CHARACTERIZATION OF HOT ISOSTATICALLY PRESSED Bi–Sr–Ca–Cu–O AS A FUNCTION OF CONSOLIDATION VARIABLES*

K. C. Goretta, D. J. Miller, R. B. Poeppel, and A. S. Nash**
Materials and Components Technology Division
Argonne National Laboratory, Argonne, IL 60439
**Marquette University, Milwaukee, WI 53233

ANL/CP--73717

DE92 006980

November 1991

Paper intended for submission to 1991 Materials Research Society Fall Meeting, Boston, MA, December 2–6, 1991; proceedings of Symposium S: Gas Pressure Effects on Materials.

*Work supported by the U.S. Department of Energy (DOE), Conservation and Renewable Energy, as part of a DOE program to develop electric power technology (KCG, RBP), and Basic Energy Sciences-Materials Science (KCG, DJM), under Contract W-31-109-Eng-38; and by the College of Engineering, Marquette University (ASN).

CHARACTERIZATION OF HOT ISOSTATICALLY PRESSED Bi–Sr–Ca–Cu–O AS A FUNCTION OF CONSOLIDATION VARIABLES

K. C. GORETTA, D. J. MILLER, R. B. POEPPEL
Argonne National Laboratory, Argonne, IL 60439
and A. S. NASH
Marquette University, Milwaukee, WI 53233

ABSTRACT

Fully dense, bulk $Bi_2Sr_{1.7}CaCu_2O_x$ (2212) superconductor pellets were made by hot isostatic pressing in an inert atmosphere. Electron microscopy revealed that rotation and bending of the platelike 2212 grains were responsible for much of the densification. Under processing conditions of 825°C and 105 MPa, dense pellets were obtained in 15 min. Many dislocations, planar faults, and, perhaps, intergrowths of the $Bi_2Sr_2CuO_x$ phase were produced during pressing. The dislocations were largely present in subgrain boundaries when the pressing times were increased to 45–120 min.

INTRODUCTION

The phases in the Bi–Sr–Ca–Cu–O system have highly anisotropic electrical and physical properties [1]. The $Bi_2Sr_2CaCu_2O_x$ (2212) phase [1], which has a superconducting transition temperature of ≈90 K, has proved to be very difficult to consolidate by pressureless sintering [2,3]. At the sintering temperature, rapid grain growth occurs in two dimensions (along the a–b planes of the unit cell), and a compact can actually become less dense with sintering time [3]. The 2212 phase and other Bi-based superconductors have, however, been successfully densified by hot isostatic pressing [4-8] or hot pressing [9,10].

The mechanisms by which the 2212 and similar phases consolidate are now under investigation. In addition, it has been shown that metallic Ag additions can promote densification of 2212 [11,12], and the effects of Ag additions are also being examined [13]. This study is a continuation of previous work [5,8,13,14] on hot isostatic pressing (HIPing) of 2212. Specific questions that are addressed are the extent to which plastic bending of the platelike 2212 grains promotes densification, the evolution of dislocation structures during pressing, and the effects of pressing time on phase formation. Bending of grains and formation of complex dislocation networks have been documented for room–temperature deformation of 2212 [14]. Dislocation structures are of particular interest because dislocations may have significant effects on the superconducting properties of high–temperature superconductors [15-17].

EXPERIMENTAL METHODS

The composition that was used was $Bi_2Sr_{1.7}CaCu_2O_x$, which yields 2212 of excellent phase purity [18]. The 2212 powder was synthesized from a mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO. The powders were ball–milled for 18–24 h in polyethylene jars containing methanol and ZrO_2 grinding media. The milled powders were pan–dried, ground lightly with an agate mortar and pestle, and heated in air for 48–72 h at 815–820°C. The resulting powder was ground in a tungsten carbide rotary mill [14]. No $Bi_2Sr_2CuO_x$ (2201) phase was observed by X–ray diffraction.

A similar routine was applied to obtain 2212 with 15 wt.% Ag additions. A mortar and pestle were used to mix 2–μm metallic Ag particles into the fully synthesized 2212 powder [8]. The 2212 and 2212 + Ag powders were processed into bulk forms by HIPing in an inert atmosphere. The pressure was 105 MPa, the temperature was 825°C, and the times at temperature and pressure were 15, 45, and 120 min.

Geometric densities were obtained for all of the specimens. Many of the specimens were examined by X–ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). In addition, ultrasonic measurements were made to determine the effective Young's modulus of some of the samples [19].

RESULTS AND DISCUSSION

As shown in Fig. 1, 2212 powder consists of thin platelike grains that can have large aspect ratios. The c–axis of the orthorhombic unit cell is perpendicular to the plane of the plate. These grains bend easily under stress, and virtually all of the dislocation activity occurs in the a–b planes of the cells [14]. It is likely that substantial bending of the grains occurs during HIPing, but this has not been confirmed.

In previous work on 2212, HIPing was conducted for 120 min. In the current work, it was found that fully dense pellets could be formed within 15 min (Fig. 2). (Times of less than 15 min were not investigated because of experimental difficulties in determining an accurate time at temperature and pressure.) TEM of the HIPed pellets clearly revealed substantial bending of many of the 2212 grains. The lack of bending in the other grains, however, suggests that grain rotation plays a significant part in the deformation process. TEM also revealed high concentrations of dislocations within the grains. In the 15–min samples, several types of complex dislocations, primarily in the a–b planes, were observed (Fig. 3). In the 45–min (Fig. 4) and 120–min samples, the dislocations were largely present at subgrain boundaries.

Figure 1. SEM photograph of platelike 2212 grains.

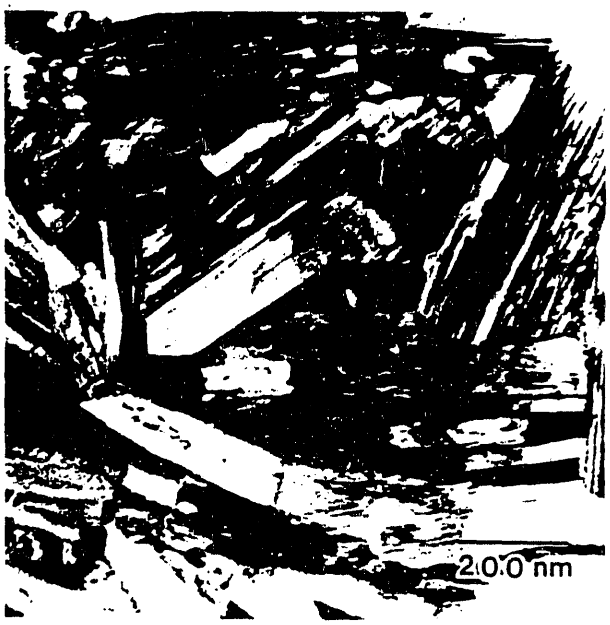

Figure 2. TEM photograph of 2212 HIPed for 15 min.

Figure 3. TEM photograph of complex dislocations in 2212 HIPed for 15 min.

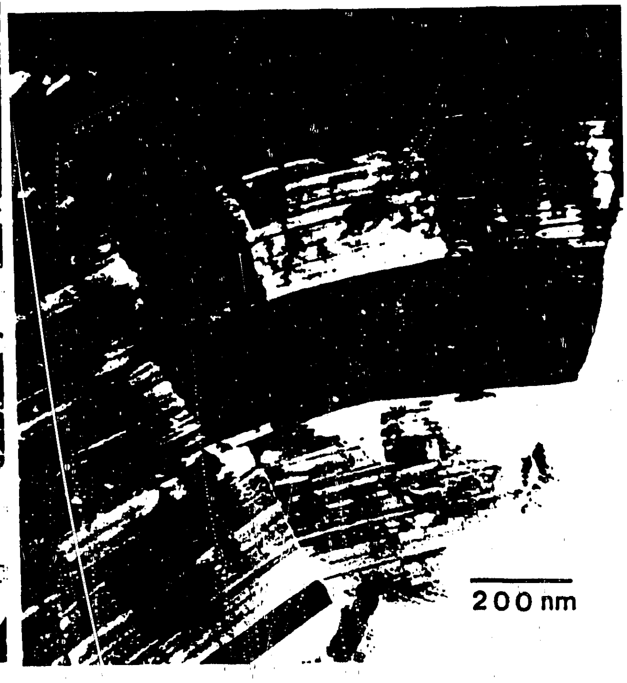

Figure 4. TEM photograph of subgrains in 2212 HIPed for 45 min.

It is likely that the vast majority of the dislocation motion occurred by glide along the a–b planes. Measurements have shown that diffusion of oxygen and Ag occurs approximately as slowly in 2212 [20,21] as in the superconductor $YBa_2Cu_3O_x$ [22,23]. Therefore, if diffusional creep were as slow in 2212 as in $YBa_2Cu_3O_x$ [24], as might be expected, the distances that the dislocations moved in 15 and 45 min cannot be accounted for by diffusion.

Diffusional considerations may also be related to an additional difference observed among the specimens that were HIPed for 15, 45, and 120 min. Although each sample was nominally fully dense, the calculated Young's modulus was 65 ± 1 GPa for a 15–min pellet and 73 ± 1 GPa for a 120 min pellet. A value of 74.3 GPa for the Young's modulus of fully dense 2212 has been reported [25]. This value can be affected by the oxygen and cation contents of the 2212 phase, which has a range of composition [25,26]. Thus, agreement between the two studies is surprisingly good. The decrease in modulus for the 15–min sample is probably due to the presence of microcracked or poorly sintered grain boundaries. Diffusion is very slow in 2212. It appears that during HIPing, 2212 densifies very quickly, largely because of rotation and bending of the individual grains. Diffusion is then needed to bond the grains, and more than 15 min is required for adequate diffusion to occur.

It should be mentioned that diffusion in high–temperature superconductors is highly anisotropic. In the most extensively studied compound, $YBa_2Cu_3O_x$, for Y, Ba, Cu (and elements such as Ni and Co that substitute on the Cu sites), and O diffusion, the *smallest* anisotropy between diffusion in the a–b plane and in the c direction is a factor of 50. The largest anisotropy is approximately a factor of 10^6. For all of the elements, diffusion is much slower in the c direction. One may therefore view bulk diffusion as occurring by motion only along the a–b planes and grain boundaries. To our knowledge, this type of mass–transport mechanism has not been modeled for processes such as sintering or creep. Experiments may be needed to provide the data needed to support modeling efforts.

X–ray diffraction has indicated that measurable amounts of the $Bi_2Sr_2CuO_x$ (2201) phase were formed during HIPing of 2212 [13]. The mechanism for the formation is not clear. TEM observations of the current specimens failed to reveal the presence of distinct 2201 grains, but did reveal that all of the samples contained many planar faults (Fig. 5). These faults have yet to be identified, but they may possibly be 2201 intergrowths in the 2212 matrix. (The difference between the two phases is the stacking of planes: one fewer Cu–O plane is present in 2201 than in 2212 and, as a result, no Ca layer is needed to separate adjacent Cu–O layers [1].) Given the slow diffusion in 2212 and the absence of a clear grain–boundary phase in the HIPed 2212, the formation of 2201 intergrowths appears to be a likely possibility. It has been reported that pressures as low as 0.3 MPa can cause some formation of 2201 from 2212 [27]. (In addition, it was reported recently that hot pressing at 200 MPa causes similar partial decomposition of the 110 K superconducting phase in the Bi system [28].) The 2201 phase has a superconducting transition temperature of ≈10 K [1]. It has been reported that HIPed 2212 pellets have very low critical current densities at 77 K [5,13]. The presence of 2201 intergrowths, with their low superconducting transition temperature, may be responsible. Measurements of current densities at 4.2 K and additional TEM analyses are in progress.

The effects of Ag additions on the kinetics of deformation could not be examined in these studies because all of the samples were fully dense within 15 min. SEM and TEM indicated that most of the Ag existed in discreet regions. Sharp boundaries were observed between the 2212 and the Ag (Fig. 6). Although Ag is known to occupy Cu sites, and some interdiffusion may have occurred between the 2212 and Ag, no reaction to form a new phase was observed. Ag additions may possibly improve the mechanical properties and

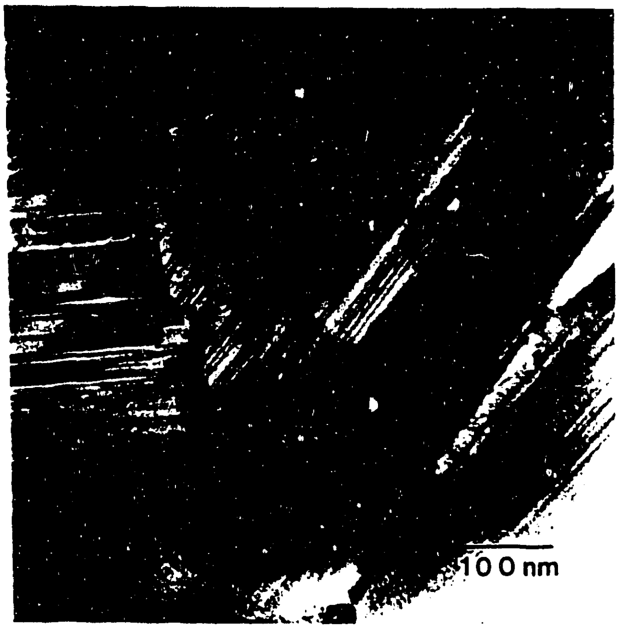

Figure 5. TEM photograph of planar faults in 2212 grains.

Figure 6. TEM photograph of 2212/ Ag interface.

some electrical properties of high-temperature superconductors [29,30]. TEM offers no evidence, such as formation of a deleterious grain-boundary phase, to indicate that incorporation of Ag into 2212 may degrade electrical properties.

CONCLUSION

Fully dense 2212 pellets were made by HIPing. Electron microscopy revealed that rotation and bending of the platelike 2212 grains were responsible for much of the densification. Under HIPing at 825°C and 105 MPa, dense forms were obtained in 15 min, but additional time at temperature was needed to bond the grains well. Many dislocations and planar faults were produced during pressing. The effects of these defects on superconducting properties are under investigation.

ACKNOWLEDGMENTS

Experimental assistance at Argonne was provided by M. T. Lanagan, C.-T. Wu, C.-Y Chu, and E. J. Zamirowski. The HIPing was performed at Industrial Materials Technology, Andover, MA, by J. Suber. This work was supported by the U.S. Department of Energy (DOE), Conservation and Renewable Energy, as part of a DOE program to develop electric power technology (KCG, RBP), and Basic Energy Sciences-Materials Science (KCG, DJM), under Contract W-31-109-Eng-38; and by the College of Engineering, Marquette University (ASN).

REFERENCES

1. R. Beyers and T. M. Shaw, Sol. State Phys. 42, 135 (1989).
2. U. Balachandran, M. J. McGuire, K. C. Goretta, C. A. Youngdahl, D. Shi, R. B. Poeppel, and S. Danyluk, in *Superconductivity and Applications*, eds. H. S. Kwok, Y.-H. Kao, and D. T. Shaw (Plenum Press, New York, 1990) p. 265.
3. D. W. Johnson Jr. and W. W. Rhodes, J. Am. Ceram. Soc. 72, 2346 (1989).
4. H. Seino, K. Ishizaki, and M. Takata, Jpn. J. Appl. Phys. 28, L78 (1989).
5. A. S. Nash, P. Nash, H. Shi, R. B. Poeppel, and K. C. Goretta, Supercond. Sci. Technol. 3, 556 (1990).
6. K. Ishizaki, M. Takata, and H. Seino, J. Mater. Sci. Lett. 9, 16 (1990).
7. S. X. Dou, H. K. Liu, J. Wang, and W. M. Bian, Supercond. Sci. Technol. 4, 21 (1991).
8. A. S. Nash, P. Nash, R. B. Poeppel, and K. C. Goretta, in *High Temperature Superconducting Compounds III*, eds. S.H. Whang, A. DasGupta and E. W. Collings, (The Metall. Soc., Warrendale, PA, 1991) p. 77.
9. N. Murayama, E. Sudo, M. Awano, K. Kani, and Y. Torii, Jpn. J. Appl. Phys. 27, L1856 (1988).
10. R. Yoshizaki, H. Ikeda, K. Yoshikawa, and N. Tomita, Jpn. J. Appl. Phys. 29, L753 (1990).
11. J. Joo, Argonne National Laboratory, private communication (1991).
12. A. S. Nash, K. C. Goretta, and R. B. Poeppel, in *Advances in Powder Metallurgy-1989, Vol. 2*, eds. T. S. Gasbarre and W. F. Janeska (Met. Powder Ind. Fed., Princeton, NJ, 1989) p. 517.
13. A. S. Nash, K. C. Goretta, R. B. Poeppel, D. Shi, and P. Nash, in *High-Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, eds. D. Christen, J. Narayan, and L. Schneemeyer (Mater. Res. Soc., Pittsburgh, PA, 1990) p. 1287.

14. A. S. Nash, K. C. Goretta, R. Wheeler IV, B. M. Moon, C.–T. Wu, and P. Nash, in *Advances in Powder Metallurgy–1991* (Met. Powder Ind. Fed., Princeton, NJ, 1991) in press.
15. Y. Takahashi and T. Suga, Jpn. J. Appl. Phys. 29, L2006 (1990).
16. M. J. Kramer, R. W. McCallum, and L. S. Chumbley, Physica C 162-164, 552 (1989).
17. D. Shi, K. C. Goretta, S. Salem–Sugui, P. McGinn, W. H. Chen, and N. Zhu, Appl. Phys. Lett. 59, 225 (1991).
18. I. Bloom, J. R. Frommelt, M. C. Hash, M. T. Lanagan, C.–T. Wu, and K. C. Goretta, Mater. Res. Bull. 26, 1269 (1991).
19. J. Krautkrämer and H. Krautkrämer, *Ultrasonic Testing of Materials* (Springer–Verlag, New York, 1977) p. 580.
20. M. Runde, J. L. Routbort, S. J. Rothman, K. C. Goretta, J. N. Mundy, X. Xu, and J. E. Baker, Phys. Rev. B, in press (1992).
21. J. L. Routbort, Argonne National Laboratory, private communication (1991).
22. S. J. Rothman, J. L. Routbort, and J. E. Baker, Phys. Rev. B 40, 8852 (1989).
23. N. Chen, Ph.D. thesis, Illinois Institute of Technology, Chicago, IL (1991).
24. K. C. Goretta, J. L. Routbort, A. C. Biondo, Y. Gao, A. R. de Arellano–López, and A. Dominguez–Rodriguez, J. Mater. Res. 5, 2766 (1990).
25. C. Fanggao, M. Cankurtaran, G. A. Saunders, D. P. Almond, P. J. Ford, and A. Al–Kheffaji, Supercond. Sci. Technol. 3, 546 (1990).
26. S. Lin, Y. He, C. Wei, and Z. Shen, Supercond. Sci. Technol. 2, 145 (1989).
27. F. A. Karbarz, O. D. Lacy, K. C. Goretta, U. Balachandran, D. Shi, J. G. Chen, M. Xu, and M. C. Hash, Mater. Res. Bull. 25, 251 (1990).
28. K.–H. Song, C. C. Sorrell, S.–X. Dou, and H.–K. Liu, J. Am. Ceram. Soc. 74, 2577 (1991).
29. J. P. Singh, H. J. Leu, R. B. Poeppel, E. Van Voorhees, G. T. Goudey, K. Winsley, and D. Shi, J. Appl. Phys. 66, 3154 (1989).
30. D. Lee and K. Salama, Jpn. J. Appl. Phys. 29, L2017 (1990).

END

DATE FILMED

3 / 3 / 92