Internally Oxidized Ag/1.2 at.% Mg Sheaths for Bi-2223 Tapes*

B. C. Prorok, J.-H. Park, K. C. Goretta, R. E. Koritala, and U. Balachandran
Argonne National Laboratory, Argonne, IL, USA

M. J. McNallan
University of Illinois, Chicago, IL, USA

September 2000

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Paper to be presented at Applied Superconductivity Conference ASC 2000, Virginia Beach, VA, September 17-22, 2000; to be published in IEEE Trans. Appl. Supercond.

*Work supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, and by the Argonne Division of Educational Programs with funding from DOE, under Contract W-31-109-Eng-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Internally Oxidized Ag/1.2 at.% Mg Sheaths for Bi-2223 Tapes

B. C. Prorok, J.-H. Park, K. C. Goretta, R. E. Koritala, U. Balachandran, and M. J. McNallan

Abstract—Bi-2223 tapes sheathed in dispersion-hardened Ag alloys that contain Mg have not generally achieved superconducting properties comparable to those of tapes sheathed in pure Ag. Factors involved in the internal oxidation process, such as oxygen diffusion and evolution of the grain structure of the sheath, appear to affect phase development of the Bi-2223 superconductor. Ag and Ag/1.2 at.% Mg sheaths, and alloy/Bi-2223 composite tapes, have been prepared and heat treated. Thermal processing procedures were optimized with respect to the diffusion of oxygen and strength profiles of the sheaths.

Index Terms—Ag alloy, wire, tape, mechanical properties

INTRODUCTION

To obtain sufficient electrical performance in high magnetic fields, high-temperature superconductor composite wires and tapes sheathed in Ag alloys must exhibit substantial tolerance to stress and strain. Dispersion hardening of Ag alloy sheaths through internal oxidation of reactive solute species can substantially improve strength [1]–[6]. Improved strain tolerances have been reported for Bi-2223 tapes with hardened sheaths, but the electrical performance of these composite conductors was degraded because of reduced phase purity of the superconducting core [5]–[8].

Mg is most often selected as the solute species in Ag because its elemental and oxide forms are relatively inert with respect to Bi-2212 and Bi-2223 superconductors [1], [9]. Use of an alloyed Ag sheath in place of a pure Ag sheath would likely lead to a shift in the O exchange between the treatment environment and superconducting phase during the internal oxidation process [10]–[12]. As has been shown in many

studies [13]–[16], there is only a narrow window of processing conditions, such as O₂ partial pressure and temperature, in which a nearly pure Bi-2223 phase can be synthesized. Although studies of the process variables involved in internally oxidizing Ag/Mg alloys have been presented [10]–[12], heat treatment procedures for Ag/Mg-sheathed high-temperature Bi-2223 superconductors have yet to be optimized. Effects of heat treatment time and temperature in an atmosphere of 8% O₂/N₂ are presented, and an optimal schedule for maximizing the sheath hardening and O transport is identified.

EXPERIMENTAL PROCEDURES

Square coupons (≤ 0.5 g and 0.5 mm thick) of Ag/1.2 at.% Mg were prepared from cold-rolled sheets. Thermogravimetric analysis (TGA) was performed in a flowing atmosphere of 8% O₂/N₂ at 450–835°C. The oxidation front was tracked by quenching samples at a designated time and then observing grain structure by sectioning, polishing, etching, and examining the resultant specimens by optical microscopy and scanning electron microscopy (SEM). The etchant was one part H₂O₂ (3% solution), one part NH₄OH, and one part H₂O.

Specimens for transmission electron microscopy (TEM) were prepared in a vertical single-jet polisher, in which a solution of 430 mL of ethyl alcohol, 50 mL of perchloric acid, and 30 mL of butyl cellosolve was used. The potential was 260 V and the temperature was –30°C. The polish was not completely uniform because of inhomogeneities in the specimen. To determine mechanical properties, cross-sectional microhardness profiles were obtained with a Knoop indenter; a load of 10 g was applied for 10 s.

RESULTS AND DISCUSSION

A. Kinetics and Microstructural Features

Fig. 1 is a plot of TGA data for the Ag/Mg alloy that was heat-treated at various temperatures in flowing 8% O₂/N₂. Samples treated at 500, 700, and 825°C were taken to their maximum O saturation limits. The maximum O saturation in the alloy decreased with increasing temperature. The lattice of Ag, and those of most metals, can support a higher concentration of O with increasing temperature [17]–[20]. Weight gains, as shown in Fig. 1, are a clear indication of an internal oxidation process that involves the retention of O atoms around the solute species (Fig. 2) [21].

Oxygen diffusion rates in the AgMg alloy are approximately identical to those in pure Ag; this equality can be demonstrated by applying Wagner's model of internal oxidation [11], [12]. Instead of simply examining apparent

Manuscript submitted September 18, 2000. Work supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, and the Argonne Division of Educational Programs with funding from DOE, under Contract W-31-109-Eng-38.

B. C. Prorok was with Argonne National Laboratory, Argonne, IL 60439, USA. He is now with the Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA (telephone: 847-467-7673; e-mail: bprorok@northwestern.edu).

J.-H. Park is with the Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA (telephone: 630-252-5104; e-mail: jhpark@anl.gov).

K. C. Goretta is with the Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA (telephone: 630-252-7761; e-mail: goretta@anl.gov).

R. E. Koritala is with the Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA (telephone: 630-252-5379; e-mail: koritala@anl.gov).

U. Balachandran is with the Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA (telephone: 630-252-4250; e-mail: balu@anl.gov).

M. J. McNallan is with the University of Illinois at Chicago, Chicago, IL 60607, USA (telephone: 312-996-2436; e-mail: mcnallan@uic.edu).

diffusion coefficients, the concentration of Mg and the solubility of O in the AgMg must be considered. One can then calculate a solubility product (k_p) in AgMg, which can be directly compared with a diffusion coefficient in Ag (Fig. 3). The question is why O fixation in the AgMg takes 50–400 times longer, depending on temperature, to penetrate

Fig. 1. Weight gain vs. temperature for Ag-Mg alloy treated in 8% O_2/N_2 at various temperatures.

Fig. 2. Two-dimensional schematic representation of smallest and larger Mg-O clusters in an Ag lattice; gray circles = Ag, wavy circles = Mg, open circles = O in cluster, and black circles = O dissolved in Ag.

Fig. 3. Diffusion coefficients (D) for O in Ag (filled circles), apparent diffusion coefficients measured for O in AgMg (open circles), and calculated k_p values for O uptake in AgMg (filled triangles); agreement between calculation and measurements is excellent.

through the alloy than through pure Ag. The extra time, and hence additional uptake of O, is the result of Mg atoms trapping superstoichiometric amounts of O, thus slowing the penetration rate of the oxidation front [11,12].

Fig. 4 shows a composite photomicrograph that illustrates differences in grain size obtained at various oxidation temperatures for the Ag/Mg alloy annealed in 8% O_2/N_2 . Based on the assumption that the samples were initially uniformly cold-worked, several conclusions can be drawn. Recrystallization without appreciable grain growth occurred at 450 and 500°C. At higher temperatures, however, grain growth did not continue uniformly throughout the specimen. Annealing temperatures of 600, 700, and 825°C induced regions of notably differing grain size. Specimens annealed at these temperatures contained zones of fine grains directly beneath the surface, whereas in the interior, recrystallization and grain growth proceeded normally. In the fine-grained zones, O had an opportunity to diffuse into the sample, combine with Mg atoms to form Mg-O clusters, and impede grain growth.

At some temperature between 500 and 600°C, the dominance of grain growth over internal oxidation in controlling microstructure was established, which can be inferred because the size of the fine-grained zone decreased with increasing temperature. These trends resulted from different temperature-dependent rates for the processes of internal oxidation and grain growth. As temperature increased, grain growth occurred more and more rapidly in

Fig. 4. SEM photomicrographs of AgMg treated in 8% O_2/N_2 at various temperatures, showing oxidation fronts and regions of grain growth.

the interior, before O had an opportunity to diffuse a significant distance within the sample and restrict grain growth through formation of Mg-O clusters. The result was a shrinkage of the fine-grained region with increasing temperature.

TEM revealed the formation of 10–30 nm Mg-O clusters that were uniformly distributed (Fig. 5). This size agrees well with what has been predicted for Mg-O clusters [13]. In Fig. 5, each dark-appearing cluster was surrounded by a gray layer, which represents the strain field that a coherent cluster should induce. The clusters appeared to form in doublets. Such apparent doubling can occur if the cluster is oriented such that the Bragg equation is satisfied by a strain misfit vector that is identical to the diffraction vector. If so, the planes through the centers of the clusters exhibit no misfit with respect to the matrix, which results in no contrast [22].

B. Property Characterization

Fig. 6 is a microhardness profile across the thickness of a specimen in which the internal oxidation process was terminated by air-quenching. The oxidation front penetrated $\approx 140 \mu\text{m}$ into the specimen. In this oxygenated region, the Knoop hardness was $\approx 160 \text{ MPa}$. Immediately ahead of the oxidation front, the hardness dropped abruptly to $\approx 40 \text{ MPa}$, which agrees well with the annealed hardness of pure Ag [23]. The hardness of the oxidized region is as much as four to five times higher. The presence of O caused an increase in lattice strain, from both free interstitial O and O associated with the Mg solute; the result was significant obstruction of dislocation motion [22],[23].

A point of interest in Fig. 6 is the peak in hardness, which appears to trail just behind the oxidation front. This peak was observed in every quenched sample that was studied. This region of increased hardness is attributed to the presence of Mg-O clusters that had not yet reached their equilibrium size. Thus, relatively more, finer clusters were more effective in hardening than fewer, larger clusters. This peak in hardness could have been predicted from the weight-gain data in Fig. 1; after each specimen attained a maximum O saturation, weight loss, i.e., O release, followed until equilibrium was reached through formation of clusters of a stable size [12].

Fig. 5. TEM photomicrograph of AgMg specimen annealed at 825°C, showing Mg-O clusters; inset is electron diffraction pattern.

A Knoop hardness-vs.-hardness plot was constructed from the base-line hardness values of specimens heat-treated at the various temperatures (Fig. 7). For this plot, a two-step heat treatment was used. Each specimen was first saturated with O in the 8% O_2/N_2 mixture at a given temperature, and then the specimen was heated at 825°C for 50 h, as would be typical for a sheathed Bi-2223 superconductor [12],[16]. Hardness increased with initial annealing temperature to a peak value at 600°C, and then decreased with further increases in temperature. The hardness trend from 600 to 825°C agrees well with hardness data published for an Ag-Mg alloy of slightly higher Mg content (1.3 at.%) [24]. These trends indicate that a certain cluster size and distribution provide maximum obstruction to dislocation motion.

The driving force for diffusion into the AgMg is proportional to the square root of the oxygen partial pressure. Thus, to enhance kinetics, if one's furnace allows, one can accomplish O saturation at 600°C in pure O_2 [12]. The atmosphere can then be switched to 8% O_2/N_2 during heating to 825°C.

The kinetic, microstructural, and hardness data can be combined to create an optimal heat-treatment schedule, by which appreciable sheath hardening can be accomplished without substantially affecting the phase purity of the Bi-2223

Fig. 6. Microhardness profile across depth of representative sample; the oxidation front has penetrated $\approx 140 \mu\text{m}$ into the alloy.

Fig. 7. Hardness-vs.-temperature data for Ag/Mg alloy; the dashed line represents data from Hirschhorn [24] for 1.3 at.% Mg in Ag alloy.

superconductor. The maximum hardness was obtained at an oxidation temperature of 600°C. Thus, a composite tape of wire of average sheath can first be annealed in O₂ at ≈600°C to harden the sheath. This temperature is sufficiently low to minimize O loss from the precursor components that will form the Bi-2223 superconducting phase during subsequent heat treatment [15]. Upon hardening the sheath, the composite can undergo normal annealing procedures in 8%O₂/N₂ for Bi-2223 phase formation, sintering, and oxygenation of the superconducting phase [13],[15].

Composite tapes obtained from Intermagnetics General Corporation [25], fabricated with Ag/Mg sheaths, have been annealed by the procedures described above. Preliminary critical-current results at 77 K indicate that these tapes yield nearly identical transport critical current as those fabricated with pure Ag sheaths. Further experiments are needed to confirm this finding and to determine the effects of sheath hardness on stress and strain tolerance.

CONCLUSIONS

Study of the internal oxidation process of an Ag/1.2 at.% Mg alloy and Bi-2223 literature allows several conclusions pertinent to the processing of high-temperature-superconducting composite wires and tapes.

(1) Internal oxidation at low temperature (≤600°C) is likely to precipitation-harden the sheath without the consumption of O from the core components that will form the superconducting phase.

(2) After complete internal oxidation, penetration of O through the alloy returns to a relationship with time identical to that of pure Ag. This relationship should allow for the normal oxygenation of the superconductor.

(3) Maximum sheath hardness is obtained with initial oxidation at 600°C, with further heat treatment at 825°C for periods of 50 h, which are ideal conditions for forming the superconducting phase.

(4) An ideal thermal treatment procedure can be designed. Such a procedure would involve first heating to ≈600°C in 8%O₂/N₂ or pure O₂; second, a dwell at ≈600°C to completely internally oxidize the sheath; and third, heating in 8%O₂/N₂ to ≈825°C for ≥50 h, followed by controlled cooling to room temperature.

REFERENCES

- [1] Tenbrink, J., Wilhelm, M., Heine, K., and Krauth, H., "Development of technical high-T_c superconductor wires and tapes," *IEEE Trans. Appl. Supercond.*, vol. 3, pp. 1123-1126, 1993.
- [2] Parrell, J. A., Dorris, S. E., and Larbalestier, D. C., "The effect of sheath material and deformation method on the oxide core density," *Adv. Cryo. Engr.*, vol. 40A, pp. 193-198, 1994.
- [3] Schwartz, J., Heuer, J., Goretta, K. C., Poeppel, R. B., Gou, J., and Raban, Jr., G. W., "High-temperature mechanical properties and high-strength sheaths for powder-in-tube tapes," *Appl. Supercond.*, vol. 2, pp. 271-280, 1994.
- [4] Guo, J., Lewis, J. A., Goretta, K. C., and Schwartz, J., "Properties and chemical stability of hot-rolled Ag(7 at.% Cu)-sheathed Bi₂Sr₂Ca_{0.64}Cu_{1.64}O_x powder-in-tube tapes," *J. Appl. Phys.*, vol. 78, pp. 4596-4607, 1995.
- [5] Goldacker, W., Keßler, J., Ullmann, B., Mossang, E., and Rikel, M., "Axial tensile, transverse compressive and bending strain experiments on Bi(2223)/AgMg single core tapes," *IEEE Trans. Appl. Supercond.*, vol. 5, pp. 1834-1837, 1995.
- [6] Goldacker, W., Mossang, E., Quilitz, M., and Rikel, M., "On the phase formation in Ag and AgMg sheathed BSCCO (2223) tapes," *IEEE Trans. Appl. Supercond.*, vol. 7, pp. 1407-1410, 1997.
- [7] Keßler, J., Blüm, S., Wildgruber, U., and Goldacker, W., "High critical currents in Bi(2223) tapes with Ag and hardened Ag sheaths," *J. Alloys Comp.*, vol. 195, pp. 511-514, 1993.
- [8] Schwartz, J., Amm, B. C., Garmestani, H., Hilton, D. K., and Hascicek, Y., "Mechanical properties and strain effects in Bi₂Sr₂CaCu₂O_x/AgMg composite conductors," *IEEE Trans. Appl. Supercond.*, vol. 7, pp. 2038-2041, 1997.
- [9] Nakajima, H., Yamaguchi, S., Iwasaki, K., Morita, H., and Fujimori, D., "Interdiffusion and interfacial reaction between a YBa₂Cu₃O_x thin film and substrates," *Appl. Phys. Lett.*, vol. 53, pp. 1437-1439, 1988.
- [10] Prorok, B. C., Park, J.-H., Goretta, K. C., Balachandran, U., and McNallan, M. J., "Hardness and microstructure of internally oxidized silver alloys," *IEEE Trans. Appl. Supercond.*, vol. 10, pp. 1178-1181, 2000.
- [11] Park, J.-H., Prorok, B. C., Goretta, K. C., Balachandran, U., and McNallan, M. J., "High temperature internal oxidation of Ag/1.2 at.% Mg and Ag/0.25 at.% Mg-0.25 at.% Ni," *Electrochem. Soc. Proc.*, vol. 99-38, pp. 107-114, 2000.
- [12] Prorok, B. C., "Internal oxidation of dilute Ag/Mg alloys for strengthening composite superconductor wires," Ph.D. Thesis, University of Illinois at Chicago, Chicago, IL, USA, 2000.
- [13] Merchant, N. N., Luo, J. S., Fischer, A. K., Maroni, V. A., Podtburg, E. R., Carter, W. L., Li, Q., Otto, A., Rupich, M. W., and Riley, Jr., G. N., "Phase formation and microstructure development in silver-clad Bi-2223 multifilament composite conductors," *Supercond. Sci. Technol.*, vol. 12, pp. 327-336, 1999.
- [14] Tanaka, Y., Asano, T., Yanagiya, T., Fukutomi, M., Komori, K., and Meada, H., "Fabrication and superconducting properties of AgCu alloy-sheathed BiSrCaCuO oxide tapes," *Jpn. J. Appl. Phys.*, vol. 31, pp. L235-L241, 1992.
- [15] Dorris, S. E., Prorok, B. C., Lanagan, M. T., Sinha, S., and Poeppel, R. B., "Synthesis of highly pure Bi-2223 by a two-step process," *Physica C*, vol. 212, pp. 277-283, 1993.
- [16] Dou, S. X. and Liu, H. K., "Ag-sheathed Bi(Pb)SrCaCuO superconducting tapes," *Supercond. Sci. Technol.*, vol. 6, pp. 297-302, 1993.
- [17] Gou, Y. C., Liu, H. K., and Dou, S. X., "Interactions of Ag with the BSCCO system," *Physica C*, vol. 212, pp. 198-207, 1993.
- [18] Steacie, E. W. R., and Johnson, F. M. G., "The solubility and rate of solution of oxygen in silver," *Proc. Roy. Soc.*, vol. 112A, 543-558, 1926.
- [19] Eichenauer, W. and G. Müller, G., "Diffusion und Löslichkeit von sauerstoff in silber," *Z. Metallkd.*, vol. 53, pp. 321-325, 1962.
- [20] Ramanarayanan, T. A. and Rapp, R. A., "The diffusivity and solubility of oxygen in liquid tin and solid silver and the diffusivity of oxygen in solid nickel," *Met. Trans.*, vol. 3, pp. 3239-3246, 1972.
- [21] Park, J.-H., "Measuring oxygen diffusivity and solubility in solid silver with a gas-tight electrochemical cell," *Mater. Lett.*, vol. 9, pp. 313-316, 1990.
- [22] Martin, J. J., *Precipitation Hardening*, 2nd edition, Butterworth-Heinemann, Oxford, p. 32, 1998.
- [23] Goretta, K. C., Routbort, J. L., Thayer, R. L., Carroll, J. P., Wolfenstine, J., Kessler, J., and Schwartz, J., "Deformation of Ag/1.2 at.% Mg," *Physica C*, vol. 265, pp. 201-206, 1996.
- [24] Hirschhorn J. S. and Lenel, F. V., "Observations on the hardness, lattice parameter and microstructure of internally oxidized silver magnesium and silver aluminum alloys," *ASM Trans.*, vol. 59, pp. 208-222, 1966.
- [25] Selvamannickam, V., Intermagnetics General Corporation, private communication, 2000.