PROCEEDINGS OF THE IV INTERNATIONAL CONFERENCE/HIGH TEMPERATURE CAPILLARITY

JOURNAL OF MATERIALS SCIENCE **40** (2005) 2361 – 2365

Grain boundary wetting in ceramic cuprates

V. V. BELOUSOV
Department of Materials, Institute of Steel, 127411 Moscow, Russia; Department of Materials Science, Moscow State University, 119992 Moscow, Russia
E-mail: vvbel@inorg.chem.msu.ru

Grain boundary (GB) wetting by a chemically compatible liquid in ceramic cuprates and its influence on transport properties of ceramics are considered, using model Bi_2CuO_4-Bi_2O_3 system as an example. It is shown that the GB wetting transition enhances significantly ionic conductivity and diffusional permeability of the ceramics. The experimental data on grain boundary wetting transition, electrical conductivity, diffusivity, and high temperature corrosion of copper are discussed. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

During the last decade there has been a growing interest in different aspects of grain boundary (GB) wetting, stimulated by intensive development of electroceramic materials [1]. For example, high temperature superconductivity in ceramic cuprates, where GBs limit the critical current density, has been discovered [2]. Wetting of GBs can take place at the synthesis of high-temperature superconducting ceramic composites. This may have a profound effect on their electrical conductivity [3]. Ion-conducting ceramic cuprates with liquid channel grain boundary structure have been obtained [4–5]. High ionic conductivity and plasticity of ceramic cuprates with liquid channel grain boundary structure are also related to the GB wetting.

Most interesting is GB wetting by a chemically compatible liquid in the two-phase area of the bulk phase diagram where the liquid and solid are in equilibrium. In this case the interfacial tension is substantially reduced [6]. In the presented paper the GB wetting of $Bi_2CuO_4$by eutectic liquid and its influence on transport properties are considered, Bi_2CuO_4-Bi_2O_3 composite ceramics as an example. The experimental data on GB wetting transition, electrical conductivity, diffusivity are discussed.

2. Grain boundary wetting transition

The GB wetting transition in Bi_2CuO_4 can be realized when ceramic composite formed of Bi_2CuO_4 and Bi_2O_3 components at eutectic melting temperature between them is heated [7]. Fig. 1a shows the starting microstructure of such composite. The light phase of Bi_2O_3 is randomly distributed in the dark composite bulk. However, this picture can change greatly under heating. Fig. 1b and c show the microstructure of same composite, but when heated higher than the melting point of the eutectic between oxides. In this case bismuth oxide is localized on the triple grain junctions. Evidently, it is the result of the grain boundary wetting transition in Bi_2CuO_4 by the eutectic liquid. The kinetics transition study shows that it has stick-slip nature [8].

Most likely, that GB wetting transition is analogous to the critical point wetting studied by Chan [9–11]. According to the phase diagram of Bi_2O_3-CuO system [12–13], the melting temperature of the eutectics between $Bi_2CuO_4$and Bi_2O_3 is 770° C. The microstructure of the solidified liquid at the triple grain junctions is presented in Fig. 2. Micrograph shows that this is a typical eutectic microstructure. In Fig. 3 the microstructure of the ceramics fracture surface is shown. The fracture is of intercrystalline nature (Fig. 3a). The grain surfaces are seen to bear eutectic traces (Fig. 3b). Note that, above solidus temperature, the ceramic composite became super plastic and may flow even due to gravity [4, 5]. It is known that one of the main conditions of super plasticity for ceramics is the presence of a liquid or glass phase along the GBs [14]. It should also be noted that the ceramic composite after cooling from temperatures above GB wetting transition has cracks (Figs 1b and c).

3. Thin intergranular films

The GB study of the ceramic Bi_2CuO_4–Bi_2O_3 composites cooled from temperatures above melting point of the eutectic by high resolution transmission electron microscopy showed the presence of thin intergranular films in Bi_2CuO_4 (Fig. 4). Thickness of intergranular films is approximately 1–2 nm. Such intergranular films were discovered in many oxide, nitride and carbide ceramics sintered with various impurities and dopants [15–21]. It was established that thickness of intergranular films is approximately constant 1–2 nm [22, 23]. This implies that the film thickness slightly depends on the GB misorientation except low angle and certain special GBs where intergranual films were not disclosed.

The equilibrium thickness of the intergranual wetting films in ceramics was calculated by Clarke [24, 25]. Within the framework of continuum approximation, Clarke proposed the approach based on the balance of forces normal to the boundary

$$P_{app} + P_{cap} + \Pi_{vdw} + \Pi_{edl} + \Pi_{st} = 0 \qquad (1)$$

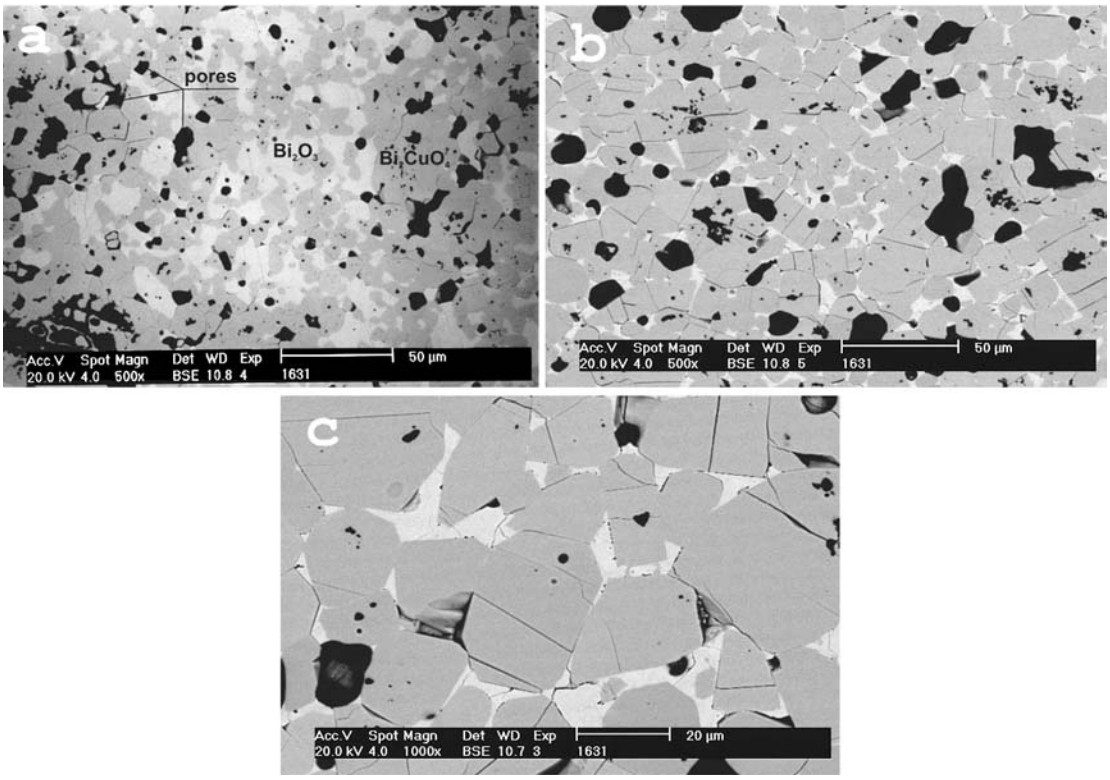

Figure 1 Scanning electron micrograph of polished cross section of $Bi_2CuO_4 + 20$ mass% Bi_2O_3 composite ceramics (a) after cooling from 700°C, (b and c) after cooling from 780°; dark, light and black areas are Bi_2CuO_4, Bi_2O_3, and pores, respectively.

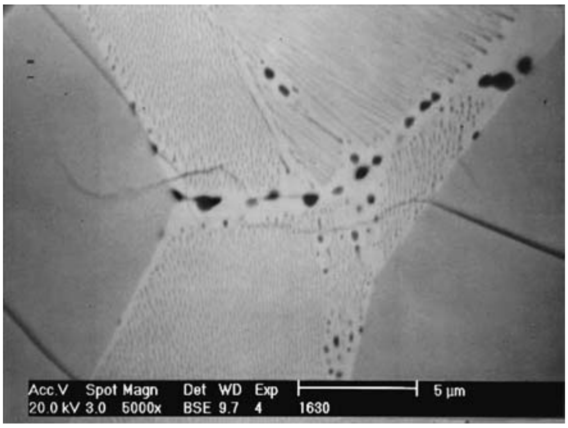

Figure 2 Microstructure of solidified liquid at triple grain junctions.

where P_{app} is the external pressure, P_{cap} is the capillary pressure, Π_{vdw} is the van der Waals pressure, Π_{edl} is the osmotic pressure due to the presence of any electrical double layer, and Π_{st} is the structural disjoining pressure. The thickness of the intergranual wetting films thus calculated is close to that obtained in experiment. Nevertheless, much should be done to elucidate whether experimentally observed intergranual films are wetting, or prewetting, or adsorption films. Most likely that these are adsorption films formed on the grain boundaries in equilibrium with the liquid phase at high temperature. Presumably, these adsorption films are left on grain boundaries after dewetting transition and retracting wetting liquid to the triple and quadruple grain junctions upon ceramics cooling. This hypothesis can be confirmed by the experimental data testifying that in many ceramics the composition of intergranular films and second phase at the triple grain junctions differs considerably [15, 18, 19, 21]. It should also be noted that the value of the thickness of wetting intergranual films, 1 nm, calculated by Clarke [24] within the framework of continuum theory of surface forces is still the matter of controversy. Derjaguin [26] showed that the applicability of continuum approximation is

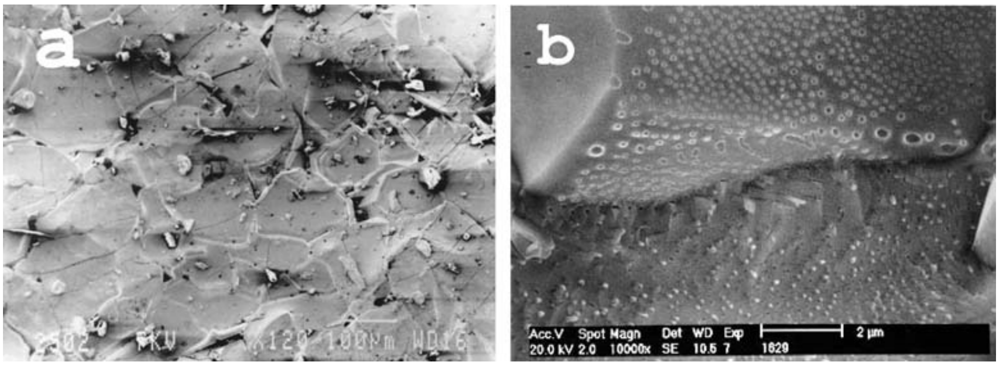

Figure 3 Scanning electron micrograph of fracture surface of $Bi_2CuO_4 + 20$ mass% Bi_2O_3 composite ceramics after cooling from 780°C.

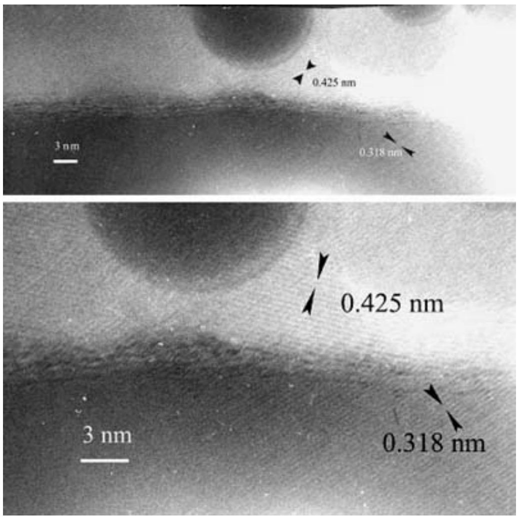

Figure 4 High resolution transmission electron micrograph of Bi_2CuO_4 + 20 mass% Bi_2O_3 composite ceramics after cooling from 780°C illustrating the presence of thin intergranular film.

limited in the region of spatial scales one nanometer; hence, quantitative estimates are unreliable. It remains to be established whether these thin intergranual films are truly wetting, or prewetting, or adsorption films.

Thus, upon heating of composite Bi_2CuO_4 and Bi_2O_3 based ceramics, the GB wetting transition by eutectic liquid takes place. The result is a solid/liquid composite consisting of solid matrix grains and liquid channels at the GBs. This is called a liquid channel grain boundary structure [4, 5]. The presence of continuous intergranular liquid channels can ensure high diffusional permeability and ionic conductivity of the material.

4. Transport

The GB wetting transition can affect significantly on transport properties of ceramics. Fig. 5 presents an electrical conductivity of Bi_2CuO_4–Bi_2O_3 composites measured versus temperature and average grain size of Bi_2CuO_4 by the conventional four-point DC technique in air [27]. The curves feature jumps at 730° and 770°C. The first jump is caused by the polymorphic transition of α-Bi_2O_3 to δ-Bi_2O_3, which is accompanied by an abrupt increase in the oxygen ionic conductivity. The second is induced by the GB wetting transition and liquid channel grain boundary structure formation

TABLE I Oxygen ionic conductivity (σ) and transference numbers (t_i) of Bi_2CuO_4-Bi_2O_3 composite ceramics with liquid channel grain boundary structure measured versus average grain size (d) at 770°C.

Composition (mass %)	t_i	σ(S/m)	$d(\mu m)$
Bi_2CuO_4 + 5% Bi_2O_3	0.02	0.12	20
Bi_2CuO_4 + 5% Bi_2O_3	0.01	0.07	10
Bi_2CuO_4 + 10% Bi_2O_3	0.03	0.22	20
Bi_2CuO_4 + 10% Bi_2O_3	0.05	0.42	10
Bi_2CuO_4 + 15% Bi_2O_3	0.14	1.26	20
Bi_2CuO_4 + 15% Bi_2O_3	0.18	1.68	10
Bi_2CuO_4 + 20% Bi_2O_3	0.26	2.91	20
Bi_2CuO_4 + 20% Bi_2O_3	0.32	6.50	10

The oxygen ionic conductivity and ion transference numbers of Bi_2CuO_4-Bi_2O_3 composites measured versus average grain size of Bi_2CuO_4 at 780°C by Coulomb-volumetric technique are presented in the Table I [28]. The higher ionic conductivity of composites with smaller average grain size is due to higher density of intergranular liquid channels. These intergranular liquid channels can serve as diffusion ways for ions as the activation energy of ion diffusion in a liquid is lower than in a solid.

In Fig. 6 the effective diffusion coefficient of ions in the liquid channel grain boundary structure was calculated as a function of the volume fraction of the liquid phase [29]. The diffusion coefficients of ions in the liquid and solid were assumed to be 10^{-5} and 10^{-9} cm^2/s, respectively. At a 15% volume fraction of liquid the effective diffusion coefficient of ions was determined to be approximately 10^{-6} cm^2/s. Therefore, intergranular liquid channels give the composite high diffusional permeability and ionic conductivity.

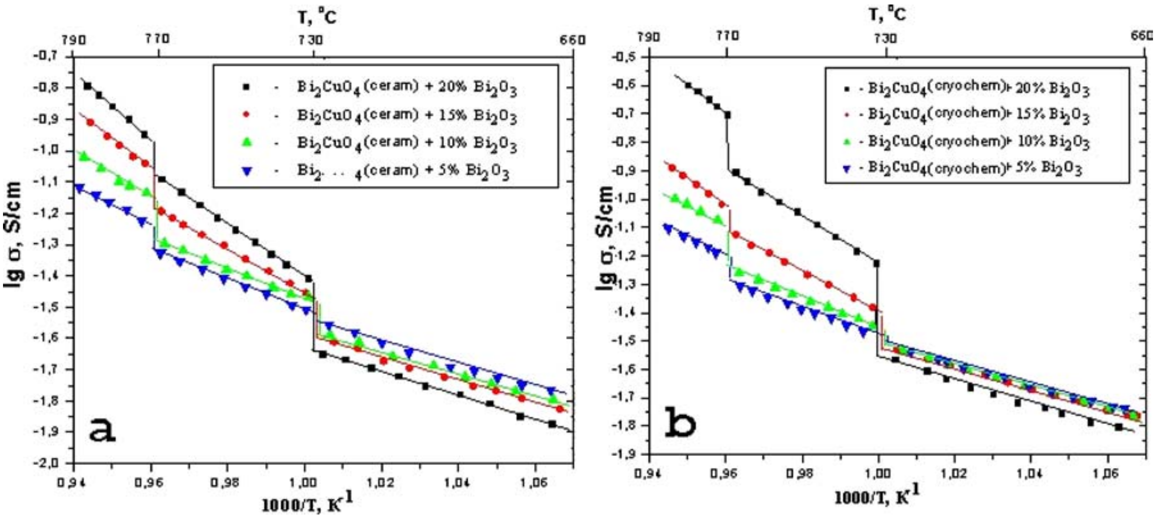

Figure 5 Temperature (T) dependence of electrical conductivity (σ) of $Bi_2CuO_4 + x$ Bi_2O_3 (x–5, 10, 15, and 20 mass%) composite ceramics measured versus average grain size (d) of Bi_2CuO_4 (a)-d = 20 μm, and (b)-d = 10 μm.

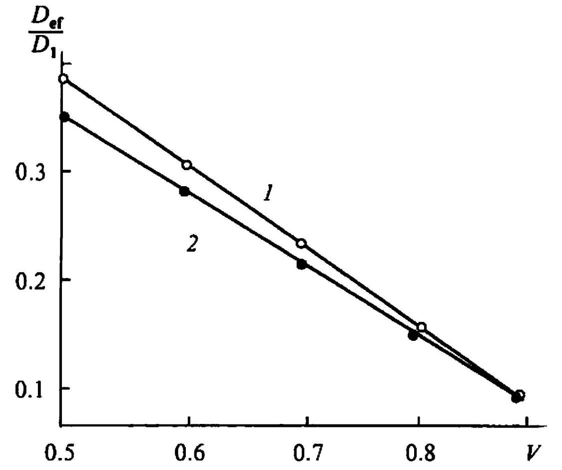

Figure 6 Effective diffusion coefficient calculated by the (1) Hart, and (2) Maxwell approaches; D_1 is the diffusion coefficient in a liquid, and *V* is the volume fraction of a solid.

Thus, GB wetting can substantially affect the transport properties of the ceramics.

5. High temperature corrosion of copper

When GB wetting occurs in the protective oxide scales on metals during high temperature corrosion, the rapid mass transport along the intergranual liquid channels results in catastrophic degradation of the metal. The GB wetting by eutectic liquid takes place in protective oxide scale containing Bi_2CuO_4 and Bi_2O_3 at high temperature oxidation of the copper-bismuth system [29, 30, 31]. As a result the copper oxidizes catastrophically. Fig. 7 presents the kinetics of copper oxidation coated with a thin film of bismuth (curve 2) and without coating (curve 1). Fig. 7 shows that the copper coated with bismuth thin film oxidizes catastrophically at 770° C. Catastrophic oxidation of copper is determined by a parabolic time law (Fig. 8), which indicates that the process is diffusion-limited.

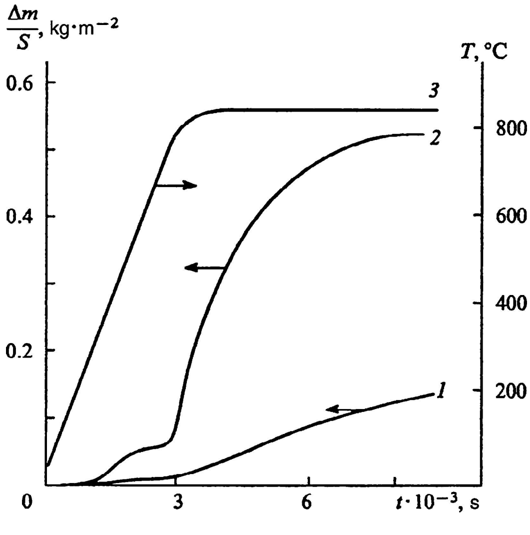

Figure 7 Oxidation kinetics of (1) uncoated and (2) Bi-coated (30 μm) copper (20 × 20 × 0.4 mm^3); m is the mass, S, the copper area, T, the temperature, and t, the time.

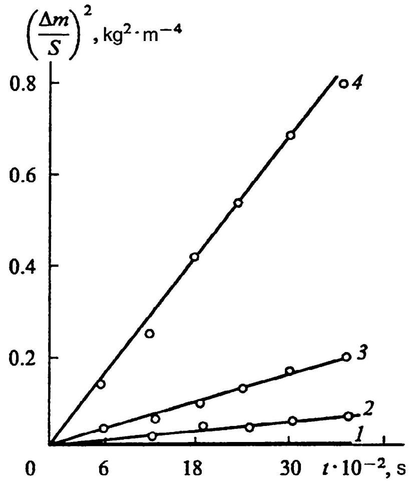

Figure 8 Copper oxidation kinetics coated with Bi_2O_3 films of different thickness at $T = 800°C$. Film thickness × 10^5 m: (1)-0; (2)-3; (3)-6; (4)-9; 10^5 k, kg^{2}m^{-4}s^{-1}: (1)-0.012; (2)-1.6; (3)-4.9; and (4)-21.

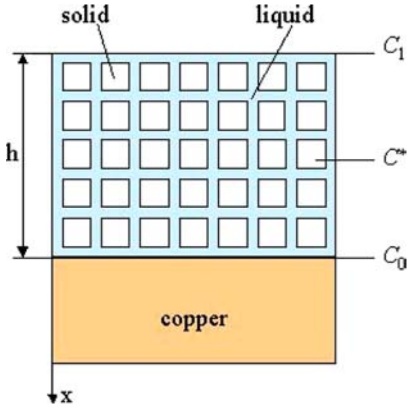

Figure 9 Schematic of protective oxide scale with liquid channel grain boundary structure formed on the Bi_2O_3—coated copper during high temperature corrosion.

Let us consider briefly the theory of copper catastrophic oxidation [29, 32]. Let us assume that at an instant t the protective oxide scale thickness is *h* (Fig. 9) and it is large in comparison with distances over which the effect of the space charge is felt. The rate of copper oxidation is limited by diffusion of oxygen ions along the liquid intergranular channels. Oxygen concentration in the corrosion product is c^*. We shall ignore oxygen dissolution in the metal. Then the mass balance equation can be written as

$$c^*(\mathrm{d}h/\mathrm{d}t) = J \qquad (2)$$

where J is the oxygen density flux.

$$J = -D(\mathrm{d}c/\mathrm{d}x) \qquad (3)$$

where D is the effective diffusion coefficient of oxygen in the liquid channel grain boundary structure, and c is oxygen concentration. Let us assume that oxygen diffusion takes place at permanent boundary conditions (stationary problem)

$$c(x = 0, t) = c_1; \quad c(x = h, t) = c_0 \qquad (4)$$

Assuming a linear distribution of oxygen concentration in the channel, one obtains

$$\mathrm{d}c/\mathrm{d}x = (c_1 - c_0)/h \qquad (5)$$

The oxygen concentration c_0 is close to zero. In view of this we obtain

$$\mathrm{d}c/\mathrm{d}x = c_1/h \tag{6}$$

Substituting expression (6) in (3) we will have

$$J = -D\,(c_1/h) \tag{7}$$

In view of (7) the equation of mass balance (2) will have the following form

$$c^*(\mathrm{d}h/\mathrm{d}t) = -D\,(c_1/h) \tag{8}$$

Separation of the variables in Equation 8 and integration gives a parabolic law for copper oxidation

$$h^2 = Kt \tag{9}$$

where is the rate constant.

$$K = 2D\,(c_1/c^*) \tag{10}$$

In actual practice, for calculation, the formula with the dimensions $\mathrm{kg}^2\mathrm{m}^{-4}\mathrm{s}^{-1}$ is more suitable

$$K = 2D\,\rho^2\,(c_1/c^*) \tag{11}$$

where ρ is the protective oxide density. The calculated $K \approx 5.2 \times 10^{-4}$ kg^2/(m^{4}s) [29] at $c_1 \approx 0.03$ and $c^* \approx 0.5$ (in atomic fraction), $D \approx 10^{-10}$ m^2/s, and $\rho \approx 6.5 \times 10^3$ kg/m^3 and experimental $K = 2.1 \times 10^{-4}$ kg ^{2}/(m^{4}s) [30, 31] values of the rate constant of catastrophic oxidation of copper are of the same order of magnitude, which testifies to the compliance of the theory and experiment. Just for comparison, the oxidation rate constant $K = 1.2 \times 10^{-7}$ kg^2/(m^{4}s) [30] for non-coated copper is over three orders less. The GB wetting enhances greatly the transport properties of the protective oxide scales formed on the metal at high temperature corrosion.

6. Conclusions

1. Thus, on the basis of the presented experimental data we can conclude that the GB wetting transition in ceramic composite based on Bi_2CuO_4 and Bi_2O_3 takes place at the melting point of the eutectic between them.
2. The GB wetting transition enhances substantially ionic conductivity and diffusional permeability of the ceramic composite.
3. The ceramic composites with liquid channel grain boundary structure could have applications as ion transport membranes in electrochemical devices such as solid oxide fuel cells, ceramic membrane reactors and oxygen separators.

Acknowledgements

Special thanks to Ms. T. Petrova and Ms. I. Kocheshkova for their assistance in preparation of the paper.

References

1. N. SETTER and R. WASER, *Acta Mater* **48** (2000) 151.
2. J. G. BEDNORZ and K. A. MULLER, *Z. Phys. B* **64** (1986) 189.
3. R. RAMESH, S. M. GREEN and G. THOMAS, "Studies of High Temperature Superconductors" (Nova Science, New York, 1990) Vol. 5, p. 363.
4. V. V. BELOUSOV, *Russ. J. Electrochem.* **31** (1995) 1343.
5. *Idem.*, *J. Amer. Ceram. Soc.* **79** (1996) 1703.
6. *Idem.*, *J. Supercond.* **15** (2002) 207.
7. *Idem.*, *Inorg. Mater.* **39** (2003) 94.
8. *Idem.*, *Colloid. J.* **66** (2004) 1.
9. R. B. HEADY and J. W. CHAN, *J. Chem. Phys.* **58** (1973) 896.
10. J. W. CHAN, *ibid.* **66** (1977) 3667.
11. M. R. MOLDOVER and J. W. CHAN, *Science* **207** (1980) 1073.
12. M. P. KULAKOV and D. YA. LENCHINENKO, *Thermochim. Acta* **188** (1991) 129.
13. B. HALSTEDT, D. RISOLD and L. J. GAUCKLER, *J. Amer. Ceram. Soc.* **79** (1996) 353.
14. R. J. XIE, M. MITOMO and G. D. ZHAU, *Acta Mater* **48** (2000) 2049.
15. R. BRYDSON, S. C. CHEN *et al.*, *J. Amer. Ceram. Soc.* **81** (1998) 369.
16. H. GU, R. M. CANNON and M. RUHLE, *ibid.* **81** (1998) 476.
17. H. GU, X. PAN, R. M. CANNON and M. RUHLE, *ibid.* **81** (1998) 3125.
18. H. WANG and Y. M. CHIANG, *ibid.* **81** (1998) 89.
19. Y. M. CHIANG, H. WANG and J. R. LEE, *J. Microsc.* **191** (1998) 275.
20. J.E. BLENDELL, W. C. CARTER and C. A. HANDWERKER, *J. Amer. Ceram. Soc.* **82** (1999) 1889.
21. J. LUO, H. WANG and Y. M. CHIANG, *ibid.* **82** (1999) 916.
22. D. R. CLARKE and M. L. GEE, in "Materials Interfaces," edited by D. Wolf and S. Yip (Chapman and Hall, London, 1992) p. 255.
23. R. H. FRENCH, *J. Amer. Ceram. Soc.* **83** (2000) 2117.
24. D. R. CLARKE, *ibid.* **70** (1987) 15.
25. *Idem.*, *ibid.* **76** (1993) 1201.
26. B. V. DERJAGUIN, N. V. CHURAEV and V. M. MULLER, "Surface Forces" (Consultants Bureau, New York, 1987).
27. N. V. LYSKOV, YU. G. METLIN, V. V. BELOUSOV and YU. D. TRETYAKOV, *Solid State Ioni.* **166** (2004) 207.
28. *Idem.*, *Doklady Chem.* **392** (2003) 63.
29. V. V. BELOUSOV, *Russ. Chem. Rev.* **67** (1998) 631.
30. *Idem.*, *Oxid. Met.* **42** (1994) 511.
31. *Idem.*, *Protect. Met.* **30** (1994) 599.
32. V. V. BELOUSOV and B. S. BOKSHTEIN, *Oxid Met* **50** (1998) 389.

Received 31 March
and accepted 20 October 2004