 1: 35
16. Zeng X. -H., Pogrebnyakov A. -V., Zhu M. -H., Jones J. E., Xi X. -X., Xu S. Y., Wertz E. and Li Q., Appl. Phys. Lett., 2003,82: 2097
17. Chen C. -P., Wang X. -F., Lü Y., Zhang J., Guo J. P., Wang X.-N., Zhu M., Xu X. -Y. and Feng Q. -R., Physica, 2004, C 416: 90
18. Wang X. -F., Guo J. -P.U., Zhang J., Lu Y., Zhu M., Wang X. -N., Chen C. P., Xu J. and Feng Q. -R., Chin. J. Low Temp. Phys., 2004, 25(4)
19. Zhang J., Guo J. -P., Lu Y., Wang X. -F., Chen C. -P., Xu J., Wang X. -N., Zhu M. and Feng Q. -R., Chin. J. Low Temp. Phys., 2005, 27(1)
20. Kolesnikov N. -N. and Kuiakov M. -P., Physica, 2001, C 363: 166
21. Rhyee J.-S., Kim C. -A., Cho B. -K. and Kim J.-T., Appl. Phys.Lett., 2002, 80: 4407