Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 1817–1824
www.elsevier.com/locate/jeurceramsoc

A study of the sintering behaviour of magnesium diboride

C.E.J. Dancer [a,*], P. Mikheenko [b], A. Bevan [b], J.S. Abell [b], R.I. Todd [a], C.R.M. Grovenor [a]

[a] *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*
[b] *Department of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

Received 26 June 2008; received in revised form 12 September 2008; accepted 12 September 2008
Available online 14 November 2008

Abstract

It is well known that a substantial increase in critical current density can be achieved by the heat-treatment of *ex situ* magnesium diboride powder-in-tube wires. However, it is not clear whether this is due to a true sintering process involving the significant transport of material and densification, or due for instance to the removal of volatile impurities from particle interfaces, limited chemical reactions at particle boundaries, or simply contact formation between particles by thermally activated direct adhesion. We believe that the term *sintering* in the magnesium diboride literature may often be used loosely when neither neck formation nor densification occurs during heat-treatment, and have designed experiments to understand what is happening during this processing step. We have studied the effect of a range of heat-treatments on the microstructure of pellets produced from commercial MgB_2 powder using X-ray diffraction, scanning electron microscopy, Vickers hardness tests and by density measurements using Archimedes' principle. The results are compared to those from a dense sample produced from the same powder by resistive sintering. No significant densification is observed in pellets produced by conventional pressure-less heat-treatment up to 1100 °C. However, a clear correlation between density and hardness is established by comparison with results for bulk MgB_2 produced by resistive sintering, which confirms that a classical sintering process has been induced in the latter samples.
© 2008 Elsevier Ltd. All rights reserved.

Keywords: MgB_2; Firing; Sintering; Porosity; Superconductivity; Borides

1. Introduction

Magnesium diboride (MgB_2) powder-in-tube (PIT) wires fabricated by the *ex situ* processing route (i.e. using pre-reacted MgB_2 powder) have been studied extensively since the discovery of superconductivity in MgB_2 in 2001.[1] In contrast to the more often studied *in situ* processing route, where the MgB_2 phase forms during processing, *ex situ* processing does not result in a large density change since there is little reaction during heat-treatment.[2] Because the superconducting phase is present from the start, it is also possible to reduce impurity formation by limiting the temperature and duration of the heat-treatment stage. *Ex situ* MgB_2 PIT tapes with critical current density (J_c) of 10^5 A/cm^2 (at 4.2 K, 0 T) have even been produced with no heat-treatment.[3] However, MgB_2 PIT wires show substantially improved superconducting characteristics following heat-treatment at moderate temperatures.[4] It has not been established whether this heat-treatment is effective due to increasing the density of the MgB_2 via conventional sintering processes, or whether some other mechanism such as removal of impurities or recrystallisation is occurring.[5]

Moderate heat-treatment temperatures of 900–1000 °C are typically used during *ex situ* processing of PIT wires because at higher temperatures a thick reaction layer is formed between the sheath metal and the core.[4,6] A wide range of grain sizes is generally evident in the cross-section of the wires.[7] The main impurity phase formed is MgO,[8] although other phases such as MgB_4[9] and the non-stoichiometric phases $MgB_{4+\delta}$ and $MgB_{7+\delta}$ [10] have been identified in *ex situ* samples following heat-treatment.

The effect of porosity in bulk *ex situ* MgB_2 samples has been studied by Grinenko et al. by systematically varying the density of bulk samples (with the same composition) between 16 and 70% of the maximum density (as calculated from the lattice parameters).[11] As the sample density was decreased, the measured onset critical temperature ($T_{c,0}$) decreased, and the width of the superconducting transition increased significantly, indicating decreased connectivity between particles and decreasing the temperature range in which MgB_2 can be used

* Corresponding author. Tel.: +44 1865 273766; fax: +44 1865 273789.
E-mail address: claire.dancer@linacre.oxon.org (C.E.J. Dancer).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.09.025

as a useful superconductor. In addition, denser material can be expected to reach higher transport critical currents than porous material processed by the same method, as the cross-sectional area of superconducting material is higher for a given sample diameter.[12] We can thus conclude that it is important to understand how to control the density of the MgB_2 in *ex situ* wires and tapes in order to achieve the optimum performance.

MgB_2 powder can be heat-treated under pressure in vacuum or inert gaseous atmosphere to produce dense bulk MgB_2, and heat-treatment at high gas pressure,[13] hot isostatic pressing (HIPing),[14] and spark plasma sintering (SPS)[15] have all been shown to be effective at improving bulk densities. Wires produced by HIPing have improved J_c values in high magnetic fields compared with wires processed identically but heat-treated conventionally at atmospheric pressure.[16] Zhu et al. studied TEM samples of bulk *ex situ* MgB_2 heat-treated in high Mg vapour pressures, and their micrographs reveal a dense structure with some regions of fine-scale porosity, nano-sized MgB_2 grains, and MgO impurities surrounding inclusions of large single-crystal MgB_2 grains.[13] There is clearly a significant difference in both microstructure and performance between MgB_2 which has undergone high-pressure processing and that produced conventionally at atmospheric pressure. One of the aims of this work is to establish reliable metrics to measure these differences in microstructure.

The approach we have taken is to use the techniques developed for conventional structural ceramics and to apply them to bulk samples of MgB_2. We designed experiments using bulk MgB_2 to model what is happening in PIT wires during heat-treatment, and as a result the maximum temperature was limited to 1100 °C. These samples were compared to those produced using a non-conventional heat-treatment process which is known to produce dense samples, resistive sintering.[17] The starting powder was also comprehensively characterized to examine the impurities and the shape and size distributions of the particles.

2. Experimental details

Commercial MgB_2 powder (Alfa Aesar, 98% purity, −325 mesh) was used to produce all the bulk materials studied in this work. Scanning electron microscopy (SEM) in a JEOL 840F was performed at 5 kV on powders dispersed on a carbon tab and coated with 2 nm of platinum to minimize charging. Transmission electron microscopy (TEM) using a JEOL 2000FX was carried out on MgB_2 powder dispersed in isopropanol onto holey carbon films on a Cu grid. The particle size distribution was measured using a Malvern Mastersizer S Laser Diffraction system, using isopropanol as the dispersion medium. Laser diffraction was used in preference to microscopy to assess particle size because it can study a very wide range of particle sizes in one fast measurement.[18]

Bulk pellets (9 mm diameter, ∼4 mm height) were prepared from this powder by uniaxial pressing at 100 bar in a stainless steel die and heat-treatment for 1 h in flowing Ar gas, with peak temperatures ranging from 200 to 1100 °C. The green pellets were placed in an MgB_2 powder bed inside a closed alumina crucible to reduce Mg loss during heat-treatment. Density measurements were carried out on pellets before and after heat-treatment using the Archimedes method with isopropanol as the immersion liquid. Hardness values on the sample surfaces were measured by Vickers indentation. Pellets were fractured, and the resulting fracture surfaces were imaged by SEM again using the JEOL 840F at 5 kV. To alleviate charging during imaging, samples were attached to aluminium stubs with silver paint and coated with 2 nm of platinum.

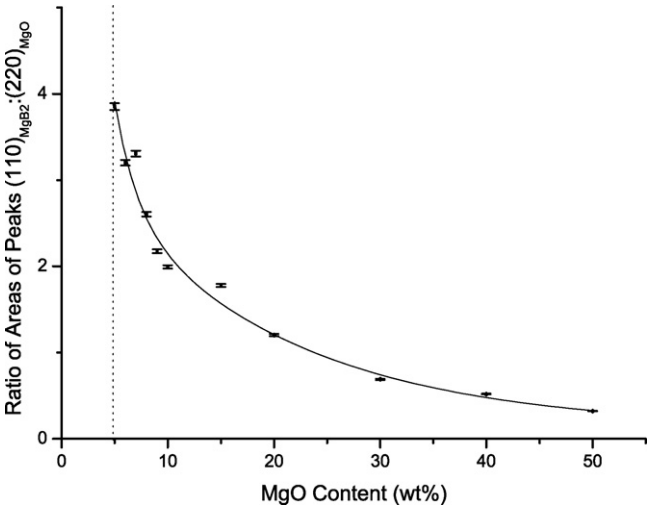

Fig. 1. MgO content XRD calibration curve.

The increase in content of crystalline MgO following heat-treatment was calculated from area of XRD peaks by comparison to known mixtures of MgO and MgB_2 content prepared from MgO powder (BDH Ltd.) mixed with Alfa Aesar MgB_2 powder. XRD scans were carried out on these calibration powder mixtures using a Philips θ–2θ diffractometer and Cu Kα radiation at 35 kV and 50 mA. The areas of the MgB_2 (1 1 0) (at $2\theta = 59.8°$) and MgO (2 2 0) (at $2\theta = 62.3°$) peaks were measured using the ProFit analysis program and their ratio calculated. The calibration curve (Fig. 1) generated was then used to measure any increase in MgO following heat-treatment in all subsequent samples. The detection limit below which the $(2\,2\,0)_{MgO}$ peak becomes indistinguishable from the background noise was established as ∼5 wt%.

A denser MgB_2 sample was also produced from the same powder at the University of Birmingham using a resistive sintering apparatus (Fig. 2) which has previously been used to produce dense MgB_2 bulk samples.[17] MgB_2 powder was placed in the centre of a graphite die and pressed from both sides with tungsten plungers. Direct current was passed through the plungers, and is thought to lead to extreme local heating at the point contacts between particles. Typical pressure and temperature ranges measured of the graphite die are 42–55 MPa and 900–980 °C, but only represent average values across the whole sample. The optimum heat-treatment temperature was assessed by monitoring the thickness of the specimen during heat-treatment. The temperature was held at the level at which a rapid decrease in the height of the specimen occurred; i.e. at the temperature at which effective densification began. Once the height of the spec-

Download English Version:

https://daneshyari.com/en/article/1476790

Download Persian Version:

https://daneshyari.com/article/1476790

Daneshyari.com