Synthesis of MgB$_2$ from elements

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Abstract

Superconducting at 40 K MgB$_2$-samples were obtained by direct reaction from elements in molybdenum crucibles under argon pressure. Pressure allows to provide annealing at temperature up to 1400$^\circ$C, that resulting in rise of $T_c$ and compactness of the ceramics, suggesting that there is a homogeneity range of composition for the compound.

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1. Introduction

Recent findings of superconductivity (SC) in MgB$_2$ [1,2] gave interest to its synthesis, doping, and phase formation and equilibrium in the system. There were reports on MgB$_2$ synthesis in sealed Ta-tubes [2], and on sintering in Ta-foils [3] with slightly different results in properties of obtained ceramics. The first attempts to sputter MgB$_2$ films [4] gave only 12 K for the SC-transition, and that contradicts to the existing phase T-x diagram of Mg-B system [5].

We report here a method of MgB$_2$ synthesis in Mo-crucibles under argon pressure, and give some properties of obtained ceramics, which support an idea of homogeneity range existing for MgB$_2$ composition.

2. Experiment

For the synthesis, we used amorphous boron powder and lump metal magnesium, both with purity better than 99.95%. Boron powder was pelletized under the load about 2 ton/cm$^2$ and placed at the bottom of Mo-crucible. Lump magnesium was laid up on the B-pellets, and the crucible (Fig. 1) was closed with a threaded cap. The inner crucible diameter was of 12.5 mm in most cases, but it could be enlarged up to 50 mm with the same wall thickness of 3 mm. The crucible was placed into the medium-pressure furnace with a resistive heater. Argon pressure is necessary at the synthesis because of Mg-vapor pressure being equal to 1 bar at 1100$^\circ$C and about 8 bar at 1400$^\circ$C, so magnesium loss during synthesis is inevitable in non-sealed systems. The furnace was preliminarily pumped out down to 10$^{-5}$ bar for 2 hours and then filled with Ar up to 10-12 bar. Actual Ar pressure was ~20 bar at 1000$^\circ$ and 27 bar at 1400$^\circ$C.

On heating, Mg melts at 650$^\circ$C, and reaction with Boron starts around 900$^\circ$C, that giving rise to the local in-crucible temperature and partial magnesium vaporization. In result, Mg-melt fills the cap threads and encapsulates the charge completely to react with boron, forming MgB$_2$. We found that the load more than 2 ton/cm$^2$ at pelletizing was ineffective, so as in this case dense ceramics at the reaction front blocked the Mg-supply to the front, and the reaction stopped, leaving the core parts of the boron charge untouched. In all other cases, the synthesized ceramics of MgB$_2$ sagged on to the bottom of the crucible as a dense cylinder which could be extracted afterwards, so as magnesium melt did not react with molybdenum. The heating could be continued up to 1400$^\circ$C with results, which are described in the next section.

Powder X-ray analysis of obtained ceramic samples was made with the Siemens D-500 diffractometer in the interval 20$^\circ$ < 20 < 80$^\circ$ with steps of 0.02$, Cu-K\alpha$ radiation being applied.

SC-transition temperature was determined by registering AC-susceptibility in the temperature interval of 4.2 to 100 K. Also the standard 4-probe method was used to obtain the resistance dependence on temperature.

The density of samples was measured by hydrostatic weighing in toluene at 25$^\circ$C.

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3. Results and discussion

The syntheses gave us compact ceramic cylinders (Fig. 2) with volume of about 30% of inner crucible volume. The output could be larger, if we had used crystalline boron for the starting material. The measured density was 2.42 g/cm$^3$ for syntheses at 1000°C with subsequent rapid cooling, and only 2.23 g/cm$^3$ after MgB$_2$ heating up to 1400°C and then keeping this temperature for an hour. This drop in density was due to Mg-evaporation and formation of numerous small voids (5-30 microns) in the ceramics.

The powder X-ray diffraction pattern (Fig. 3) shows, besides MgB$_2$, the presence of small amounts of elemental magnesium and magnesium oxide MgO. The elemental Mg comes from the condensation of equilibrium Mg-gas phase on cooling, whereas MgO, as we believe, is due to Mg-gettering of oxygen adsorbed on boron powder. In the case of 1400°C-annealing, along with Mg-evaporation the formation of MgB$_4$ is registered by XRD-data on occurrence of two the most intensive reflections of the phase.

The SC-properties of the obtained MgB$_2$ samples also reflect to some extent the synthesis conditions. The ceramics sintered at 1000°C reveals the SC transition at 36 K by AC-susceptibility (Fig. 4), whereas the ceramics annealed at 1400°C shows the SC transition at 38 K by AC-susceptibility and 40 K by resistance (Fig. 4, 5). We believe this trend in transition temperature to originate from the existence of the homogeneity range in the composition of MgB$_2$. The more the composition is shifted to B-side, the more high T$_c$ the phase reveals. This conclusion is in compliance with very low T$_c$ ~ 12 K for Mg-enriched films [4], and with higher T$_c$ for 1400°C-annealed ceramics in our experiments. It is worth noting that doping MgB$_2$ with copper at 1000°C, as in [3], gives actually the same result in T$_c$ as the high-temperature annealing (Fig. 4). Evidently, the intentional large-scale Cu-doping of MgB$_2$ gives only the phase composition shift to the B-side with possible appropriate rise of T$_c$. The repetition of the experiment, made in [3], in our conditions resulted in accumulation of Cu-rich phase MgCu$_2$ just before the front of MgB$_2$ formation, because the first one is low-melting (~819°C) and insoluble in the second.

Both the known T-x diagram of the Mg-B system [5] and its computational elucidation [6] do not suggest such a homogeneity range. We also are unable to make difference between two borders of supposed range (one with excess of Mg and the other with co-existing MgB$_4$) using our XRD-data: both give the same result $a_0=3.086(4)$, $c_0=3.520(0)$. It is also doubtful that the difference will be found by micro-probe analysis, so as Mg-counts drop only ~ 35% when the probe moves from MgB$_2$ to the pure boron phase [7]. Nevertheless, the ceramics from the sides look externally very much unlike: the one synthesized at 1000°C is brownish-black and somewhat loose for touch, whereas the other one annealed at 1400°C has light-bronze color and is very tough to break. As considered in [8], that reflects very different carrier in such samples. The study needs to be continued.

4. Conclusion

It is shown that MgB$_2$ ceramics is proven to be produced on relatively large scale in Mo-crucible under moderate argon pressure. Ceramics synthesized at 1000°C seems black and loose, and has slightly lower T$_c$, than the one annealed at 1400°C which is very durable mechanically. As yet, there are no other parameters to differentiate these two ceramics.

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References

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, et al. Nature 410 (2001) 63.
[2] S. L. Bud’ko, G. Lapertot, C. Petrovic, et al. Phys. Rev. Lett. 86 (2001) 1877.
[3] Y.P. Sun, W.H. Song, J.M. Dal, et al. Chin. Phys. Lett. 18 (2001) 587.
[4] A. Brinkman, D. Mijatovic, G. Rijnders, et al. Cond-mat/0103198.
[5] A.A. Nayeb-Hashemi and J. B. Clark, in: Phase Diagrams of Binary Mg-Alloys (ASM International, Materials Park, Oh.) (1988).
[6] Zi-Kui Liu, D. J. Schlam, Qi-Li, and X.X. Xi. Cond-mat/0103335.
[7] C. E. Cunningham, C. Petrovic, G. Lepertot, et al. Cond-mat/0103390.
[8] A. M. Cambell. Science 292 (2001) 65.
Figure captions

1. Molybdenum crucible (cross section)
2. MgB$_2$ ceramics (a scale in cm)
3. X-ray diffraction pattern of MgB$_2$ powder
4. AC-susceptibility of MgB$_2$ ceramics
5. Resistance of 1400$^\circ$-annealed MgB$_2$ ceramics as function of temperature
