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Mechanical and physical properties of sintered YBCO–metal bulk composites with silver powder and fibres

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Silver powder and continuous fibres were used in developing sintered $YBa_2Cu_3O_{7-x}$ (YBCO)–metal composites because applications require further improvement in mechanical and physical properties of the bulk superconducting elements without affecting the critical current capacity. The weight ratios of silver powder to YBCO and silver fibre to YBCO were varied up to 50% and 5%, respectively, in the beam elements. The effect of silver addition on the density of the composite has been quantified. Stress–strain–critical current properties of bulk YBCO–metal composite elements were investigated in bending at 77 K. The addition of silver powder reduced the sintering temperature, increased the dimensional changes after sintering and also improved the strength, toughness and critical current capacity compared to the monolithic. Silver fibres, (aspect ratios varying between 70 and 110), aligned along the length of the element restricted the changes in dimensions of the composite after sintering and also influenced the stress–strain–current capacity relationship, strength and toughness of the composite to varying degrees. The mixture theory was used to predict the composite flexural strength based on the composition of the composite, constituent properties and porosity.

1. Introduction

Difficulty in manufacturing large single crystals of the superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) phase has generated interest in developing bulk superconducting elements by aggregation of the superconducting powder. The mechanical properties and critical current capacity of the bulk YBCO superconducting elements must be improved to withstand the working stresses induced by the current and magnetic field and external loads in various applications such as power generation and storage, medical diagnostics, transportation, large magnets, and microelectronics [1]. Compared to other structural ceramics, the bulk YBCO superconductor elements developed up to date have low strength, low modulus and low strain to failure [2–9]. Several methods have been used to improve the strength and the modulus of the bulk superconducting materials. The methods include polymer impregnation [2, 3] and addition of metal powder in the matrix [4–8]. Some of the additives used with the YBCO are silver, silver oxide and zirconia. Also stainless steel fibres have been used with YBCO to improve the strain-to-failure and post-peak current-carrying capacity with large strains [9]. Because processing temperature for the sintered superconducting material is about 900 °C (1173 K) and the performance temperature is − 196 °C (77 K), developing metal composites is considered a real challenge, as the metal selected should be chemically and thermally stable within these temperature ranges. In developing bulk superconducting elements, it is the critical current capacity, I_c, and not the current density, J_c, which is of major interest.

The reactivity of YBCO at high processing temperatures also limits the selection of metals for developing composites. Singh *et al.* [4] added silver and Ag_2O to the $YBa_2Cu_3O_{7-x}$ superconductor and observed the following results: an increase in flexural strength from approximately 40 MPa to 75 MPa and a two-fold increase in critical current density, J_c, by adding 20 vol % Ag. When 30 vol % Ag was added the strength was further increased to 87 MPa, but it was associated with a decrease in J_c. It was also observed that the modulus, hardness and fracture toughness were improved with the addition of silver. Nishio *et al.* [5] observed that by adding silver powder, the flexural strength was increased for 18 MPa (monolithic with no silver) to 59 MPa (with 50 vol % Ag) when compacted at 0.4 GPa. When compacted at 1 GPa the strength increased from 42 MPa (no silver) to 106 MPa (with 50 vol % Ag). They also varied the silver content up to 92 vol % and reported a strength of 210 MPa. Lee and Salama [8] observed that the flexural strength increased from 40 MPa to 60 MPa and the Young's modulus from 81 GPa to 96 GPa by adding 15 wt % Ag. Matsumuro *et al.* [6] also added varying amounts of silver to the $YBa_2Cu_3O_{7-x}$ powder and concluded that the compressive strength increased by three times and the maximum strain increased by about four times compared to the monolithic YBCO (the comparison here is made with a composite which was compacted using pressures as high as 5.4 GPa, while the monolithic was compacted at 0.5 GPa). Yeh and White [7] observed that by adding 30 wt % Ag_2O to the $YBa_2Cu_3O_{7-x}$ powder the fracture toughness, K_{IC}, increased from 1 MPa $m^{1/2}$ to 2.4 MPa $m^{1/2}$. The composite also showed a rising R-curve behaviour, indicative of an improvement in the cumulative toughening efficiency. However, very little work has been performed on improving the strain-to-failure and toughness of the bulk superconductor [9]. Toughness is defined as the area under the complete stress–strain relationship of the material. Toughness can be used to represent the relative improvement in energy absorption capacity due to the addition of silver powder and fibres. The monolithic YBCO has low strength, strain-to-failure (approximately 0.2%) and exhibit brittle failure and hence improving these properties is of interest in this study.

The method used in conventional structural ceramics in improving strain-to-failure and ductility is by fibre reinforcement of the matrix [10]. The fibres/whiskers often used in a structural ceramic matrix are silicon carbide (SiC) and carbon (C) [11, 12]. However, Hing and Groves [13] reinforced polycrystalline magnesium oxide with metal fibres to utilize the toughness of the metal fibres. Vipulanandan and Salib [9] showed that the toughness, strain-to-failure and post-peak behaviour (stress–strain–current capacity) of bulk YBCO can be substantially improved using continuous stainless steel fibres in the bulk YBCO matrix. The microcracks in the ceramic matrix and the reaction between the stainless steel fibres resulted in reduced current-carrying capacity and lower strength and modulus for the composite. Hence, in the present study, silver powder was used to reduce the microcracking in the ceramic matrix and silver fibres were used to reduce or prevent chemical reaction between the YBCO matrix and to improve the strain-to-failure and post-peak behaviour. Other factors that influenced the selection of silver fibres for this study are : (1) the ductility of silver fibres with a failure strain of 54% [14], (2) the thermal expansion coefficient of 20.6 $\times 10^{-6}\,°C^{-1}$ from 0–500 °C [14], which is higher than the YBCO matrix to avoid cracking while processing and testing, (3) paramagnetic, and (4) good thermal and electrical conductors.

2. Experimental procedure

A commercially available YBCO powder was used in this study with the particle size varying from 8–10 μm. Three different sets of specimens were fabricated: (1) YBCO monolithic, (2) YBCO mixed with silver powder up to 50 wt %, and (3) YBCO with 3 or 4.9 wt/wt % Ag fibres and 18 wt % Ag powder. Commercially available silver powder was used which was 99.9% pure with particle size varying from2–3.5 μm and a melting temperature of 961 °C. The silver fibres, 0.5 mm diameter and 35–55 mm long, were longitudinally aligned at the centre of the YBCO beam specimens in multiple layers. The thermal expansion coefficients of YBCO material varies from 11×10^{-6}–$25.5 \times 10^{-6}\,°C^{-1}$ above room temperature and between 130 K to room temperature varies from 5.2×10^{-6}–$15.7 \times 10^{-6}\,C^{-1}$ [15]. The monolithic YBCO beam elements were 65 mm in length with a cross-section of 13 mm × 9.4 mm before sintering. The fibre-reinforced composite was fabricated by uniaxial pressing at room temperature up to 30 MPa in a hardened steel mould and approximately 25 g powder was used for preparing each beam specimen. In the case of the 3.0 wt % Ag fibres (six fibres), the powder was divided into three equal parts (by weight) and placed in the mould in three layers with three fibres in between each layer. The minimum centre-to-centre spacing between fibres was 3 mm. The mould with the constituents and the die was first vibrated using a vibrating table at 25 Hz for 30 s and then compacted using up to 30 MPa uniaxial pressure. Relatively low uniaxial pressure was enough to compact the specimen because vibration was used. In fabricating the specimen with 4.9 wt % Ag fibres (12 fibres) the powder was divided into four equal parts with three layers of fibres each containing four fibres and the centre-to-centre distance between fibres was 2 mm. When silver powder was used in the matrix, the silver was mixed with the $YBa_2Cu_3O_{7-x}$ powder in the desired proportions in a mortar and pestle. After compaction the specimens were sintered between 881 ± 1 °C (silver composites) and 895 ± 3 °C (monolithic) for 12 h with 15 °C hr^{-1} heating and cooling rates. The sintering temperature was based on producing specimens with relative density greater than 80% (5.0 Mg m^{-3}) without any microcracking (shrinkage) on the surface. Fig. 1 shows the processing steps for the specimens. After sintering, the beam specimens were ground using 180 grit silicon carbide grinding paper to achieve parallel sides and then polished using 320 and 600 grit silicon carbide paper to remove any surface flaws. Gravimetric method was used for density measurements. The dimensions were measured using a vernier caliper with an accuracy of 0.025 mm and the specimens were weighed accurately to 1 mg. For current capacity measurements, silver contact wires were wrapped around the specimen as current leads and glued in place using silver paste. A total of two current leads and two voltage leads were placed on the specimens.

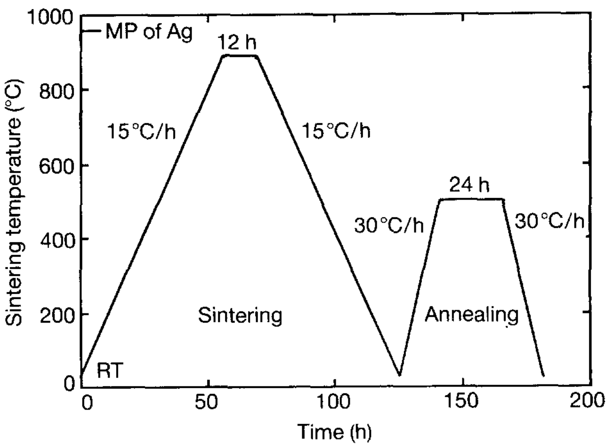

Figure 1 Temperature–time relationship for sintering and annealing monolithic YBCO and composites.

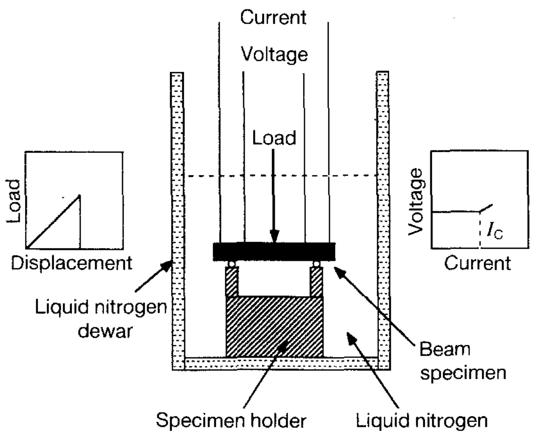

Figure 2 Electro-mechanical testing configuration for testing at 77 K.

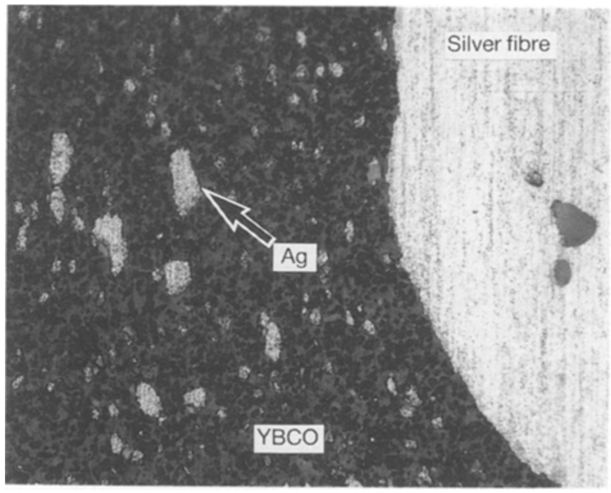

Figure 3 Optical micrograph of YBCO–Ag composite cross-section. ×400.

Specimens with silver contacts were then annealed in oxygen at 500 °C for 48 h. The current capacity was measured from the voltage–current relationship using a 1 μV cm^{-1} (cut-off) criteria. An HP model 6011A d.c. power supply 0–20 V/0–120 A, 1000 W and a Keithley model 181 nanovoltmeter were used. The current capacity was measured at 77 K to an accuracy of ± 0.1 A.

Three-point bending tests were performed on beam specimens in liquid nitrogen to evaluate the electro-mechanical properties. A schematic illustration of the experimental apparatus used for the electro-mechanical testing at liquid nitrogen temperature is shown in Fig. 2. X–Y recorders were used to collect the data continuously. The machine displacement was corrected to obtain the test specimen displacement using the compliance method. Before loading the specimen, the change in resistance with reducing temperature was measured to determine the T_c. The testing span used for the bending test was either 48 or 56 mm, depending on the specimen length. While loading the specimens in liquid nitrogen, the current capacity was also measured to develop the electro-mechanical property relationship. Several specimens were tested under various conditions studied. The changes in microstructure and the interaction between the YBCO powder and silver powder and fibres were studied using a Nikon (optiphot) optical microscope.

3. Results and discussion

Inspection of the cross-section of the composite using an optical microscope (× 1000 magnification), as shown in Fig. 3, indicates that the silver powder is well distributed within the YBCO matrix. Also, the bonding between the YBCO matrix and silver fibre is good and void free. Fig. 4 shows the variation of resistance with temperature for the monolithic and YBCO–Ag (30 wt %) composite. The monolithic and YBCO–metal composite showed similar T_c and transition width. Addition of silver reduced the normal resistance of the composite compared to the monolithic form. The relative density is defined as the ratio of bulk density/theoretical density of superconductor (6.30 Mg m^{-3}) or the composite.

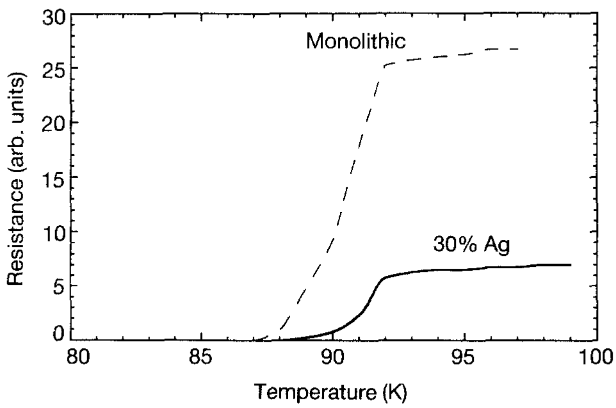

Figure 4 Resistance–temperature relationship for a monolithic YBCO and a Ag-YBCO composite.

3.1. Monolithic YBCO

Several specimens were compacted between 15 and 30 MPa and the green relative density varied from 40% –50%. And the density of the sintered specimens varied from 75%–90%. Sintering resulted in a volume strain (reduction) which depended on the initial green density. The shrinkage strain due to sintering was greatest along the length of the beam. The higher the sintered density the greater the potential for cracks and degradation of the monolithic composite. Hence, the development of YBCO composites to avoid cracks during sintering is in the pipeline. The sintered monolithic specimens were tested in liquid nitrogen in three-point bending (displacement control test) with critical current measurement, and a typical result is shown in Fig. 5. The stress–strain relationship was linear up to the peak stress and failure was sudden. The critical current capacity remained constant throughout the loading phase up to the peak stress, and dropped to zero after brittle failure. The critical current capacity was not affected by the flexural stress and remained constant up to failure. Rapid loss of strength and current capacity at a strain of 0.25% warrants improvement of strength, current capacity, post-peak behaviour, toughness and increase of the strain-to-failure (ductility). Hence reinforcing the matrix with silver powder and fibres was evaluated.

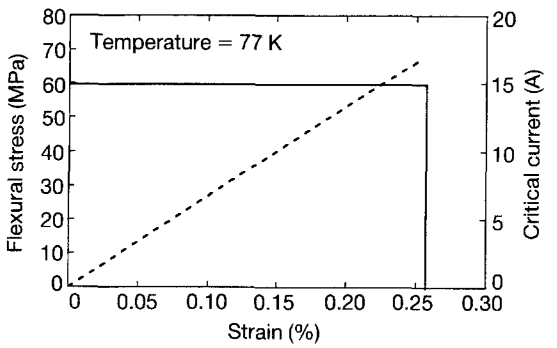

Figure 5 Typical flexural stress–strain–critical current relationship for monolithic YBCO. (- - -) stress–strain, (——) current–strain.

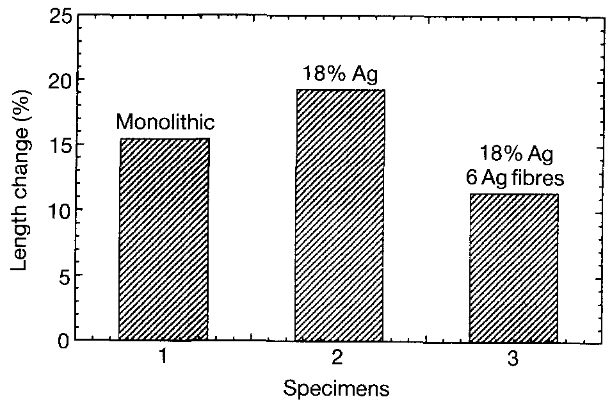

Figure 6 Change in length after processing for monolithic YBCO and composites.

3.2. YBCO–Ag composites

3.2.1. *Silver powder*

Silver powder was used in this study because it does not react with the YBCO [16]. Addition of 18% Ag powder resulted in 18% reduction in length of the sintered beam specimen compared to 15.5% for the monolithic. The change in length is due to densification at sintering temperature followed by thermal contraction due to cooling thereafter. The addition of silver powder resulted in higher green and sintered densities. The sintered relative density increased from 77% (4.85 $Mg m^{-3}$) for the monolithic to 86% (5.87 $Mg m^{-3}$) for the 18 wt % Ag powder composite and to 89% (7.05 $Mg m^{-3}$) for the 50 wt % Ag powder composite. The sintered density of 50% Ag powder composite was 7.05 $Mg m^{-3}$. The change in length after sintering for the monolithic and 18 wt % Ag powder/YBCO composites is compared in Fig. 6. The porosity (volume of void/total volume) of the specimens after sintering varied from 0.1–0.2 with the amount of silver powder added. Fig. 7 shows the effect of silver powder on the flexural stress–strain–critical current relationship of the composites. The composite with 18 wt % Ag showed the highest current capacity. Compared to the monolithic the strength and the modulus increased for both (18 and 50 wt %) composites. The 50 wt % Ag powder/YBCO composite had the highest strength but lower modulus than the 18 wt % Ag powder/YBCO composite. The 50 wt % Ag powder composite showed about a five-fold increase in toughness while the composite with 18 wt % Ag powder showed a 50% increase over the monolithic (Fig. 8). The toughness of the 50 wt % Ag powder/YBCO composite was very close to the toughness reported for the stainless steel fibre/YBCO composites [9], and is compared in Fig. 8. Even though some mechanical properties were improved, still no post-peak behaviour was observed for the silver powder composites. This indicated that silver powder by itself would not improve ductility. Therefore, the YBCO matrix had to be fibre reinforced to improve the ductility, as suggested by Vipulanandan and Salib [9].

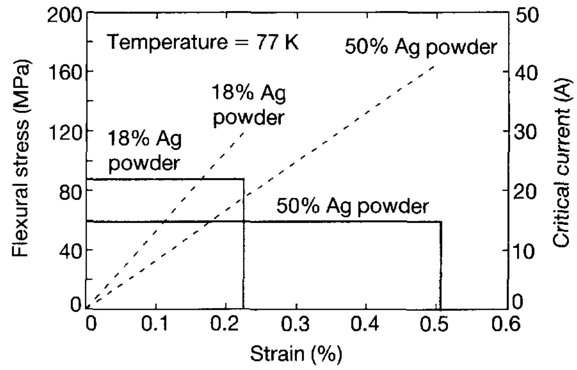

Figure 7 Typical stress–strain–critical current relationship for silver powder composites. (- - -) stress–strain, (——) current–strain.

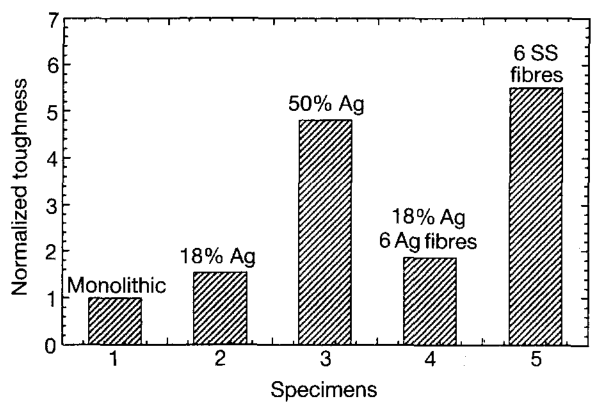

Figure 8 Toughness for monolithic and silver composites.

3.2.2. *Silver fibres*

Initially 3 wt % (six fibres) were added to the YBCO/Ag powder (18 wt %) matrix, a typical configuration is shown in Fig. 9 (insert). Addition of silver fibres reduced the change in length of the specimens after sintering as shown in Fig. 6. The change in length of the fibre composites with 3.0 wt % Ag fibres (six fibres) was 12%, even lower than the YBCO monolithic sample. This is because the fibres may interfere with the densification at sintering temperature and subsequent thermal contraction during cooling of the composite. Hence this will induce residual stresses in the YBCO matrix. Typical stress–strain relationships for YBCO with continuous silver fibres are shown in Fig. 9. The composite with 3.0 wt % Ag fibres neither affected the strength of the 18 wt % Ag powder/YBCO composite nor improved the brittle failure of the composite and hence the fibre content was increased

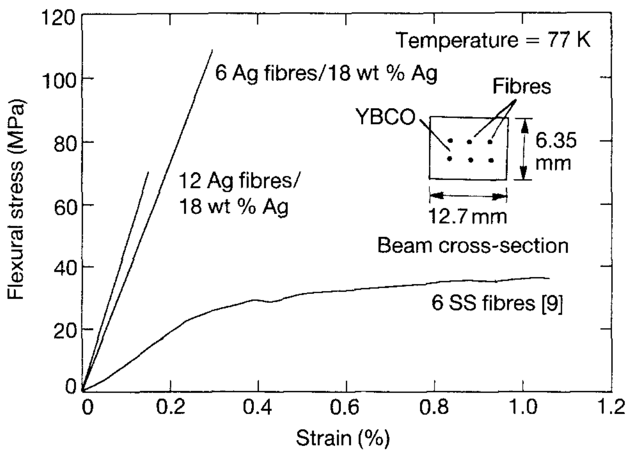

Figure 9 Typical stress–strain relationships for silver fibre composites.

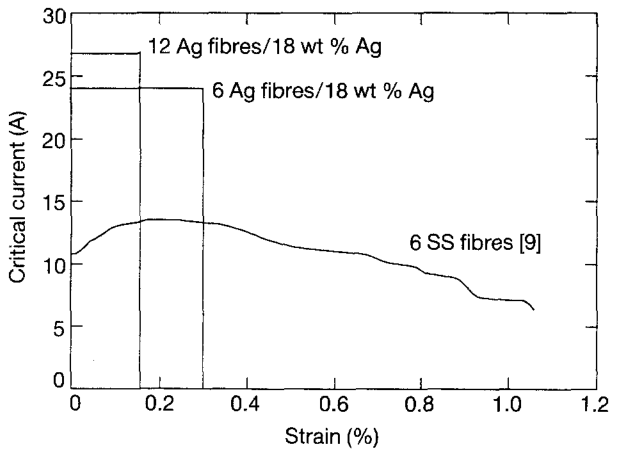

Figure 10 Typical critical current–strain relationship for silver composites.

to 4.9 wt % composite (12 fibres). Even when 4.9 wt % (12 fibres) were placed in the YBCO matrix, the composite showed a similar brittle failure to the YBCO/Ag powder composite. As stated in the literature, stainless steel (ss) fibres (2 wt % composite) with a modulus of 200 GPa were very effective in improving the post-peak behaviour (both load and current capacity) of the composites as shown in Figs 9 and 10. The main reason for the brittle behaviour of silver fibre/YBCO composite is because silver fibre has a modulus (71 GPa) [14] not high enough, when compared to the YBCO matrix, to share the load (compared to the ss fibres). In general for fibre-reinforced composites, the fibres must have a higher modulus than the matrix to perform effectively. When compared to the ss-fibre/YBCO composites, silver fibre composites investigated in this study showed higher strength and modulus but lower toughness and ductility. The composite specimens with 4.9 wt % Ag fibres/18 wt % Ag powder did not affect the current capacity but lowered the strength and failure strain more than the other YBCO/Ag composites with (i) 3.0 wt % Ag fibres/18 wt % Ag powder or (ii) 18 wt % Ag powder. This could be due to higher residual stresses developed in the YBCO matrix during sintering and cooling in the presence of 4.9 wt % continuous silver fibres. These results also suggest that there is an optimum weight percentage of fibres that could be used in the composite without significantly degrading the mechanical properties.

4. Analysis

The green and sintered densities and the strength of the YBCO monolithic and YBCO/Ag composites are quantified in terms of the processing conditions, porosity, composition and constituents properties.

4.1. Density–pressure relationship

The variation of relative density, (γ) (bulk density/theoretical density), with the uniaxial compaction pressure, σ_c (MPa), for the monolithic YBCO can be represented by a power law [2]. In this study, it was proposed to verify this relationship for YBCO/Ag composites and if necessary modify the relationship to include the effect of silver addition. The power-law relationship can be represented as follows [2]

$$\gamma = \mu \sigma_c^{\eta} \quad (1)$$

where μ (a density parameter) and η are dependent on the method of processing and are determined from linearized least square fit of the test data. The theoretical densities for the composite beams were calculated based on volume fraction of YBCO (density $= 6.30\ \mathrm{Mg\,m^{-3}}$) and silver (density $= 10.5\ \mathrm{Mg\,m^{-3}}$) in the composite. The theoretical densities were $6.83\ \mathrm{Mg\,m^{-3}}$ and $7.90\ \mathrm{Mg\,m^{-3}}$ for the 18% and 50% (wt/wt%) Ag powder composites, respectively. Using the test data from this study and other published data on density [2, 17] the parameters were determined. The data on the monolithic composite was available up to a uniaxial pressure of 350 MPa. The parameter η was determined to be 0.145 and 0.10 for green (dry compact) and sintered monolithic specimens, respectively [2]. The parameter μ was 30 for the dry compact ($T = 25\,°\mathrm{C}$). The measured and predicted (Equation 1) green densities for the monolithic and YBCO/Ag composites are compared in Fig. 11 and the agreement is good.

The value of μ had to be modified to predict the sintered density of the monolithic and YBCO/Ag

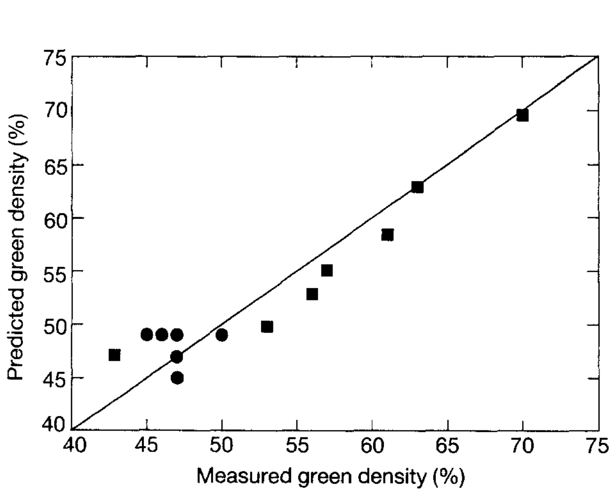

Figure 11 (■) Predicted [17] and (●) measured green density for the monolithic and YBCO–Ag composites.

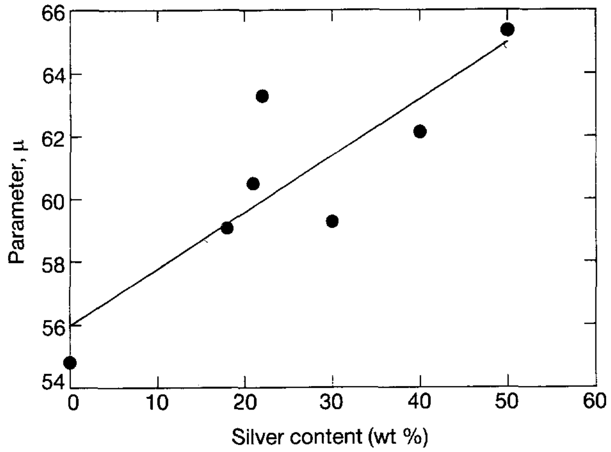

Figure 12 Variation of sintered density parameter, μ, with silver content.

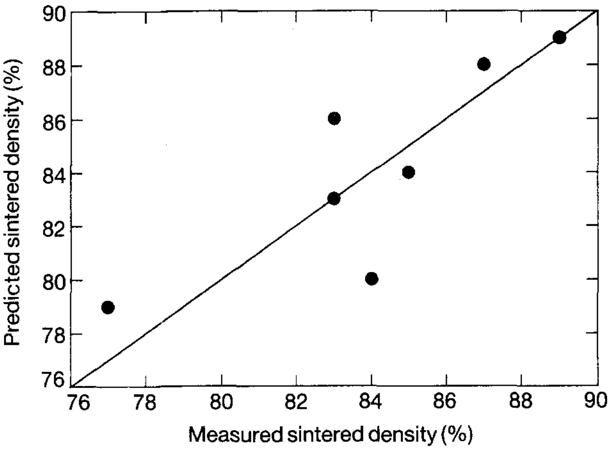

Figure 13 Predicted and measured sintered density for the monolithic and YBCO–Ag composites.

composite beam specimens. The parameter μ increased with the addition of silver powder and showed a linear variation (coefficient of correlation of 0.85) as shown in Fig. 12. The relationship can be represented as follows

$$\mu = 56 + 0.18\omega \qquad (2)$$

where ω is the weight percentage (wt/wt%) of silver powder in the composite ($0 < \omega < 50\%$). The measured and predicted sintered densities using the parameter μ (Equation 2) for the monolithic and YBCO/Ag composites are compared in Fig. 13. This comparison is made to evaluate the assumptions and approximations made in developing the relationships in Equations 2 and 3.

4.2. Strength–porosity relationship

During the last two decades, several semi-empirical functions have been used to describe strength–porosity relationships of ceramic materials [2]. The following relationship is proposed, based on the mixture theory, and is used to estimate the strength of the monolithic and the YBCO/Ag powder composites

$$\sigma_c = \sigma_0(1 - A\alpha)\beta + \sigma_{Ag}(1 - \beta - \alpha) \qquad (3)$$

where the strength σ_c, of the monolithic YBCO is

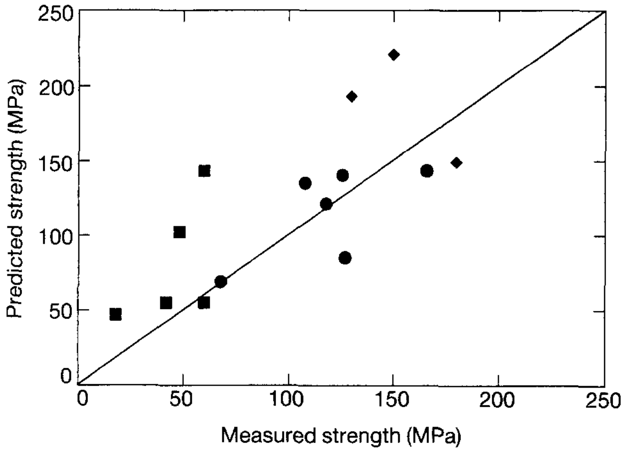

Figure 14 Predicted and measured flexural strength for the monolithic and silver composites. (■) [17], (●) present work, (◇) [6].

assumed to vary linearly with the porosity, α, which varied from 0.1–0.25. Volume fraction of YBCO in the composite is $\beta (0.55 < \beta < 0.87)$. Volume fraction of silver in the composite, equal to $(1 - \beta - \alpha)$, was varied up to 0.34 (50 wt % composite). The strength of silver, σ_{Ag}, is 55 MPa [14]. Note that Equation 3 does satisfy the limiting condition that $\sigma_c = 0$ when $\alpha = 1$ and $\beta = 0$. In the current study the parameters σ_0 and A were obtained from least square fit of the test data on 65 mm long beams of monolithic and YBCO/Ag powder composites and the values were 340 MPa and 3.13, respectively. The parameter A indicates the dependency of the strength on the porosity. The monolithic and YBCO/Ag composite flexural strength predicted using Equation 3 is compared to the measured strength from the current study and other published data [6, 17] in Fig. 14.

5. Conclusions

Methods to improve the mechanical properties and critical current capacity of bulk YBCO superconductors using silver powder and continuous fibres were investigated. The electro-mechanical properties of the monolithic and composites were studied at 77 K. Based on the experimental and analytical studies the following conclusions can be drawn.

1. A linear stress–strain relationship was observed for the monolithic YBCO and the failure was brittle. The critical current capacity was not affected by the flexural stress up to failure.

2. Addition of silver powder reduced the sintering temperature by more than 10 °C. The change in length after sintering of YBCO/Ag powder composites was greater than in the monolithic composites. Addition of silver powder improved the strength, modulus, critical current capacity and toughness of the composite, but no improvement in post-peak behaviour was observed.

3. Silver fibres restricted the change in length during sintering. Continuous silver fibres bonded well to the YBCO matrix and the failure of the composite at 77 K was by fibre breakage. A 20% increase in toughness was observed when 3 wt % Ag fibres were used in

the 18 wt % Ag powder/YBCO composite. The silver fibres (up to 4.9 wt % composite) did not improve the post-peak behaviour (stress–strain–current capacity) within the range of variables studied.

4. Both linear and non-linear relationships for the monolithic and YBCO/Ag composites have been developed to represent the green and sintered densities, and the flexural strength in terms of processing parameters and constituent properties.

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