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ARTICLE

Effect of Graphene Doping and Sintering Temperature on Microstructure and Superconducting Properties of MgB_2 Bulks

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Abstract: The effect of graphene doping on the microstructure and superconducting properties of MgB_2 bulks was examined in comparison with the case of un-doped MgB_2. The correlation among annealing temperatures, microstructures and superconducting properties in graphene doped MgB_2 bulks was investigated. The phase, microstructure and superconductivity of MgB_2 were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and superconducting quantum interference device (SQUID), respectively. The results show that the graphene doping results in an obvious improvement of the critical current density. The highest critical current density reaches 1.8×10^5 A/cm^2 at 20 K and 1 T.

Key words: MgB_2; doping; sintering; microstructure; critical current density

Since the discovery of superconductivity in MgB_2 at 39 K[1], it has been considered one of the most promising candidates for engineering applications due to its low material cost and relatively high critical transition temperature[2-4]. However the critical current density of pristine MgB_2 drops rapidly with increasing the magnetic field, which is mainly due to its poor pinning and low upper critical field.

Carbon doping is the most effective and relatively simple way to improve the superconducting properties of MgB_2 [5-9], as it has a great influence on carrier density and impurity scattering. Graphene (G) is a single layered carbon with a honeycomb arrangement of carbon atoms. The ability to improve flux pinning at low doping levels has made graphene very significant among other carbon sources. Graphene has become an effective dopant improving the critical current density and flux pinning with only a slight reduction in the critical temperature[10,11].

In this work, we presented a study of the effects of graphene on improving the superconducting properties of MgB_2. Synthesis temperature for MgB_2 is an important parameter to improve the quality of powders and subsequently to enhance performances. In this work, we also investigated the effect of synthesis temperature on morphology, and how this is reflected in superconducting properties.

1 Experiment

Magnesium powder (99.81%, 37 μm, Tangshan Weihao), amorphous nano boron powder (98.99%, <350 nm, Pavezyum) and homemade graphene (99.5%, 3~5 layer) were used in this work. The mixture powders with a stoichiometry of $MgB_{1.92}C_{0.08}$ or MgB_2 were well mixed and ground in an agate mortar for 30 min in a glove box under argon atmosphere. The mixture powders were pressed into disks with 20 mm in diameter and approximately 1.5 mm in thickness under a pressure of 10 MPa. Then these disks were enveloped in a niobium foil and put into a horizontal tubular furnace. The

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disks were sintered at 700~850 °C for 2 h. After sintering, the disks were cooled naturally.

The phase composition was identified by X-ray diffraction (XRD) with Cu Kα radiation. The microstructure was observed by scanning electron microscope (SEM). The magnetization was measured using a dc superconducting quantum interference device (SQUID). In order to compare the physical properties of samples with different composition, the samples used in this study were shaped to dimensions of 2 mm × 2 mm × 1 mm. The critical current density (J_c) values of the samples were deduced from the hysteresis loops using the Bean model [12]. $J_c = 20\Delta M/(va(1-a/3b))$ ($a<b$), where ΔM is width of the hysteresis loop (emu), v is volume of the sample (cm^3), and a and b are the sample dimensions perpendicular to the field direction (cm).

2 Results and Discussion

Fig.1 is the XRD patterns of un-doped and G-doped MgB_2 samples sintered at 750 °C for 2 h. It can be seen that MgB_2 is the main phase in the two samples. A small graphene peak can be observed from the XRD pattern of G-doped MgB_2 sample. No significant peak shift is observed for the sample, due to the low doping level. In the XRD peaks, the full width at half maximum (FWHM) of the (110) diffraction peak reveals information about the crystallinity. The FWHM value of the (110) peak for the G-doped sample (0.348) increases compared to that for the un-doped samples (0.340), proving a decrease in the grain size for G-doped sample, which gives evidence that grain refining occurs due to graphene doping.

Fig.2 shows the SEM micrographs of un-doped MgB_2 sample (a, a′), and G-doped MgB_2 sample (b, b′) sintered at 750 °C for 2 h. Porosity is clearly visible in two samples, and SEM images show that their grain size is about 300 nm. However, the grain structure and the morphology of the G-doped MgB_2 sample seem to be slightly different from those of the un-doped MgB_2 sample. The G-doped MgB_2 sample has more homogeneous grains and most grains merge

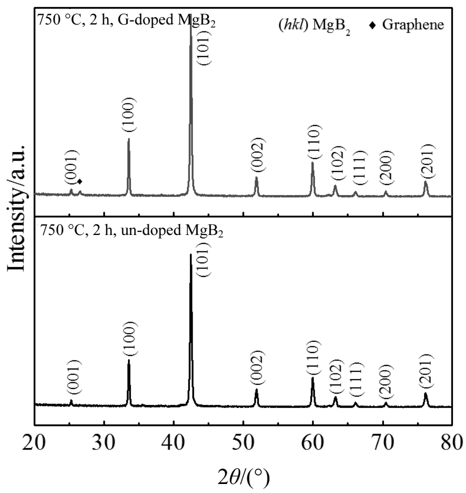

Fig.1 XRD patterns for un-doped and G-doped MgB_2 samples

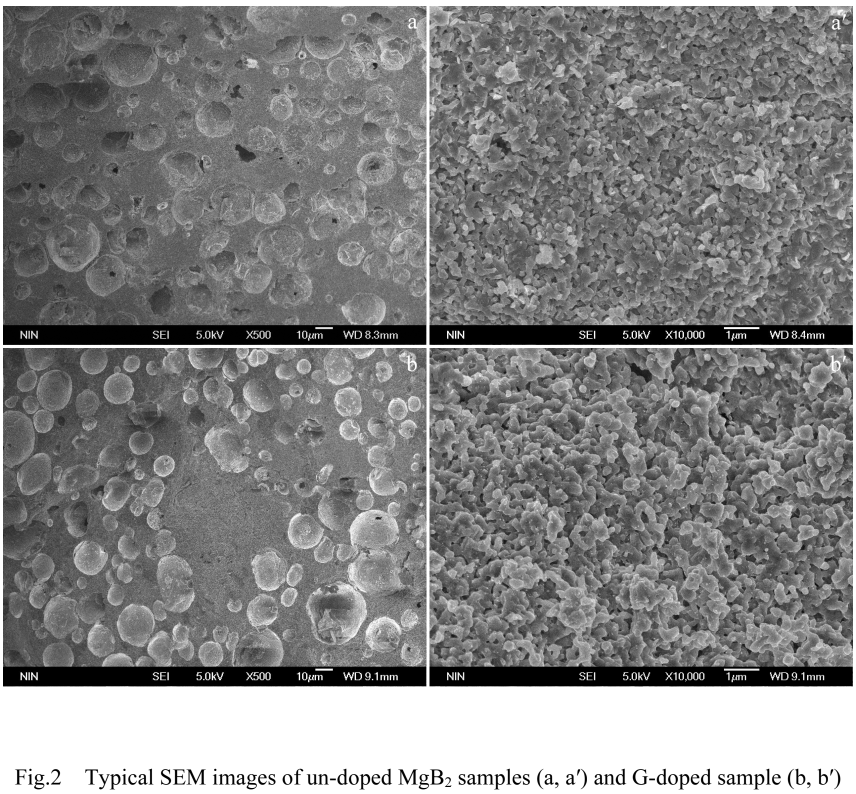

Fig.2 Typical SEM images of un-doped MgB_2 samples (a, a′) and G-doped sample (b, b′)

together into big clusters. A specific feature in graphene doping of MgB_2 is that it improves the inter-grain connectivity.

Fig.3 shows the variation of the critical current density J_c with the applied field for un-doped and G-doped MgB_2 samples sintered at 750 °C for 2 h. J_c of G-doped MgB_2 sample is increased due to graphene doping, which has improved J_c both in low field and high field.

Fig.4 is the XRD patterns of G-doped MgB_2 samples sintered at different temperatures. Analysis of the XRD patterns of G-doped MgB_2 powder samples shows that all samples consist of a main phase of MgB_2 together with graphene, indicating complete formation of MgB_2 under the sintering conditions. The FWHM value of the (110) peak is 0.353, 0.348, 0.297, 0.236 at four sintered temperatures. The decrease in FWHM value of the (110) peak proves an increase in the grain size with increasing the sintered temperatures.

Fig.5a~5d show the SEM micrographs of G-doped MgB_2 samples sintered at 700, 750, 800, and 850 °C, respectively.

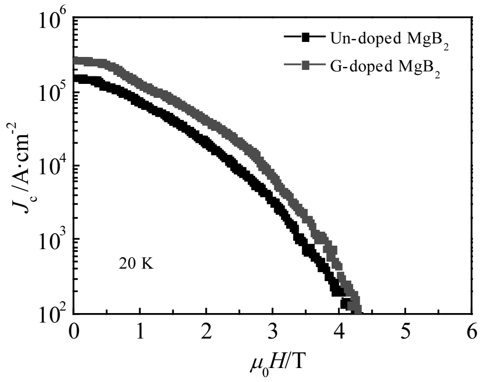

Fig.3 Variation of critical current density J_c with applied field for un-doped and G-doped MgB_2 samples

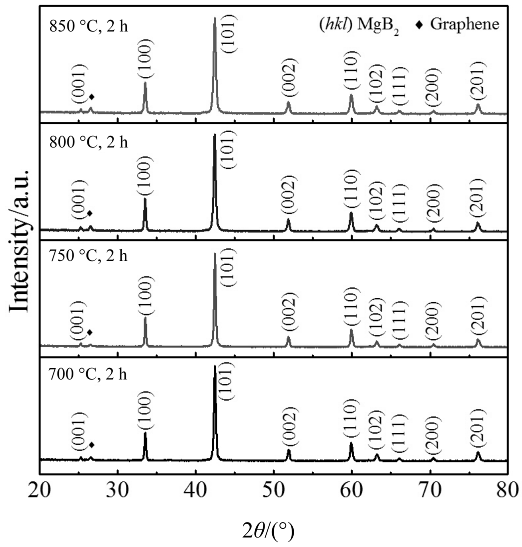

Fig.4 XRD patterns for G-doped MgB_2 samples sintered at different temperatures

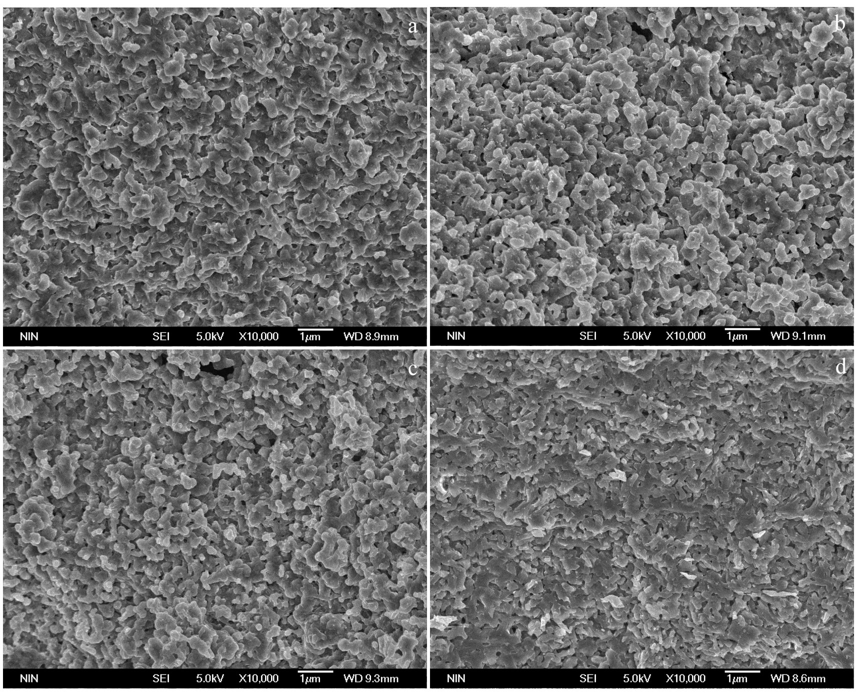

Fig.5 Typical SEM images for G-doped MgB_2 samples sintered at different temperatures: (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 850 °C

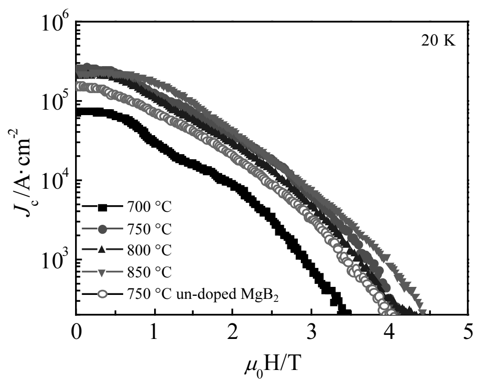

Fig.6 Variation of the critical current density J_c with the applied field for un-doped MgB_2 sample and G-doped MgB_2 samples sintered at different temperatures

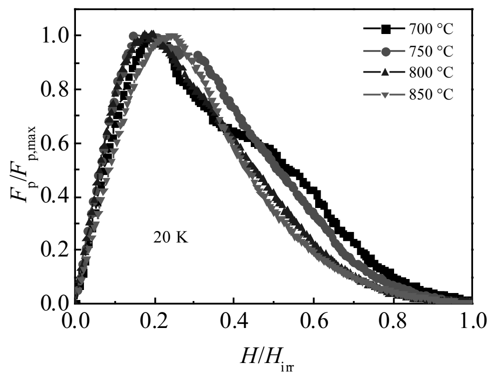

Fig.7 Normalized flux pinning force $F_p/F_{p,max}$ as a function of field H/H_{irr} at 20 K for G-doped MgB_2 samples sintered at different temperatures

As predicted higher synthesis temperature would lead to an enhancement in average grain size, the effect is slightly appreciable. The merging of several grains into a cluster is more visible in the samples that are sintered at higher temperatures. The SEM results indicate that the porosity of MgB_2 samples improves obviously.

The effect of sintering temperature on the superconducting properties of graphene doped MgB_2 was also studied. Fig.6 shows the variation of the critical current density J_c with the applied field for un-doped MgB_2 sample sintered at 750 °C and G-doped MgB_2 samples sintered at 700, 750, 800, and 850 °C. It can be clearly seen that the sintering temperature 700 °C of the doped MgB_2 sample is not sufficient to obtain the benefit of doping of graphene. With increasing the temperature, a significant improvement in J_c of samples sintered at 750 °C can be seen due to the graphene doping, and the critical current density J_c improves both in low field and high field, reaching 2.7×10^5 A/cm^2 at 20 K and self field. With continually increasing the sintering temperature to 800 °C, the J_c value is slightly reduced in low field from 0 T to 0.6 T. However, the critical current density J_c for the sample sintered at 850 °C improves obviously in higher field, and the highest critical current density reaches 1.8×10^5 A/cm^2 at 20 K and 1 T. The doping of graphene and high sintering temperature improve the connectivity of samples, so the highest J_c in high field is observed in the G-doped MgB_2 samples sintered at 850 °C.

Fig.7 shows normalized flux pinning force $F_p/F_{p,max}$ as a function of field H/H_{irr} at 20 K for G-doped MgB_2 samples sintered at different temperatures. For MgB_2 system, the main pinning source is the surface pinning[13,14]. The pinning mechanism is not changed by doping in the initial powder, whereas the strengths of the pinning centers are increased with increasing the sintering temperatures.

3 Conclusions

1) A significant enhancement of critical current density can be observed in G-doped MgB_2 samples sintered at 750 °C for 2 h. The porosity of MgB_2 samples improves obviously.

2) The graphene doping can effectively improve the superconducting properties of MgB_2 sample.

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石墨烯掺杂和烧结温度对 MgB_2 块体微观结构和超导性能的影响

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摘　要：采用未掺杂石墨烯的粉末制备 MgB_2 块体作对比，研究了石墨烯掺杂对 MgB_2 块材微观结构和超导性能的影响，以及退火温度对石墨烯掺杂 MgB_2 块材微观结构和超导性能的影响。对烧结后的样品采用 XRD，SEM，SQUID 进行相组成，微观结构和超导性能等的分析检测。研究发现，石墨烯掺杂明显提高了 MgB_2 超导材料的临界电流密度，在 20 K 和 1 T 磁场下，最大的临界电流密度达到 1.8×10^5 A/cm^2。

关键词：MgB_2；掺杂；烧结；微观结构；临界电流密度

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