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Effect of the Starting Boron Powder on the Superconducting Properties of MgB$_2$

A thesis submitted in fulfillment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

From the

UNIVERSITY OF WOLLONGONG

By

XUN XU, B. Eng., M. Eng.

Institute for Superconducting and Electronic Materials

2008
DECLARATION

This is to certify that the work presented in this thesis was carried out by the candidate in the laboratories of the Institute for Superconducting and Electronic Materials (ISEM), at the University of Wollongong, NSW, Australia, and has not been submitted for a degree to any other institution for higher education.

Xun Xu
2008
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Abstract

The effect of the properties of the starting boron powders on the superconducting properties of MgB$_2$ has been studied. Low grade boron powders are attractive because of their low cost, but produced lower surface reactivity and larger particle size than high purity (99%) amorphous boron powder, indicating that the low grade powders cannot be used to achieve the same superconducting properties as those of samples made from pure 99% boron powder. However, the low purity boron powders can be improved by using simple physical and chemical processes, leading to enhanced magnetic critical current density, $J_c$. In order to get high performance MgB$_2$, it is obviously important to control the phase composition and microstructure of the boron starting powders and the solid state reaction conditions.

Ball milling is an effective method to reduce the boron particle size, so, the effects of ball milling boron powders in different media, such as acetone, ethanol, and toluene, on the superconducting properties of MgB$_2$ needed to be considered and studied. It was observed that toluene was the most effective medium of them all for enhancing $J_c$. $J_c$ was estimated to be $5 \times 10^3$ A cm$^{-2}$ at 8 T and 5 K for a sample that was ball milled in toluene. This value is much higher than that of the pure MgB$_2$ reference sample that was not ball milled, by a factor of 20. It was considered that ball milling B using toluene leads to smaller MgB$_2$ grains, resulting in enhanced $J_c$ at low operating temperatures and high fields.

MgB$_2$ samples were prepared using as-supplied commercial 96% boron with strong crystalline phase and the same 96% boron (B) after ball milling. The effects of the properties of the starting B powder on the superconductivity were evaluated. It was
observed that samples using ball-milled 96% B, in comparison with the reference sample made from the as-supplied 96% B, were characterized by small grain size and enhanced magnetic critical current density ($J_c$), which reached $2 \times 10^3$ A cm$^{-2}$ at 5 K and 8 T. The improved pinning seen in these samples seems to be caused by enhanced grain boundary pinning at high field. MgB$_2$ samples were also prepared by using 96% boron powder with strong crystalline phase that had been ball milled for various times. Based on Rowell connectivity analysis, when the ball-milling time increased, the connectivity factor, described as the active cross-sectional area fraction ($A_F$), was decreased. This implies that the inter-grain connectivity became worse. These properties could lead to poor $J_c$ in low field. However, the pinning force strength of samples using ball-milled 96% B is larger than that of the reference sample using as-supplied commercial 96% B powder. These results accompany enhanced irreversibility ($H_{irr}$) and upper critical fields ($H_{c2}$).

Furthermore, the magnetic field dependence of the transport critical current density ($J_{ct}$) and the grain connectivity of MgB$_2$/Fe wires fabricated from ball-milled boron have been investigated in detail, and strong correlations have been found, as evidenced by differences in grain size, critical transition temperature, and resistivity. It was observed that the samples fabricated by ball milling had relatively small grain sizes, resulting in a weaker field dependence of the $J_{ct}$ in the high field region. On the other hand, the ball-milled boron was associated with poor connectivity between adjacent grains. It is clearly shown that the observed reduction in low field $J_{ct}$ is related to the reduction in the superconducting area fraction that is reflected by the connectivity factor. Even though high temperature sintering could always compensate for the degradation of the $J_{ct}$ in the low field region, the subsequent grain growth in this case was mainly responsible for the degradation of $J_{ct}$ in the high field region. The strong correlation
between the grain size and the connectivity can change the field dependence of the $J_c$, and both these factors are primarily affected by the sintering temperature and by the presence and extent of ball milling.

In the MgB$_2$ field, chemical doping is the most popular way to improve the superconductor properties. It has been reported that significantly enhanced critical current density in MgB$_2$ superconductor could be easily obtained by doping with a hydrocarbon, highly active pyrene (C$_{16}$H$_{10}$), while using a sintering temperature as low as 600°C. The processing advantages of the C$_{16}$H$_{10}$ additive include production of a highly active carbon (C) source, an increased level of disorder, and the introduction of small grain size, resulting in enhancement of $J_c$.

Using the same concept, low purity boron powders were used to fabricate pure and submicron-sized carbon sphere doped MgB$_2$ superconductor. The boron powders used showed low reactivity towards MgB$_2$ formation, as compared to high purity (99%) amorphous boron, which might result from the larger grain size and the existence of crystalline boron or boron oxide in the former. However, the samples prepared from this boron powder showed comparable $J_c$ values at 20 K and in low field ($<1$ T) to those from a sample prepared from 99% amorphous boron. Doping submicron-sized carbon spheres successfully introduced carbon substitution for boron, and so improved the $H_{c2}$, $H_{irr}$, and in-field $J_c$ properties of the MgB$_2$. 