TMS Conference Feb 1996, Anaheim, Ca.

CONF-960202--27

ISM 850

The Effect of Ag on the Decomposition Pathway of $Bi_2Sr_2CaCu_2O_x$ in Air

L. Margulies, K.W. Dennis, M.J. Kramer, and R.W. McCallum
Ames Laboratory*
Department of Materials Science and Engineering
Iowa State University, Ames, IA 50011 U.S.A.

RECEIVED
APR 25 1996
OSTI

Abstract

The decomposition pathway of $Bi_2Sr_2CaCu_2O_x$ (Bi2212) in .21 bar O_2 with 0, 2, and 10 wt.% Ag added has been determined by performing SEM/EDS and microprobe analysis on oil quenched samples. A series of quaternary phase diagrams were constructed to describe the evolution of the phase assemblage with temperature. It was found that the first decomposition products are $Bi_9Sr_{11}Ca_5O_x$ (9115), $(Sr_{1-x}Ca_x)CuO_2$ (11), and liquid. The addition of Ag acted to depress the first peritectic temperature by 16-20°C and slightly modified the order in which some of the subliquidus solid phases nucleate and decompose. The effect of C on the peritectic melting temperature was examined through thermal analysis of powder samples.

---

* The work was performed at Ames Laboratory, Iowa State University was supported by the Director of Energy Research, Office of Basic Sciences, U.S. Department of Energy under Contract No. W-7405-ENG-82

Introduction

Melt-processed $Bi_2Sr_2CaCu_2O_x$ (Bi2212) wires and tapes often contain a variety of second phases which may have deleterious effects on the superconducting critical current [1]. The size, distribution, and type of second phases that exist in the final material is highly dependent on both the maximum processing temperature and the cooling schedule [2,3]. Without a clear understanding of the partial melt phase relations, it is often difficult to separate the effects of the maximum processing temperature with that of cooling. To properly control the second phase content of the fully processed wires and tapes, it is necessary to understand the origins of each of the second phases, that is, whether they existed in the partial melt before cooling or crystallized from the melt at some point during cooling.

Previously, we have reported the decomposition pathway of Bi2212 in 100% O_2 [4]. Most processing, though, is done in air (.21 bar O_2), and as the partial melt phase relations are highly dependent on oxygen partial pressure (PO_2), it is important to determine the decomposition pathway of Bi2212 in .21 bar O_2. Most melt processing utilizes Ag as a sheathing material, and often additional Ag powder is mixed with the Bi2212 precursor to assure greater texture throughout the thickness of the wire or tape [5]. It is also important, then, to understand the effect of Ag content on the decomposition pathway of Bi2212.

There have been a number of studies on the melting pathway of Bi2212 in air, but no studies have been done which examine the effect of Ag content. Of the results that have been reported, there are numerous discrepancies as to what second phases exist in the subliquidus melt. Most high temperature x-ray diffraction studies report the first peritectic reaction as Bi2212 --> $(Sr_{1-x}Ca_x)CuO_2$ (11) + liquid [6-8]. Other studies suggest that the first decomposition products are $Bi_2(Sr_{1-x}Ca_x)_4O_x$ (24x), (11), and liquid [9] or even $Bi_2Sr_2Ca_2Cu_3Ox$ (Bi2223) and liquid [10]. The lack of consistency between these studies is of concern and will be addressed below. The goal of this paper is to present comprehensive data on the effect of Ag content on the decomposition pathway of Bi2212 in .21 bar O_2.

Experimental Procedures

Commercial Bi2212(Kalichemie) was heat treated in flowing (10 l/min) air at 860°C-870°C to minimize second phases and increase homogeneity. The CO_2 and hydrocarbon content of the flowing air was reduced to below 2 ppm by a commercial molecular sieve filter. The resulting powder was thoroughly mixed with 2 and 10 wt.% Ag powder (<5μm). ICP-AES analysis was done to determine the composition of the starting material. The cation ration was determined to be $Bi_{2.01}Sr_{2.04}Ca_{0.98}Cu_{2.00}$. The Ag contents of the three batches were measured at <.005, 2.4, and 9.6 weight percent respectively.

Samples consisting of approximately 50-100 mg of powder in a MgO tube (2mm ID, 3mm OD) were suspended in the hot zone of a vertical furnace. The quartz tube in the furnace was evacuated and backfilled with 21% O_2 (N_2 balance) to a total pressure of 1 bar. All gases used in this study were rated to below .5 molar percent hydrocarbons and 3.5 molar percent H_2O. Samples were held at temperature in a flowing atmosphere for 30 minutes and then dropped into an oil bath. Cross sections of the tubes were mounted and polished for SEM-EDS and microprobe analysis. Standardless semi-quantitative EDS data was collected for each sample. Microprobe analysis was done on a number of samples to verify the compositions of the solid phases. $Al_4Bi_2O_9$, CuO, $CaCO_3$, and $SrSO_4$ were used as internal standards. Identified phases and their approximate composition ranges are given in Table I.

Table I Nomenclature and Composition of Solid Phases as Measured by Electron Microprobe.

Phase	Nomenclature	observed solid solution range	Avg. composition by microprobe (Bi/Sr/Ca/Cu)
(11)	$(Sr_{1-x}Ca_x)CuO_2$	x= .32 - .45	.02/.29/.20/.51
(21)	$(Sr_{1-x}Ca_x)_2CuO_3$	x= .63 - .80	.04/.20/.46/.34
(10)	$(Ca_{1-x}Sr_x)O$	x= .02 - .05	.01/.02/.96/.01
(9<u>11</u>5)	$Bi_9(Sr_{1-x}Ca_x)_{16}O_x$	x= .30 - .35	.36/.41/.20/.03

Thermal analysis was performed using a Perkin Elmer DTA-7. Pressed pellets (20mg) were run in MgO cups and were surrounded with MgO powder to minimize discontinuities in thermal contact between the sample and cup. Unlike Pt and Al_2O_3, MgO does not react with the partial melt. This effect is evident in Figure 1 as peaks after the first thermal event are obscured due to reaction between the liquid and Al_2O_3 crucible. Surrounding the pellet with MgO powder does delay this reaction, but it is necessary to use a MgO crucible to assure clean thermal events in the partial liquid regime. All thermal analysis was done at a heating rate of 5°C/min.

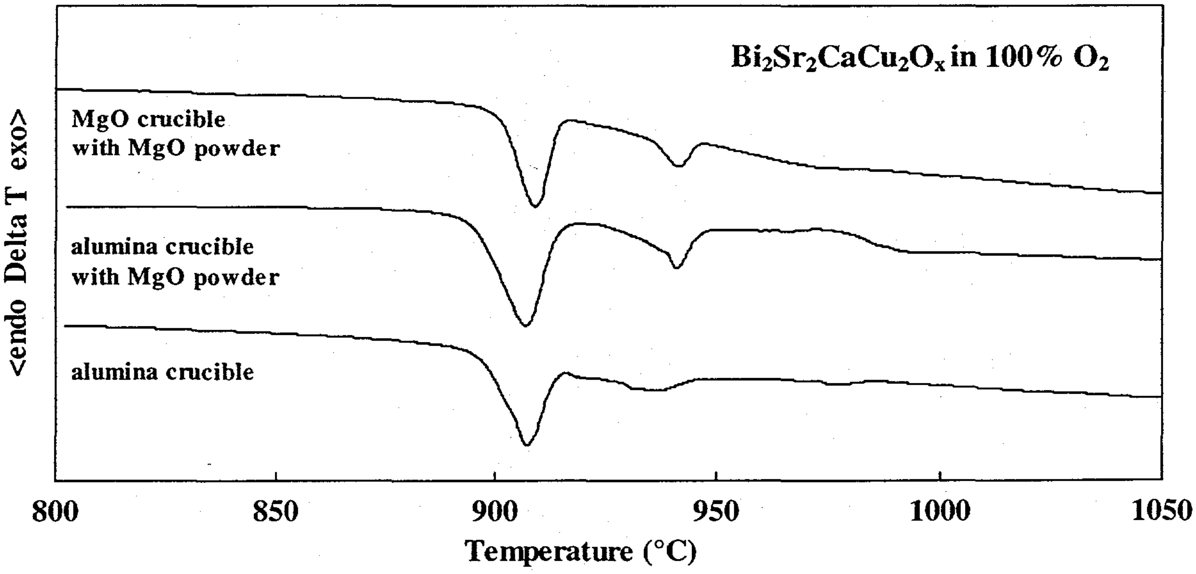

Figure 1- The use of nonreactive crucible materials maximizes the sensitivity of thermal analysis to events occurring in the partial melt regime.

The oxygen partial pressure was controlled by mass flow controllers and monitored with a zirconia oxygen analyzer. The carbon content of all samples was measured by a Horiba EMIA-520 carbon analyzer.

Results

Phase Relations

Isothermal cuts of the $1/2Bi_2O_3$-SrO-CaO-CuO phase diagram have been constructed for each of the major phase regions (Fig. 2). Phases identified in the drop tube samples by SEM/EDS are presented with respect to Ag content and temperature in Table II. The first peritectic reaction, Bi2212 --> (11) + (9115) + L, occurs at 887°C. By 900°C, (21) has begun to nucleate from the liquid. The (9115) completely dissolves by 925°C and a region is entered in which (11), (21), and liquid are in equilibrium. As the temperature increases, the (11) slowly dissolves. By 937°C, the (11) has completely gone and (10) begins to nucleate from the liquid. The (21) then begins to dissolve while the (10) continues to nucleate. By 965°C the (21) has disappeared leaving just (10) and liquid. DTA results show that the peritectic decomposition temperature is lowered with the addition of Ag (Fig. 3). The first peritectic reaction is depressed to 871°C with 2 wt.% Ag and 867°C with 10 wt.% Ag added. At 2 wt.% Ag, all of the Ag is soluble in the ceramic liquid. No solubility of Ag in any of the solid phases was found up to the detectability limits of EDS. With 10 wt.% Ag added, the solubility limit of Ag in the liquid is exceeded, and the excess Ag remains as either a separate solid phase or as an immiscible liquid above 941°C. The presence of Ag seems to have a much greater effect on the stability of the (11) and (21) than on the (9115) so that with the addition of 10 wt.% Ag the decomposition order of (9115) and (11) switches creating a new phase region in which (9115), (21), (10), and liquid are in equilibrium. The nucleation temperature of (10) is lowered by 30°C with 10 wt.% Ag added which also causes slight modifications in the decomposition pathway. Table III summarizes the decomposition pathway of Bi2212 with respect to Ag content. Phase regions marked with an asterisk were not directly observed but are expected to exist due to thermodynamic considerations.

Table II SEM/EDS determined solid phases of samples quenched from .21 bar O_2.

0% Ag		2% Ag		10% Ag	
Temp(°C)	Phases	Temp(°C)	Phases	Temp(°C)	Phases
890	9115+11	880	9115+11	872	9115+11
900	9115+11+21	895	9115+11+21	877	9115+11
910	9115+11+21	910	9115+11+21	884	9115+11+21
920	9115+11+21	915	9115+11+21	890	9115+11+21
925	11+21	920	11+21+10	900	9115+11+21
930	11+21	925	11+21+10	905	9115+21+10
937	21+10	930	11+21+10	910	9115+21+10
943	21+10	935	21+10	920	21+10
945	21+10	941	21+10	930	21+10
950	21+10	950	21+10	942	10
965	10	962	10		

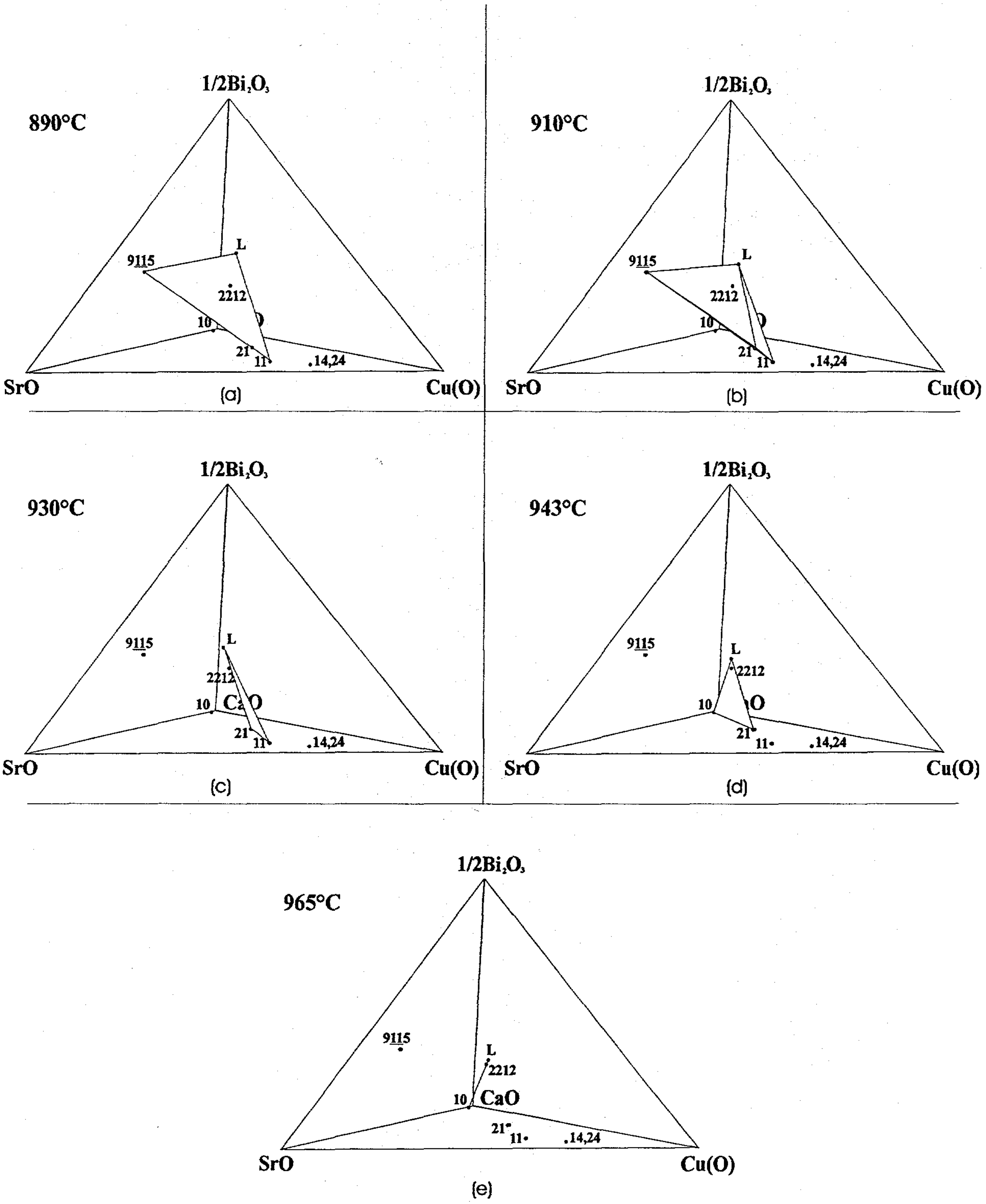

Figure 2 - Pseudo-quaternary phase relations of the $1/2Bi_2O_3$-SrO-CaO-CuO system in air.

Table III Summary of decomposition pathways with respect to Ag content.

0% Ag	2% Ag	10% Ag
Bi2212 -->	Bi2212 -->	Bi2212 -->
(9115)+11+L -->	(9115)+11+L -->	(9115)+11+L -->
(9115)+11+21+L -->	(9115)+11+21+L -->	(9115)+11+21+L -->
11+21+L -->	*_(9115)+11+21+10+L_ -->	*_(9115)+11+21+10+L_ -->
21+10+L -->	11+21+10+L -->	(9115)+21+10+L -->
10+L	21+10+L -->	21+10+L -->
	10+L	10+L

* These phase regions were not directly observed but are expected to exist due to thermodynamic considerations.

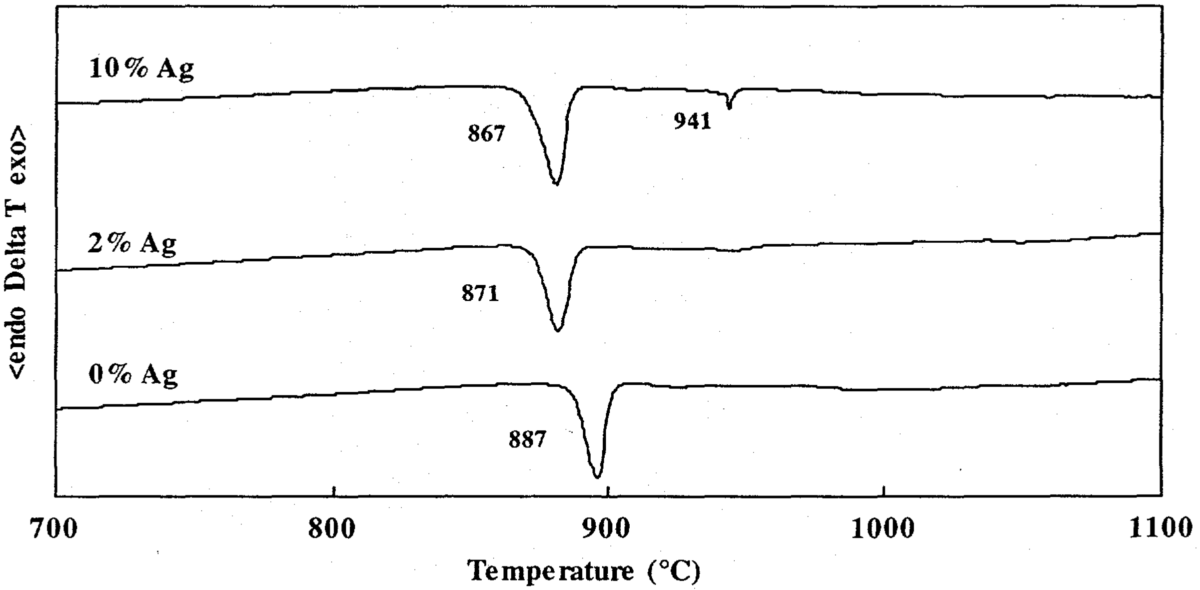

Figure 3 - Thermal analysis of Bi2212 with 0, 2, and 10 wt.% Ag added at .21 bar O_2.

Effect of C

The material used in this study was analyzed for C content. The material had been periodically exposed to air during the course of the study and showed C contents ranging from 250 to 1500 ppm by weight. It has been suggested that Ag alone does not have any effect on the decomposition temperature of Bi2212 and that both C and Ag are needed to lower the melting temperature [11]. A high temperature x-ray diffraction study by Misture, *et al.* [12] demonstrated that Bi2212 with 1600 ppm C showed no depression of the melting temperature with the addition of 20 wt.% Ag. Although all the material used in this study had C levels below 1600 ppm, thermal analysis and the drop tube experiments showed a significant and reproducible depression of reaction temperature with the addition of Ag.

In order to determine whether this effect would disappear at lower C levels, additional material was heated in flowing O_2 at 800°C for 3 days. Analysis of this material showed a C content of 30 ppm for the Ag free material and 81 ppm for 10 wt.% Ag added material. This low C material was then exposed to air and water saturated air for a controlled amount of time and re-analyzed for C content (Table IV). The presence of H_2O in the atmosphere increases the rate at which Bi2212 picks up C for both Ag and Ag free material. The presence of Ag, though, lowers the rate at which C is picked up, which is directly opposite to the effect observed in low humidity. The combined role of H_2O and Ag in this reaction is not known, but it is clear that exposure to humidity must be minimized to assure low C material.

Table IV The C content of samples used in this study.

	C content (ppm)	
sample history	**0% Ag**	**10% Ag**
original material	270	1470
800°C 72hrs	30	81
3 days in H_2O saturated air	1770	990
3 weeks in H_2O saturated air	6980	1030
3 days in air	111	273

Thermal analysis was performed at a number of C levels in .21 bar O_2 (Fig. 4). Lowering the C content of Bi2212 and Bi2212 + 10% Ag did produce a slight increase in decomposition temperature, but the depression of the peritectic onset with the addition of Ag remained identical at all C concentrations. In .21 bar O_2, we previously reported a 20°C depression with the addition of 10% Ag. With the C content lowered to below 100 ppm, a depression of 19°C was observed. These results suggest that down to at least 80 ppm C, the addition of Ag does act to depress the melting temperature of Bi2212, and this effect is negligibly effected by an increase in C content up to 1500 ppm. It should be noted that only one composition in the solid solution range of Bi2212 was analyzed. It may be the case that compositions nearer to the solubility limit are more sensitive to the addition of C. A more complete analysis of this work is being prepared [13].

Discussion

The disagreement between the results presented here and those previously reported are significant and need to be addressed. Most of the high temperature x-ray diffraction work has been done in air and the results suggest that the first peritectic reaction is Bi2212--> (11) + liquid [6-8,14]. The (9115) is not observed at any point along the decomposition path. In the melt, the position of the solid phases relative to the surface of the liquid during in situ XRD experiments will depend on their relative densities. If the (9115) has a higher density than the liquid it will sink to the bottom and may be below the penetration depth of an x-ray beam.

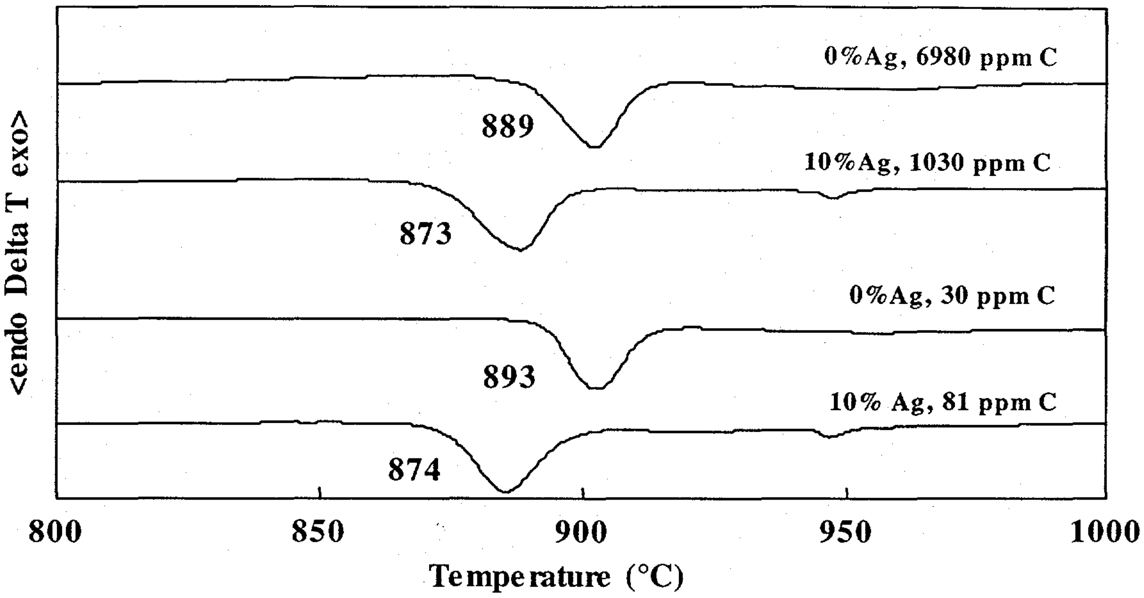

Figure 4 - The effect of C content on the melting temperature of Bi2212 with 0 and 10 wt.% Ag added.

This may explain why the (9115) has only been observed in quenching experiments. The Cu free phase reported in quenching experiments has been labeled 24x [9] or (9115) [15]. In fact, a variety of (Sr,Ca):Bi ratios ranging from 1.71 to 2.33 have been reported with similar XRD patterns indexed to a monoclinic unit cell [13,16-19] The atomic positions and occupancies of the unit cell have not been solved in any of these studies. All of these phases are very close in composition and slight deviations in EDS standardization could easily cause confusion. Standardless semi-quantitative EDS analysis is not accurate enough to differentiate between these compositions. Microprobe analysis suggested that the true composition of this phase was closer to (9115), although there seemed to be approximately 3 mole % Cu substituting for Sr. It has been suggested that the (9115) phase is really the 24x with some solubility of Cu for Sr or Ca [20]. It seems likely that this Cu free phase has a solid solution range that extends not only along the Sr-Ca direction, but also along the Bi-(Sr,Ca) and even Cu-(Sr,Ca) directions. In this case, the various nomenclatures used in the literature are misleading and must remain so until the exact structure and solubility range of this phase is determined. It should also be noted that a variety of compositions have been used as starting materials in the literature. The dependence of the melting pathway on exact composition has not been examined well, and may play an important role in melt processing. The range of compositions used within the Bi2212 stability region is quite large and may explain some of the conflicting results reported in the literature.

Summary

Bi2212 undergoes a series of peritectic decompositions between the solidus and liquidus. The addition of Ag depresses the temperature at which these reactions occur and slightly modifies the order in which the equilibrium solid phases nucleate and decompose. The presence of C in levels from 30 to 1500 ppm does not seem to have any significant effect on the decomposition of Bi2212 with and without Ag.

Acknowledgments

We would like to acknowledge Alfred Kracher, who provided microprobe measurements, and Bob Hofer, who performed ICP and carbon analysis.

References

[1] P. Majewski, S. Elschner, and F. Aldinger, Physica C, **249** (1995), 234.

[2] T. Holesinger, D. Miller, and L. Chumbley, "Melt Processing of the $Bi_2Sr_2CaCu_2O_y$ Superconductor in oxygen and argon Atmospheres," IEEE Trans. Appl. Supercond, **3** (1993), 1178.

[3] R. D. Ray II and E. E. Hellstrom, "Microstructurally optimized heat treatment for melt-processed Ag clad $Bi_2Sr_2CaCu_2O_y$ tape Step-solidification melt processing," Physica C, **251** (1995), 27-49.

[4]..L. Margulies, K. W. Dennis, M. J. Kramer, R. W. McCallum, "Effect of PO_2 and Ag content on the Peritectic Decomposition of $Bi_2Sr_2CaCu_2O_x$" submitted to Physica C.

[5] B. Heeb and L. Gauckler, "Partial Melting of Bulk Bi-2212" (Paper presented at the 4th Congress on Superconductivity, Orlando, FL, USA, June 27 - July 1 1994).

[6] J. Polonka, M. Xu, Q. Li, A. Goldman, D. Finnemore, "In situ x-ray investigation of the melting of Bi-Sr-Ca-Cu-O phases," Appl. Phys. Lett, **59** (1991), 3640-3642.

[7] Yoshio Oka, Naoichi Yamamoto, Yoichi Tomii, Hitoshi Kitaguchi, Kiichi Oda, and Jun Takada, "Crystalline Phases Formed in the Partially Melted States of Bi-Sr-Ca-Cu-O," Jap. J. Appl. Phys, **28** (1989), L801-L803.

[8] Ming Xu, J. Polonka, A. I. Goldman, and D. K. Finnemore, "Investigations of crystalline phases in the melting of $Bi_2Sr_2CaCu_2O_x$," Applied Superconductivity, Vol 1, No. 1/2 (1993), 53-60.

[9] W. Zhang, E. Hellstrom, "The Effects of Oxygen On Melt-Processing Ag-Sheathed $Bi_2Sr_2CaCu_2O_8$ Conductors," to appear in Superconductivity Science and Technology, June 1995.

[10] Hiroshi Komatsu, Yuki Kato, Satoru Miyashita, Tetsuo Inoue, and Shigeyuki Hayashi, "In situ observations of crystal growth of Bi-based oxide superconductors," Physica C, **190** (1991), 14-17.

[11] C. Park and R. L. Snyder, "Relation between silver and residual carbon content in the surface FTIR study of the effect of silver and carbon on the processing of $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_{7-\delta}$," preprint.

[12] S. T. Misture, D. P. Matheis, R. L. Snyder, T. N. Blanton, G. M. Zorn, B. Seebacher, "High-Temperature X-Ray Diffraction Study of the Peritectic Reactions of Bi-2212 With and Without Ag Additions," Physica C, **205** (1995), 175-183.

[13] L. Margulies, R. Hofer, K. W. Dennis, M. J. Kramer, R. W. McCallum, "The Effect of Carbon on the Decomposition of Bi2212 and Bi2212 + Ag," submitted to Physica C.

[14] T. Hasegawa, T. Kitamura, H. Kobayashi, H. Kumakura, H. Kitaguchi, and K. Togano, "High-temperature x-ray diffraction analysis for $Bi_2Sr_2CaCu_2O_y$," Appl. Phys. Lett, **60** (1992), 2692-2694.

[15] T. Lang, D. Buhl, M. Cantoni, L. Gauckler, "Decomposition and reformation of Bi-2212 during the partial melt processing in oxygen" (Paper presented at the European Conference on Applied Superconductivity, Edinburgh, Scotland, July 3-6, 1995).

[16] D. Buhl, T. Lang, B Heeb, and L. Gauckler, "Tape Casting and Partial Melting of Bi-2212 Thick Films" (Paper presented at the 4th Congress on Superconductivity, Orlando, FL, USA, June 27 - July 1 1994).

[17] C. J. Rawn, R. S. Roth, B. P. Burton, M. D. Hill, "Phase Equilibria and Crystal Chemistry in Portions of the System $SrO-CaO-1/2Bi_2O_3-CuO$: V, The System $SrO-CaO-1/2Bi_2O_3$," J. Am. Ceram. Soc, **77** (1994), 2173-2178.

[18] F. Abbattista, C. Brisi, D. Mazza, and M. Vallino, "The Subsolidus Equilibria in the Most Basic Zone of the $Bi_2O_3-SrO-O$ System," Mat. Res. Bull, **26** (1991) 107-117.

[19] R. Muller, M. Cantoni, L. J. Gauckler, "Phase compatibilities in the Bi-poor region of the system Bi-Sr-Ca-O at 820 and 900°C in air," Physica C, **243** (1995), 103-112.

[20] J. L. MacManus-Driscoll, J. C. Bravman, R. B. Beyers, "Pseudo-quaternary phase relations near $Bi_2Sr_2CaCu_2O_{8+x}$ in reduced oxygen pressures," Physica C, **251** (1995), 71-88.