Effect of composition on the melting behaviour of Bi2212-Ag conductors

M O Rikel1, S Arsac1, E Soileux1, J Ehrenberg1, J Bock1, K Marken2, H Miao2, C-E Bruzek3, S Pavard3, A Matsumoto4, E E Hellstrom4, and L Motowidlo5

1Nexans SuperConductors GmbH, Chemiepark Knapsack, Hürth, 50351 Germany; 2Oxford Superconducting Technology, Carteret, NJ 07008, USA 3Nexans, 31 rue de l’industrie, Jeumont, 59460 France; 4University of Wisconsin-Madison, 1500 Engineering Dr, Madison, WI 50706 USA 5SupraMagnetics, 125 South End Rd., Southington, CT 06489 USA

Mark.Rikel@Nexans.com

Abstract. Using DTA measurements and SEM/EDX and XRD of isothermally annealed and rapidly cooled/quenched 2212/Ag conductors, we study the effect of precursor composition on the melting temperatures, composition and abundance of phases in the partially molten state.

1. Introduction
Ag-sheathed Bi2212 conductors produced via the powder-in-tube method are promising materials for high-field applications [1, 2]. Partial melt processing (PMP) in which round wire or flat tape is heated above the peritectic decomposition temperature of the Bi2212 phase and then cooled down to form well connected and aligned 2212 is used to make them conductors [3]. The conductor engineering critical current density $J_c$ is known to be strongly dependent on the maximum processing temperature $T_{max}$ [4, 5], which is considered to be a significant constraint for processing conductor for large-scale applications [6]. It was shown, however, that the sensitivity of $J_c$ to $T_{max}$ could be significantly affected by precursor stoichiometry [6, 7]. This opens the prospect of widening the processing-temperature window by optimising the precursor composition. Better understanding of melting and solidification of the Bi2212 phase as a function of its composition is an important prerequisite for such optimisation. In this paper, we present some of the first results of this project, which show the importance of the effect and help to formulate the direction of further work.

2. Experimental
Precursor powder/rods were fabricated on an industrial scale at Nexans SuperConductors using the melt casting process and subsequent thermomechanical treatment to closely approach equilibrium. 85-filamentary flat tape and 7×85-filamentary round wire conductors were fabricated at Nexans (Jeumont) and Oxford Superconducting Technology [7, 8], respectively. Table 1 shows the overall composition determined by x-ray fluorescence analysis (XFA) of precursor powder used to fabricate the two tape and four wire conductors used in this study. Tape T45 has the nominal 2212 stoichiometry and T32 is
Table 1. Composition (XFA data) of precursor powders in the wire (W) and tape (T) conductors studied. $T_m$(DTA) was measured using powder mixed with 50 wt% Ag and in the Ag-sheathed conductor. All DTA runs were done at 5°C/min in 1 bar O$_2$. $T_m$(vol% 2212 left) was determined by rapidly cooling samples to room temperature from $T_{max}$, and using SEM/XRD analysis to determine the vol% of 2212 present in the rapidly cooled sample. $T_{on}(J_e>0)$ was determined as shown in Fig. 1.

| Conductor | Composition | $T_m$(DTA) (°C) | $T_m$(% 2212 left) (°C) | $T_{on}(J_e>0)$, ±2°C (°C) |
|-----------|-------------|----------------|--------------------------|-----------------------------|
| W521      | Bi 2.17, Sr 1.94, Ca 0.89, Cu 2.00 | 879.5 | 882.0 | 883(1) | 886(1.5) | 885 |
| W522      | Bi 2.17, Sr 1.82, Ca 1.04, Cu 1.97 | 884.0 | 889.0 | 887(1.5) | 891(2) | 889 |
| W523      | Bi 2.15, Sr 1.98, Ca 0.88, Cu 1.99 | 877.0 | 880.0 | 882(1.5) | 886(1.5) | 885 |
| W524      | Bi 2.14, Sr 1.66, Ca 1.24, Cu 1.96 | 883.0 | 889.0 | 889(1) | 892(2) | 891 |
| T32       | Bi 2.18, Sr 1.89, Ca 1.00, Cu 1.93 | 878.0 | 882.0 | 880(1) | 884(1) | 882 |
| T45       | Bi 2.00, Sr 2.00, Ca 1.00, Cu 2.00 | 873.0 | 875.0 | 880.9(5) | 882.5(5.5) | 880 |

$^a$Precursor powder mixed with 50 wt % Ag powder, $^b$after preannealing 48 h at 835°C in 100% O$_2$.

a Bi-rich composition [6]. Both of these precursor powders contain multiple phases. The precursor powders used in wires W521–W524 were almost single-phase (<1 vol. % second phases by SEM).

The melting and solidification behaviour of conductors and mixtures of powder + 50 wt.% Ag was studied using DTA (Netzsch STA 409) and by isothermal annealing followed by rapid cooling (in the DTA unit) or quenching in oil (see [9] for details). Samples were characterized by SEM/EDX and XRD. Comparison of compositions determined from XFA and EDX, show EDX has an absolute accuracy in of 0.5 at. %.

The furnaces were calibrated so that $T_{max}$ was known with an absolute accuracy of ±2°C. The DTA unit was calibrated using the melting point of 99.99% pure Ag (in N$_2$ and O$_2$) and Au to have an absolute accuracy of ±0.5°C.

3. Results

Figure 1 shows $J_e$ as a function of $T_{max}$ for tape T45 and wires W521–W524. $J_e$ for tape T45 has a sharp step-like behaviour that is observed for many other batches of tape fabricated with precursor powder with the nominal 2212 composition. For wires W521 and W522, we also observe a step-like increase in $J_e$, but the $J_e(T_{max})$ curves are different showing a rather broad region of $J_e$ increasing with increasing $T_{max}$. Despite this difference, we may in all cases define the temperature $T_{on}(J_e)$, within ±1°C such that for $T_{max} > T_{on}$, $J_e > 0$, whereas for $T_{max} < T_{on}$, $J_e = 0$. $T_{on}$ is listed in Table 1 where we also present the melting temperatures $T_m$(DTA) determined from DTA traces and from the isothermal.

Figure 1. Engineering critical current density $J_e$(4.2 K sf) as a function of $T_{max}$ in (a) various batches of tape conductors made using precursor powder with 2212 composition and (b) in wires W521–W524.
annealing experiments \((T_m(\text{vol \% 2212 \text{ left}}))\). For a given wire, all of these temperatures are different, but show the same trends as a function of composition as observed for \(T_m(J)\).

Tape T45 made with precursor powder with the nominal 2212 stoichiometry shows the sharpest melting event (Table 1, figures 2a and 2b). Note that this is the only composition where rapid cooling at \(-9^\circ\text{C/sec}\) in the DTA unit was sufficient to quench-in the morphological features of the molten state (cf Figs. 2b and 2c) with liquid crystallized as a 2201 matrix containing \(\approx 2\) vol. \% 4413 phase (identified by XRD, see [10]). Conductors with other compositions cooled from the molten state, contained 10 to 30 vol. \% 4413 phase of the solidified liquid matrix, which can be identified by both XRD and EDX. The presence of the 4413 grains in rapidly cooled samples, which have a very similar contrast to that of the 2212 phase in BSE images, contributed to the error in \(T_m(0\% 2212)\) for samples W521–W524 (Table 1).

**Table 2** EDS/SEM analysis of composition and volume fraction of phases in wire and tape conductors quenched in oil after annealing 0.5 h at \(T_{\text{max}} = T_m(\text{DTA}) + 7^\circ\text{C}\) in 100\% \(\text{O}_2\) (\(T_m(\text{DTA})\) for BSCCO + 50\% Ag).

| Sample/Tmax (Sr/Ca) | Phases | Cation Composition | Mol\%a | Vol. \% from EDSb SEM |
|---------------------|--------|--------------------|--------|------------------------|
| W523/885 (2.25)     | L(q)c  | Bi 2.15(2) Sr 1.28(1) Ca 0.47(1) Cu 1.09(3) Ag 5.2(5) | 56(2) 60(3) 62(5) |
|                     | 14-24AEC | 0.24(3) 9.36(5) 4.81(4) 23.5(1) | 26(1) 20(2) 16(3) |
|                     | 2-4CF | 2.16(1) 2.59(1) 1.17(1) 0.08(1) | 18(2) 20(2) 23(4) |
| W521/885 (2.18)     | L(q)   | 2.11(3) 1.26(2) 0.49(1) 1.14(5) 6.0(8) | 58(2) 62(3) 58(7) |
|                     | 14-24AEC | 0.22(2) 9.21(5) 5.05(5) 23.5(1) | 24(1) 19(1) 18(4) |
|                     | 2-4CF | 2.17(1) 2.57(1) 1.21(1) 0.06(1) | 16(1) 19(2) 24(6) |
| T45/885 (2.00)      | L(q)   | 2.06(2) 1.21(2) 0.49(1) 1.23(3) 4.5(4) | 44(1) 47(3) 52(5) |
|                     | 14-24AEC | 0.43(7) 9.06(3) 5.35(4) 23.1(1) | 27(1) 21(1) 19(3) |
|                     | 2-4CF | 2.14(1) 2.46(1) 1.21(1) 0.19(2) | 27(1) 32(3) 29(4) |
| T32/890f (1.89)     | L(q)d  | 1.87(3) 1.18(1) 0.57(1) 1.38(3) 5.7(8) | 63(3) 65(4) 60(8) |
|                     | 14-24AEC | 0.25(4) 8.75(8) 5.57(7) 23.4(1) | 16(1) 12(2) 15(4) |
|                     | 2-4CF | 2.16(2) 2.53(2) 1.22(2) 0.08(2) | 20(2) 23(3) 25(7) |
| W522/894 (1.75)     | L(q)   | 2.06(3) 1.22(3) 0.6(2) 1.12(7) 5.2(7) | 60(3) 64(5) 58(9) |
|                     | 14-24AEC | 0.40(6) 8.14(6) 5.90(7) 23.5(1) | 24(2) 18(2) 19(5) |
|                     | 2-4CF | 2.17(2) 2.48(2) 1.27(2) 0.08(2) | 16(3) 18(4) 23(7) |
| W524/892 (1.34)     | L(q)d  | 1.86(2) 1.12(1) 0.62(1) 1.40(2) 4.9(2) | 68(1) 71(3) 68(6) |
|                     | 14-24AEC | 0.28(3) 7.80(7) 6.37(6) 23.5(6) | 10(1) 8(1) 17(4) |
|                     | 2-1AEC | 0.04(1) 0.32(1) 1.65(2) 0.99(1) | 8(1) 6(1) 17(4) |
|                     | 2-4CF | 2.15(1) 2.4(3) 1.35(2) 0.1(3) | 14(1) 16(3) 15(4) |

a Mole fraction of phases calculated using the lever rule assuming one atom per formula unit; b Estimated from mole fraction assuming densities 7.0(4), 5.1(2), 6.5(3), and 4.4(3) g/cm\(^3\) for L, 14-24AEC, 2-4CF, and 2-1AEC, respectively; c Composition of quenched liquid L(q) is normalized to Bi + Sr + Ca + Cu = 5 as in 2201; d In addition to the matrix phase L(q), we observed pockets containing phases with compositions close to 2201 and thin 14-24AEC platelets. Both are believed to be formed from liquid during quenching; e AE total; f Sample quenched after heating to 890°C without dwell for 0.5 h.
Note that even quenching in oil does not completely suppress compositional changes. This is seen for example in figure 2c where the contrast changes are observed due to redistribution of Ag within the liquid as it was freezing. Another example is the presence of five phases in sample W524 quenched from 892°C (see footnote d to Table 2). The compositions of phases present in samples quenched into oil from $T_{\text{max}} = T_{\text{m}}(\text{DTA}) + 7^\circ$C are presented in Table 2. Variation in the Sr/Ca in a given phase changes linearly with respect to the overall Sr/Ca ratio. For samples with Sr-rich overall compositions, the composition of quenched liquid matrix is very close, but not equal to that of the 2201 phase. In wire W524 and tape T32, the composition of the frozen liquid matrix is Cu-rich being closer to that of 2212 ($\text{Bi}_{2.60(3)}\text{Sr}_{1.61(4)}\text{Ca}_{0.84(3)}\text{Cu}_{1.95(3)}$ when normalized to $\text{Bi}+\text{Sr}+\text{Ca}+\text{Cu} = 7$). Changes in overall composition strongly affect the volume fraction of liquid in the molten state. Note the very good agreement in Table 2 between the volume fraction of each phase determined from quantitative analysis of the SEM images and using the EDS data. Averaging the two methods, the amount of liquid can be estimated to vary from 50 ± 3 vol. % in T45 to 69 ± 4 vol. % in W524.

4. Discussion

In this study, we demonstrate that the overall precursor composition of Bi2212/Ag conductors affects its melting behaviour and determines the temperature range of optimum $J_c(T_{\text{max}})$. Table 1 suggests that to within ±2°C, $T_{\text{on}}(J_c)$ is determined by the temperature of complete decomposition of the 2212 phase $T_{\text{dil}}(0\% \ 2212)$. We can also deduce another relation: $T_{\text{on}}(J_c) = T_{\text{dil}}(\text{DTA}) + (6±2)^\circ$C ($T_{\text{dil}}(\text{DTA})$ for BSCCO+50%Ag mixture). To justify that relation, the C content in conductors [3] and possible changes in composition due to BSCCO interaction with the Ag sheath [11] should be taken into account. Note that the C content and changes in composition depend on conductor architecture and preannealing history.

The step-like change in $J_c(T_{\text{max}})$ in T45, W521 and W523 (Fig. 1) is in contrast to the dome-like $J_c(T_{\text{max}})$ observed previously [4, 5]. The sharp increase in $J_c$ above $T_{\text{on}}(J_c)$ is due to the precursor powder preserving its phase homogeneity up to the melting temperature (Fig. 2a). The step-like $J_c(T_{\text{max}})$ in T45 is somewhat similar to recently reported optimisation results [12] and could be related to the sharpness of the melting event for the nominal 2212 stoichiometric composition (Table 1).

Studying the samples quenched from $T_{\text{dil}}(\text{DTA}) +7^\circ$C, we found a strong effect of composition on the volume fraction and composition of the quenched liquid (Table 2). Differences in DTA cooling curves for samples with different compositions [8] indicate that compositional variations affect the solidification path. Further work is needed to understand the effect changing $T_{\text{max}}$ has on the solidification path and kinetics of 2212 formation on cooling. We believe those future studies will provide important basic information that will help design a more efficient, optimised heat treatment.

References

[1] Weijers H W, Trociewitz U P, Marken K et al 2004, Supercond. Sci. Technol., 17 636
[2] Hasegawa T, Koizumi T, Hikichi Y et al 2002 IEEE Trans. Appl. Supercond. 12 1136
[3] Hellstrom E E and Zhang W 1996 Physica B 216 252
[4] Polak M, Zhang W, Polianskii A et al 1997 IEEE Trans. Appl. Supercond. 7 1537
[5] Lang Th, Buhl D, and Gaukler L J 1998 Physica C, 294 7
[6] Miao H, Marken K, Meinesz M et al 2004 Adv. in Cryogenics Eng. 50, 603
[7] Bruzek C-E, Lalouet N, Flahaut E et al 2003 IOP Conf. Series No. 181 2260
[8] Miao H, Marken K, Meinesz M et al 2005 submitted to ICMC2005
[9] Zhang W, Pupyshева O V, Ma Y et al 1997 IEEE Trans. Appl. Supercond 7 1544
[10] Rikel M O and Hellstrom E E 2001 Physica C 357–360 1081
[11] Wesolowski D, Rikel M, Jiang J et al 2005 Supercond. Sci. Technol., 18 934
[12] Matsumoto A, Kitaguchi H, Kumakura H et al 2004 Supercond. Sci. Technol. 17 989