

Investigation on Phase and Microstructure Comparison of Pure and Carbon-Doped MgB_2 Superconducting Bulks during Acid Exposure

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Abstract: The phase composition and microstructure evolution of pure and carbon-doped MgB_2 bulks exposed to hydrochloric acid (pH=2) for different time were investigated by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) systematically. XRD results show the decomposition of pure and carbon-doped MgB_2 bulks exposed to acid is rapid decay with exposure time. The decomposition reaction will finish completely after 5 h exposure and the main solid products are $\text{B}(\text{OH})_3$ and $\text{MgCl}_2(6\text{H}_2\text{O})$. The SEM results demonstrate that the reaction among pure and carbon-doped MgB_2 as well as HCl occurs at grain boundaries. But the grain connection of carbon-doped MgB_2 is better than that of pure MgB_2 after acid exposure. The T_c of MgB_2 decreases after 10 min acid exposure, but T_c is almost unchanged in carbon-doped MgB_2 after the same exposure. This result indicates that substitution of C for boron in MgB_2 can improve of the resistance to the corrosion of acid.

Key words: MgB_2 superconductor; carbon-doping; acid; chemical stability

The discovery of superconductivity at 40 K in binary inter-metallic compound MgB_2 superconductor has generated great excitement among the researchers worldwide^[1]. Tremendous efforts have been made for improving the low upper critical field (H_{c2}) and critical current density (J_c) of MgB_2 ^[2,3]. It has been found that superconducting properties can be improved by doping carbon in B plane^[4]. The structure and superconducting properties of $\text{MgB}_{1-x}\text{C}_x$ have been studied for samples with various configurations (bulks, films, wires etc.) prepared by different methods^[5-7].

For the preparation and application of MgB_2 , it is possible to be exposed to acid conditions. For example, MgB_2 bulks or powders contain MgO and B_2O_3 when they are fabricated by solid state reaction method with Mg and amorphous B powder as precursor and purified by being exposed to acid solution to remove MgO , B_2O_3 impurity phase. MgB_2 superconducting Josephson junctions or electron devices can be produced by MgB_2 thin film with a chemical acid etching solution. The study on the chemical stability and behavior of pure and carbon-doped MgB_2 in acid is of great importance for preparation and engineering

applications. For this purpose, it is necessary to investigate the phase revolution, microstructure character and the degradation of the superconducting properties for MgB_2 exposed to acid.

In this paper, we report that the systematic acid-exposure time dependencies of the crystal structure, microstructure and critical temperature (T_c) of carbon-doped MgB_2 . At the same time, the possible reaction mechanism of pure and carbon-doped MgB_2 with acid was discussed.

1 Experimental

In this work, we selected composition of $\text{MgB}_{1.9}\text{C}_{0.1}$ as the study object for carbon-doped MgB_2 , which is the optimal doping level used in fabrication of films, bulks and wires^[5-7]. Pure MgB_2 and carbon-doped $\text{MgB}_{1.9}\text{C}_{0.1}$ bulk samples were prepared by solid state reaction method at ambient pressure. Magnesium (purity with 99%), amorphous boron (purity with 99%) and amorphous carbon (purity with 99%) fine powder were mixed and ground for 2 h with composition of MgB_2 and $\text{MgB}_{1.9}\text{C}_{0.1}$. Then the mixed powders were pressed into pellets (Φ 20 mm \times 2 mm) under a pressure of 20 MPa, and sealed in

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quartz tubes. Generally, a large fraction of carbon will substitute for boron site at high sintering temperature during solid state reaction at ambient pressure^[7]. Here we selected 1000 °C for fabrication of carbon-doped MgB₂. The pure MgB₂ samples were sintered in pure Ar at 750 °C for 2 h and MgB_{1.9}C_{0.1} samples were sintered at 1000 °C for 2 h respectively, and finally cooled down to room temperature in furnace. All the pellets were cut into bar-shaped samples (1 mm×2 mm×3 mm) and submerged in HCl solution at 28 °C for 10 min and 5 h. The pH value of the solution during exposure was measured at the beginning and the end of each exposure. Following every acid-exposure, the samples were immediately dried in ambient atmosphere (ambient temperature 28 °C and relative humidity about 70%) and subjected to the measurements of phase, microstructure and superconducting properties.

The crystal structures of all samples were characterized by PW1710 type powder X-ray diffraction (XRD) with the Cu K radiation. The microstructures and oxygen contents of the surfaces of the samples were investigated by JSM-6460 scanning electron microscopy (SEM). The superconducting properties measurements were carried out by a Quantum Design MPMSR2 model RF SQUID magnetometer.

2 Results and Discussion

The XRD patterns for as-prepared pure MgB₂ and MgB_{1.9}C_{0.1} samples are shown in Fig.1. It can be seen from it that the patterns for the samples sintered at 750 °C do not show significant impurities only with trace amount of MgO phase. But XRD pattern for the MgB_{1.9}C_{0.1} sintered at 1000 °C shows higher amount of MgO and MgB₄ impurity, which were induced by oxygenation of Mg and decomposition of MgB₂ phase at higher temperature respectively. The carbon-doped MgB₂ with lattice parameter $a=0.307421$ nm and $c=0.352113$ nm, which well agree with the reported in Ref[7].

The XRD patterns for MgB₂ samples exposed to acid for different time are shown in Fig.2 and Fig.3. The decrease of MgO phase can be found after 10 min exposure in Fig.2, indicating MgB₂ and MgB_{1.9}C_{0.1} were purified by short time HCl-exposure.

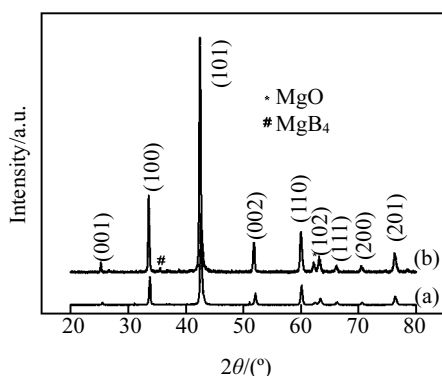


Fig.1 XRD patterns of as-prepared pure (a) and carbon-doped (b) MgB₂ samples

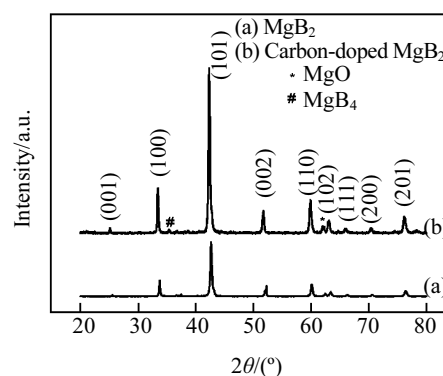


Fig.2 XRD patterns of MgB₂ samples exposed to acid for 10 min

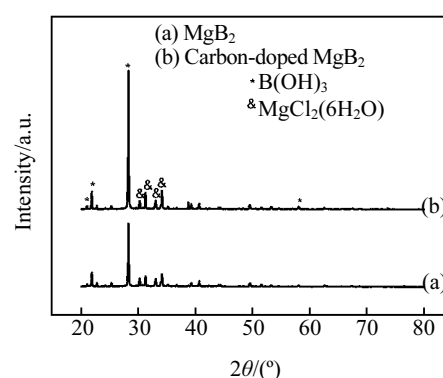
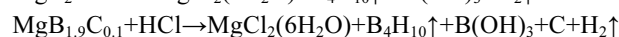
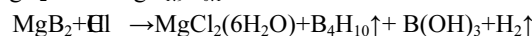


Fig.3 XRD patterns of MgB₂ samples exposed to acid for 5 h

It is clear in Fig.3 that the pure and carbon-doped MgB₂ decomposed fully into B(OH)₃ and MgCl₂(6H₂O) after 5 h exposure. It should be noted from the comparison that the solution became clouding solution in yellow color, and the pH value increased from 2 to 10 after 10 min and 5 h exposure, respectively, in our experiments. It is worth to be mentioned that a lot of bubbles were produced during the acid exposure process with a strong smell, which indicates the gas product should be tetraborane (B₄H₁₀) from analysis of Mg-B-HCl system.

Based on the analysis of the products of the pure and the carbon-doped samples reacted with HCl, the reaction among MgB₂ and MgB_{1.9}C_{0.1} as well as HCl can be written as:



It should be pointed out that the gas product of MgB₂ exposed to acid may contain poisonous B₄H₁₀ gas, which should be handled carefully for the effect of it in acid processed MgB₂ on environment.

(1) After water-exposure, it is found by visual observation that the color of the surface of as-prepared samples changes from dark gold into black, which may be induced by reaction products covering on samples.

(2) the SEM images of the as-prepared MgB₂, 10 min acid-exposed MgB₂, MgB_{1.9}C_{0.1} sintered at 1000 °C and 10 min acid-exposed MgB_{1.9}C_{0.1} are shown in Fig4a, 4b, 4c and

4d respectively.

The MgB_2 and $\text{MgB}_{1.9}\text{C}_{0.1}$ samples remained bulk-shape after 10 min exposure and decomposed into powder after 5 h exposure in acid. For the pure and carbon-doped MgB_2 samples after 10 min exposure in acid, porous structure could be observed and the grains became isolated as exposure time increased. The SEM results demonstrate that the reaction between carbon-doped MgB_2 and HCl occurred at grain boundaries, which is same as the reaction behavior between MgB_2 and water in Ref[8].

The temperature dependence of magnetization moment un-

der $5 \times 79.6 \text{ A/m}$ field with zero field cooling for the carbon-doped MgB_2 samples after acid exposure of various time intervals are shown in Fig.5a and 5b. Fig.5a presents the results of MgB_2 samples, indicating that the magnitude of magnetization moment increases after 10 min exposure and the transition width becomes broader after acid exposure. For the $\text{MgB}_{1.9}\text{C}_{0.1}$ sample exposed to acid for 10 min, the same degradation behaviors were observed in Fig.5b. But the transition broadening width is almost unchanged. This result indicates that substitution of carbon for boron in MgB_2 improves the resistance to the corrosion of acid.

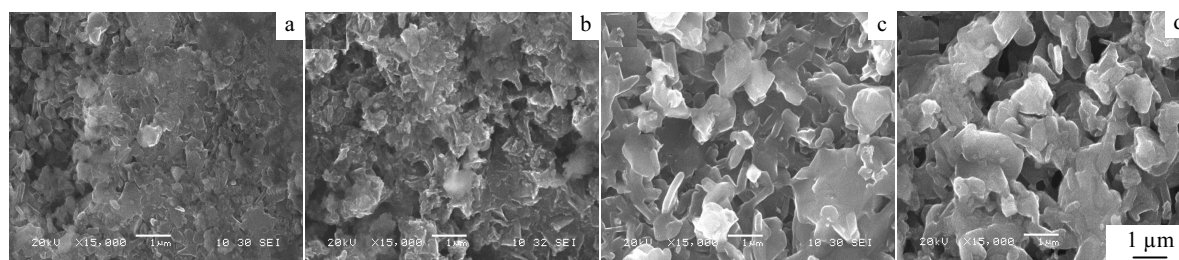


Fig.4 SEM images of the surface of as-prepared samples: (a) MgB_2 (c) carbon-doped MgB_2 ; samples after 10 min acid-exposure: (b) MgB_2 (d) carbon-doped MgB_2

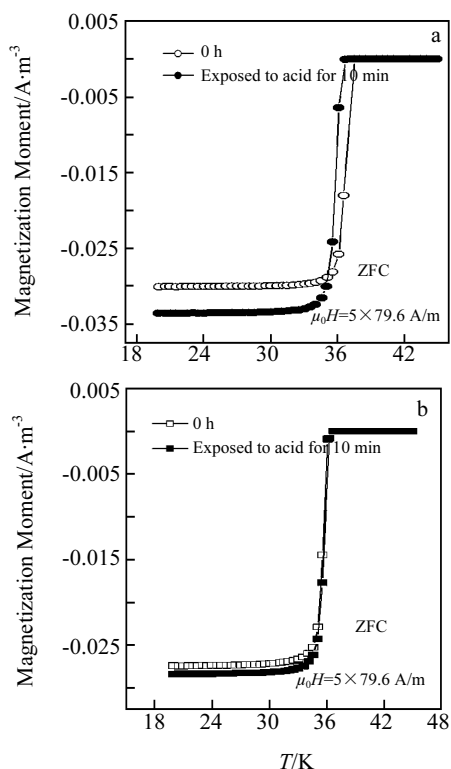


Fig.5 Temperature dependence of magnetization moment under $5 \times 79.6 \text{ A/m}$ field with zero field cooling (ZFC) for the pure and carbon-doped MgB_2 samples after 10 min acid exposure: (a) MgB_2 and (b) carbon-doped MgB_2

3 Conclusions

1) Pure and carbon-doped MgB_2 are easy to react with acid, and carbon-doping will enhance the short-time resistance to the corrosion of acid.

2) The gas product of MgB_2 exposed to acid may contain poisonous tetraborane gas.

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纯 MgB_2 和碳掺杂 MgB_2 超导块材在酸浸过程中相成分和微观结构的演变

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摘 要: 采用 X 射线衍射仪和扫描电镜系统研究了纯 MgB_2 和 碳掺杂 MgB_2 超导块材在的盐酸溶液中($\text{pH}=2$)酸浸后的相成分和微观结构演变过程。XRD 结果显示, 纯 MgB_2 和 碳掺杂 MgB_2 超导块材均迅速与盐酸反应而分解。分解反应在 5 h 后完全结束, 主要的固态产物是 $\text{B}(\text{OH})_3$ 和 $\text{MgCl}_2(6\text{H}_2\text{O})$ 。SEM 结果显示, 纯 MgB_2 和碳掺杂 MgB_2 超导块材与酸反应都是从晶界处开始, 与纯 MgB_2 块材相比, 碳掺杂 MgB_2 块材在与酸反应后仍保持致密的结构特征。而对酸浸 10 min 后纯 MgB_2 和碳掺杂 MgB_2 块材的临界超导转变温度测定结果显示, 碳掺杂 MgB_2 块材的临界超导转变温度保持不变, 说明碳掺杂可提高 MgB_2 在酸中的稳定性。

关键词: MgB_2 超导体; 碳掺杂; 酸; 化学稳定性

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