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SUPERCONDUCTING NANOSTRUCTURED MAGNESIUM DIBORIDE

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Like conventional superconductors, MgB_2 is a phonon-mediated superconductor with a relatively long coherence length. Its properties make the prospects for fabricating reproducible uniform Josephson junctions, the fundamental element of superconducting circuits, much more favorable for MgB_2 than for high-temperature superconductors. Here, we report bulk superconductivity in nanophase MgB_2, using a two-step technique of mechanically activated self-propagated high-temperature synthesis(MASHS). The conditions of synthesis and some properties of the product (structure, susceptibility, resistivity) were studied. It was shown that a single-phase product was obtained after 2 hours of intense mechanical treatment of reagents (*Mg* and *B* powders), and MASHS induced at 30 $A.cm^{-2}$.

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1. Introduction

A newly discovered 39-K superconductor [1] holds great promise for superconducting electronics. Like conventional superconductors, MgB_2 is a phonon-mediated superconductor [2] with a relatively long coherence length [3]. These properties make the prospect of fabricating a reproducible uniform Josephson junction, the fundamental element of superconducting circuits, much more favourable for MgB_2 than for high-temperature superconductors. The higher transition temperature and larger energy gap of MgB_2 [4,5] promise higher operation temperatures and potentially higher speeds than *Nb*-based integrated circuits. *Nb*-based superconductor integrated circuits using rapid single-flux quantum logic have demonstrated the potential to operate at clock frequencies above 700 GHz [6]. However, such circuits must operate at temperatures close to 4.2 K, which requires heavy cryocoolers with several kilowatts of input power, and this is not acceptable for most electronic applications. Circuits based on high-temperature superconductors (HTS) would solve this problem. However, 18 years after their discovery, reproducible HTS Josephson junctions with sufficiently small variations in device parameters have not been produced. MgB_2-based circuits operate at about 25K, achievable by a compact cryocooler with roughly one tenth of the mass and power consumption of a 4.2 K cooler of the same cooling capacity. The ultimate limit on device and circuit speed depends on the product of the junction critical current, I_C and the junction normal-state resistance, R_n. Because I_CR is proportional to the energy gap of the superconductor [7], the larger energy gap in MgB_2 could lead to even higher speeds (at very high values of critical current density) than in *Nb*-based superconductor integrated circuits. The MgB_2

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compound differs from other superconductors in its simple hexagonal crystal lattice and chemical composition. This makes it an ideal system for testing different physical theories on the superconductivity phenomenon.

The good mechanical properties of the compound, its low cost, light weight, and easy fabrication of wires further underline its practical importance. Synthesis methods are decisive for the complexity of the physical, chemical and technological properties of MgB_2. Its synthesis from powdered magnesium and boron at 1223 K for 2h or at 873 K and at 1173 K for 1h has been described [2]. Nakamori synthesized MgB_2 at 1173 K for 10 min (4h at 1000 K) under pressurized hydrogen atmosphere, thus preventing *Mg* particles from cracking during the process. The size of the product particles was comparable to that of the starting *Mg* powder (about 200 µm) [8].

During the last few years, some untraditional synthesis methods such as mechanochemical synthesis and varieties of Self propagated High-temperature Synthesis (SHS) offered new technological designs of the synthesis process [9-16]. Products obtained by these methods possess unusual properties such as chemical purity, ultra fine and nanosized particle dimensions, high chemical activity, and sinterability. Some of these properties are often inherited by the final dense body, usually obtained by the methods of powder metallurgy, and determine its workability.

The aim of this work was to study some properties of bulk MgB_2 obtained by Mechanically Activated SHS (MASHS). Also, we wanted to demonstrate that this new method gives the possibility for producing superconducting MgB_2 with nano-sized particle dimensions at relatively low temperature and cost of the synthesis.

2. Samples and experimental method

Powdered magnesium (99.8 wt.% purity, *Alfa Asear Johnson Mathey GmbH*) with an average size of about 50 µm and amorphous boron (98.0 wt.% in purity, *Merck*) with about 1 µm size were used as reagents in a stoichiometric ratio. The first step of the synthesis route was mechanical activation of reagents performed in a planetary ball mill (*Pulverizzete 5/4, Fritsch GmbH*). Stainless steel balls (ϕ10) were used for this purpose. The duration of activation processes was 120 min. and it led to homogenization of the reagents, appearance of fractures and oxygen-free surfaces, formation and accumulation of micro-strains and defects in the reagent crystal lattices. After this first procedure, cylindrical pellets (ϕ10) containing activated reagents were produced by cold pressing in a stainless steel die. The pressure force was varied between 0.1 and 1 GPa, thus changing the contact among the reagent particles. Below 0.5 MPa, the pellets lost their mechanical strength, which is necessary for manipulation and the successful carrying out of the SHS. After mechanical treatment and the pelletization, the pellets were placed in a stainless steel reactor for SHS. This procedure ran successfully at 60 V with a single current pulse of 30 $A.cm^{-2}$ under a protective atmosphere of pure (99,999) Ar for 1-2 seconds, accompanied by a faint noise. The morphology, sizes of the reagents and product particles were studied by scanning electron microscopy (SEM, *Jeol 357*) and transmission electron microscopy (TEM, *Jeol 200 CX*). XRD patterns were taken under CuK_α radiation, using a *Philips* counter diffractometer.

The critical temperatures of samples were determined by two different methods: i) a contact-free technique, employing the Meissner effect using a two coil system and; ii) resistivity measurements using a standard four-probe technique.

Within the range 4.2 - 25 K, the temperature of the sample was measured by a *Lake Shore* Sensor, Carbon Glass Resistor, Model *CGR-1-1000*. For temperatures above 25 K a *Lake Shore PT-103* platinum resistor was used. The error in the determination of $R = f(T)$ was not more that ± 0.2 %.

3. Results and discussion

A SEM image of the initial *Mg* particles, with an average size of about 50.0 µm, is shown in Fig. 1. The average size of the initial *B* particles is about 1.0 µm, and they are characterized by a relatively close size distribution. After intense mechanical treatment in a planetary ball mill and the successful conduct of self propagated high temperature synthesis, the final products possess ultra-fine and nanosized particle dimensions. Fig. 2 shows a TEM image of the product. As can be seen, the mean size of the MgB_2 particles is around 70 to 80 nm. Some of these particles conglomerate in groups, but these are not bigger than 200 nm.

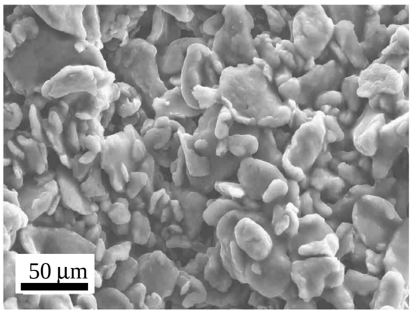

Fig.1. SEM image of the starting Mg particles.

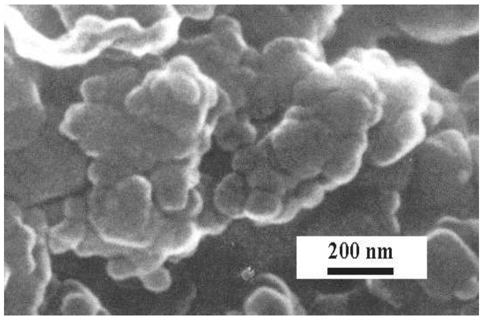

Fig.2. TEM image of the MgB_2 particles.

The XRD patterns of the product obtained by SHS at 60 V and a current density of 30 $A.cm^{-2}$ is shown in Fig. 3. It is obvious that the product mainly consist of the MgB_2 phase. All the intense peaks can be indexed assuming a hexagonal unit cell with a = 3.086 Å and c = 3.524 Å. The non-reacted reagents or contaminations comprise less than 4%, which is the sensitivity of the Philips counter diffractometer used.

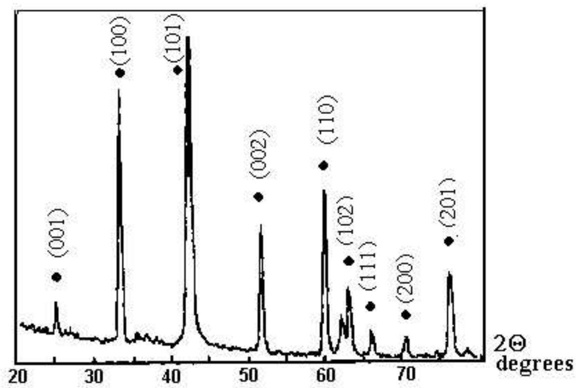

Fig.3. XRD patterns of MgB_2 obtained by MASHS with 30 A cm^{-2}.

At current densities higher than 30 $A.cm^{-2}$, the synthesis reaction proceeds violently and the product contains areas of melted aggregates. XRD analyses reveal, in addition to MgB_2, the presence of a certain amount of one of the high temperature boron compounds, namely MgB_4. The same results (with melt aggregates and MgB_4) were obtained using a classical method named field-activated combustion synthesis [10-13].

Some of the MgB_2 superconducting properties obtained by mechanical activated SHS are illustrated in Fig. 4 and Fig. 5.

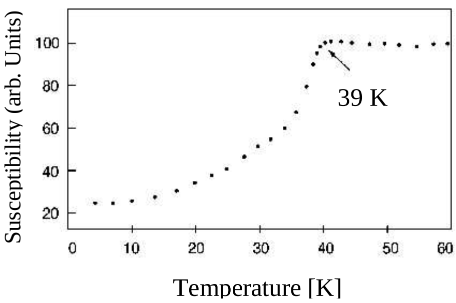

Fig. 4. Magnetic susceptibility χ of MgB_2 vs. temperature under zero field cooling.

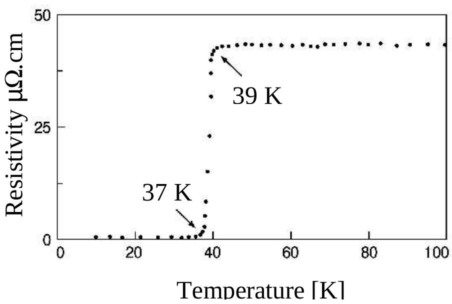

Fig. 5. Resistivity vs. temperature of MgB_2 under zero magnetic field.

Fig. 4 shows the magnetic susceptibility ($\chi=M/H$, where M is the magnetization and H is the magnetic field) of MgB_2 as a function of temperature under the condition of zero field cooling. The onset of a well-defined Meissner effect was observed at 39 K. This effect indicated that the superconductivity is bulk in nature.

The temperature dependent electrical resistance of the material from 4.2 K to 100 K is shown in Fig. 5. The room temperature resistivity has a value of 154 μΩ cm, whereas ρ(77 K) is 48 μΩ.cm and ρ(40 K) is 38.5 μΩ cm. This leads to a residual resistivity ratio (RRR) of 4. The relatively high room temperature value, along with the low RRR is probably due to some unreacted reagents or contamination. We suppose that the shoulder in $\chi(T)$ (Fig. 4) and relatively broad transition width (2 K) in R(T) (Fig. 5) have the same origin. Although comprising less than 4 %, the unreacted reagents had a considerable effect on the material properties.

4. Conclusions

The present study demonstrates that MgB_2 material with superconducting properties can be obtained by consecutive application of:

i) a mechanical activation procedure and
ii) Self-propagated High-temperature Synthesis.

It is shown that only appropriate conditions (pressure, current density) for SHS lead to a superconducting MgB_2 product with nano-sized particles (70-80 nm).

Magnetic and resistivity measurements indicate the start of the superconducting transition closed to a temperature of 39 K, as cited in the literature.

The easy and quick creation of the material, together with the low cost of production, make the method very promising.

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