Formation of magnesium diboride-based materials with high critical currents and mechanical characteristics by high-pressure synthesis

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Abstract. The developed method of high-pressure synthesis (HPS) allows producing nanostructural highly dense material based on MgB$_2$, which possesses the highest superconducting and mechanical characteristics among the known world analogues, in the form of blocks that are suitable for application in SC electromotors and pumps. Additions of Zr can increase critical current density ($j_c$) of synthesized at 2 GPa and 750-800 °C MgB$_2$ in the same manner as additions of Ta or Ti, i.e. due to the absorption of impurity hydrogen forming the ZrH$_2$. The formation of ZrB$_2$ phase at higher synthesis temperatures (about 950 °C) in HPS MgB$_2$ does not result in the $j_c$ increase. Some increase in $j_c$ of HPS MgB$_2$, at 10 K in the fields higher than 8 T was observed when nano-SiC was added. The additions of Zr, Ta or Ti can prevent the harmful MgH$_2$ impurity phase from appearing and hydrogen from being introduced into the material structure. Besides, the presence of additions in HPS MgB$_2$ promotes the formation of a larger amount of Mg-B (most likely MgB$_2$) inclusions in the Mg-B-O material “matrix” that in turn leads to the increase of $j_c$ of the material in magnetic fields.

1. Introduction

The structure of MgB$_2$, high-pressure synthesized from Mg and B, which in accordance with XRD analysis, contains mainly a well-crystallized MgB$_2$ phase, has turned out to be more complicated as shown by SEM and microprobe examinations [1] (figure 1). In parallel with Mg and B the nanostructure of the main “matrix” phase of the samples contains oxygen (Mg-B-O) and is superconducting. Mg-B (or most likely monocrystalline MgB$_2$) inclusions of size from 10 μm down to 200 nm or even smaller are distributed throughout the “matrix”. Energy-dispersive analysis (figure 1d) has shown that the amount of Mg in the “matrix” with respect to B is much higher than is needed by the MgB$_2$, stoichiometry, while the stoichiometry of “black” Mg-B inclusions corresponds well to MgB$_2$. Usually a larger amount of Mg-B inclusions in the structure of HPS MgB$_2$ corresponds to a
higher $j_c$ and irreversibility field, $H_{irr}$, at 30-10 K [1,2]. Samples, with higher SC characteristics, contain some amount of pure Mg and lesser amount of MgH$_2$ impurity or this phase is absent at all.

A number of investigations have been performed to study a possibility to produce additional pinning centers in the MgB$_2$ structure by chemical doping. Promising results have been obtained by adding Ta, Ti, Zr and nano-SiC [1-4]

![Figure 1. Characteristics of the sample synthesized at 2 GPa, 800 °C for 1 h from Mg and B (without additions): (a) X-ray pattern; (b) critical current densities ($j_c$) at different temperatures vs. magnetic field ($\mu_0H$) variation; (c) backscattering electron images obtained by SEM; (d) energy-dispersive spectra (gray-colored spectrum is the spectrum of the “black” Mg-B inclusions, white-colored spectrum is the spectrum of the “matrix” Mg-B-O phase of the structure shown in figure 1c).](image)

2. Experimental

Metallic Mg chips and amorphous B (of 1 μm, MaTecK, 95-97% purity), were taken in the stoichiometric ratio of MgB$_2$. To study the influence of Zr, Ti, Ta, or nano-SiC additions, the Zr (of 2-5 μm, MaTecK, 94-98% purity), Ti (of 1-3 μm, MaTecK, 99% purity), Ta (of 1-3 μm) or nano-SiC (20-30 nm) powders were added to the stoichiometric mixture of Mg and B in amounts of 2 or 10 wt%. Components were mixed and milled in a high-speed activator for 1-3 min. The X-ray study of the initial Mg, Zr, Ti, Ta, SiC and B showed that the materials contained no impurity phases with hydrogen (the accuracy being 3-5%). The high pressure (2 GPa) - high temperature (750-950 °C) conditions for 1 h were created in a recessed-anvil type high-pressure apparatus (HPA) (sample was in contact with hexagonal BN). The structure was studied using SEM and XRD. The $j_c$ was estimated on 3 mm samples using Oxford Instruments 3001 vibrating sample magnetometer (VSM).
Figure 2. (a-e) X-ray patterns, dependences of $j_c$ on magnetic fields, $\mu H$, and structure obtained by SEM in backscattering electron image of the HPS-MgB$_2$ with additions of SiC, Ti and Zr. (Regimes of synthesis and amount of additions are given in the pictures). In figure 1a, the letter “A” marks the phase that contains Si, C, Mg, B; (f) – the $j_c$ vs. amount of “black” Mg-B inclusions, N, for HPS-MgB$_2$ samples without additions and with additions of Ta and Ti (N, %, was calculated as a ratio of the area that is occupied by “black” inclusions in the image of the structure obtained at 1600x magnification to the total area of the image obtained by SEM in the backscattering electron regime).
3. Results and discussion

Figures 2 a-e demonstrate the results of the study of HPS MgB₂ with additions of nano-SiC, Ti, Zr and figure 2f shows the results of the quantitative investigation of the amount of “black” inclusions and \(j_c\) of the HPS MgB₂ samples without additions and with additions of Ta and Ti. All the additions under study induced an improvement of \(j_c\) in HPS MgB₂. The most pronounced improvement of \(j_c\) is observed when Ti and Zr are added. The additions of nano-SiC increases the \(j_c\) value at 10 K in the fields higher than 8 T. Usually the improvement in critical current density in the case that Ti or Zr are added to the materials synthesized at ambient pressure is explained by the formation of the TiB₂ or ZrB₂ thin layers at grain boundaries that increase the number of pinning centers, which is ascribed to a \(j_c\) improvement caused by doping with these elements [4]. The main effect of Ti, Zr and Ta in all cases for HPS MgB₂ can be explained by the absorption of impurity hydrogen (the source of which can be materials of high-pressure cell surrounded the sample during synthesis) to form TiH₁.₉₄, ZrH₂ or Ta₂H. Additions of Zr, Ti or Ta can prevent the harmful (for \(j_c\)) MgH₂ impurity phase from appearing and hydrogen from being introduced into the material structure. The appearance of ZrB₂ (at synthesis temperature \(T_s=950\) °C, figure 2 c) does not affect the \(j_c\) of HPS MgB₂ as compared to the \(j_c\) of MgB₂ synthesized at the same temperature under the same conditions when Zr was not added (curves for the latter case are shown in [1] in Fig.1a).

A decrease in \(T_s\) results in an increase of the amount of Mg-B inclusions and an increase in the amount of Ti or Ta provokes the increase in the amount of these inclusions as well (figure 2 f). The correlation between the amount of Mg-B inclusions and increase of \(j_c\) is not so strict because several factors affect the \(j_c\). For example, a decrease in the \(T_s\) results in an increase of MgH₂ phase formation (harmful to \(j_c\)) and in an increase of the amount of free Mg and Mg-B inclusions that positively affect \(j_c\). Besides, a decrease in the \(T_s\) can lead to a decrease in the material density. But many observations allow us to conclude that \(j_c\) is most strongly influenced by the amount of Mg-B inclusions.

The highest \(j_c\) for HPS MgB₂ with nano-SiC additions was observed at \(T_s=900\) °C. SiC does not absorb hydrogen and at low \(T_s\) (750-800 °C) in HPS MgB₂, MgH₂ forms and hydrogen probably enters into the structure of material decreasing the \(j_c\). At higher \(T_s\) (900 °C) hydrogen seems to be partly liberated from the pressure cell during the synthesis and the grains “A” containing Si, C, Mg, B or Mg₂Si and SiC found by X-ray (figure 2 a) may serve as pinning centers (instead of Mg-B inclusions whose amount decreases at such \(T_s\)). We do not rule out the opinion as to MgB₂ with nano-SiC addition synthesized under ambient pressure that SiC may be incorporated into the MgB₂ lattice and thus facilitate the intragrain pinning.

The hardness of the HPS material (HPS MgB₂ with 10% Ta) measured by a Vickers indenter under a load of 14.8 N is \(H_v=10.12\pm0.2\) GPa and the fracture toughness under the same load is \(K_{ic}=7.6\pm2.0\) MPa-m⁰. The HPS MgB₂, without additions has \(H_v=16.85\pm0.74\) GPa and \(K_{ic}=4.24\pm0.14\) MPa-m⁰ under a 4.96 N-load. Using the proposed method, blocks of 32 mm in diameter and up to 20 mm in height and quadratic blocks measuring 28×28×10 mm can be high-pressure synthesized. The HPS MgB₂ material tested in SC motor at 20 K has shown operating characteristics similar to those of MT-YBCO at 20 K.

4. Conclusions

Highly dense alloyed HPS MgB₂ shows \(j_c\) at 20 K higher than: \(10^5\) A/cm² up to 3 T, \(10^4\) A/cm² up to 5 T and \(10^3\) A/cm² up to 7 T fields and has high mechanical characteristics.

References

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