A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 4
DOI: 10.1515/amm-2015-0492

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MECHANICAL SPECTROSCOPY OF MgB_2 CONTAINING SiC

SPEKTROSKOPIA MECHANICZNA MgB_2 ZAWIERAJĄCEGO SiC

The compound magnesium diboride (MgB_2) has been well-known since the 1950s; however, its superconducting properties were unknown. Intrinsic characteristics of MgB_2 make this material a promising candidate for technological applications, although the low value of the irreversibility field and the decrease in critical current density with the increase in the magnetic field considerably reduce its utility. The present work aimed to study the effect of carbon-based doping on anelastic properties of MgB_2 as measured by mechanical spectroscopy. The samples were prepared by using the powder-in-tube method. The samples were made with 5, 7.5, and 10 wt.% of silicon carbide (SiC). The results reveal complex mechanical loss spectra caused by the interaction between point defects and surface defects in the crystalline lattice of MgB_2.

Keywords: Mechanical spectroscopy, internal friction, anelasticity, MgB_2, SiC

Dwuborek związek magnezu (MgB_2) jest znany od 1950 roku; jednak jego właściwości nadprzewodzące były nieznane. Swoiste cechy MgB_2 czynią ten materiał obiecującym kandydatem do zastosowań technicznych, jednak niskie wartości nieodwracalnego pola i zmniejszenie krytycznej gęstości prądu ze wzrostem pola magnetycznego znacznie zmniejszają jego użyteczność. Celem pracy było zbadanie wpływu domieszkowania związkiem węgla na anelastyczne właściwości MgB_2 mierzone metodą spektroskopii mechanicznej. Próbki zostały przygotowane za pomocą metody powder-in-tube (PIT). Wytworzono próbki o zawartości 5, 7.5 i 10 % wag. węglika krzemu (SiC). Wyniki pokazują złożone widma strat mechanicznych powodowanych przez wzajemne oddziaływanie pomiędzy defektami punktowymi i defektami powierzchniowymi w sieci krystalicznej MgB_2.

1. Introduction

Since the discovery of superconductivity in magnesium diboride (MgB_2) in 2001 by Nagamatsu et al. [1] at Tc of 39 K, several studies have been conducted on this material. As MgB_2 is a granular compound, it is fundamentally important to understand the mechanisms of the interaction between the defects and the crystalline lattice, in addition to other possible processes involving grain boundaries.

The mechanical properties of MgB_2 vary according to how it is processed because this compound can be prepared as solid samples with considerable volume (bulk) and as thin films by using different techniques. Characteristics such as grain boundaries, connectivity among the grains, and the sample porosity are of great importance to the mechanical strength of the material. For technological applications involving MgB_2, it is important to find mechanisms responsible for an increase in the mechanical strength without losing the electrical or magnetic properties of this material.

Mechanical spectroscopy [2-7] of pure Mg showed two relaxation peaks in a 2005 study conducted by Hu et al. [8]. The first one, located at around 373 K, was associated with dislocation motion in the basal plane. The second one, observed at 503 K, was associated with slipping of grain boundaries [8]. Similar results were obtained for Mg-Ni alloys, in which the same peaks were observed as in the pure MgB_2. Moreover, it was observed that when both pure MgB_2 and Mg-Ni alloys were subjected to heating above 673 K, some impurities diffused from the grain boundaries to the intra-grain region, that is, mainly to dislocations, which reduced the height of the observed relaxation peaks. Peaks with the same behavior were observed by Hu et al. [9] in Mg-Si alloys. However, no peaks were observed in Al-Mg-Si alloy. The absence of peaks was attributed to the effect of Al, which block dislocations and grain boundaries and preclude the peaks to appear. Liao et al. [10] found a relaxation peak at around 420 K, measured at 1 Hz, in Mg-9Al-Si alloys, and thermally activated features were assigned to the relaxation process caused by grain boundaries in MgB_2.

Cordero et al. [11] measured mechanical loss spectrum of MgB_2 in the temperature range from 1 to 620 K, with a frequency of 5 kHz, and observed two broad relaxation peaks that were associated with the vibration modes of atoms and with the migration of Mg atoms in the material.

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The authors also noticed traces of another relaxation process at high temperatures, probably due to the motion of grain boundaries, but it was not possible to analyze this effect due to experimental limitations. Silva and Grandini [12] reported the internal friction in pure MgB_2, in the as-cast state and after heat treatment in vacuum, and observed a broad thermally activated relaxation effect composed of almost three relaxation processes that were attributed to the interaction between point defects and dislocations, hydrogen mobility along the dislocation line, and the migration of magnesium atoms. In the case of the annealed sample, some relaxation processes disappeared after the heat treatment.

In this study, mechanical loss measurements were carried out for pure MgB_2 samples and samples doped with silicon carbide (SiC). The results showed two thermally activated relaxation peaks, which were explained in terms of the interaction between point and linear defects in the crystalline lattice of the material.

2. Experimental

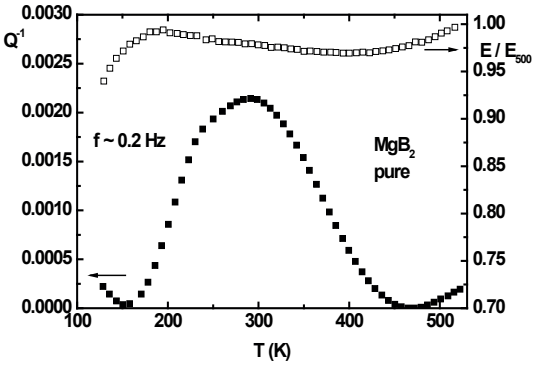
The samples were prepared by the powder-in-tube (PIT) method in an argon atmosphere glove box by using high-energy ball milling for five hours. After milling, the powders were manually injected into stainless steel tubes. For the pure sample, commercial MgB_2 powder (99.99999% Alfa Aesar) was used. For the doped samples, the same MgB_2 commercial powder was mixed with 5 wt.%, 7.5 wt.%, and 10 wt.% of SiC (99.99999% Alfa Aesar). In this paper the samples will be referred to as #0, #5, #7.5, and #10, representing the content of the SiC. After this process, the samples were swaged to consolidate the powder into the tube. The sealed tubes were heat-treated for one hour in nitrogen flux. The stainless steel tubes were removed and the samples were cut to final dimensions of 50 mm in length and 4 mm in diameter. The samples were sintered at 750ºC with a rate of 5ºC/min and annealed at this temperature for one hour. Following this, the sample was cooled at a rate of 5ºC/min.

The characterization of the samples was carried out by density measurements, mechanical spectroscopy, X-ray diffraction analysis (XRD), scanning electron microscopy, electrical resistivity, and magnetic susceptibility. The mechanical loss measurements were carried out in a dynamical mechanical analyzer by compression mode (Areva DMA 25 Metravib©01Db) operating in the multi-frequency mode at discrete selected frequencies 0.2, 2, and 20 Hz in the temperature range from 100 to 700 K with a heating rate of 1 K/min. A dynamic displacement was around 5×10^{-7} m; a static force was not applied.

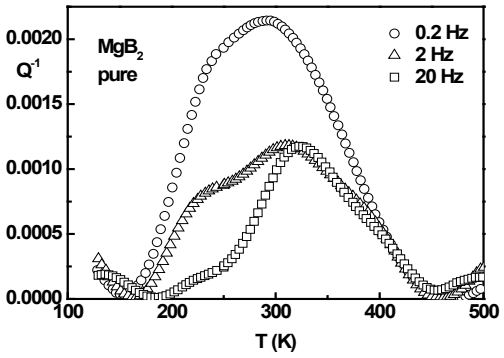
3. Results and discussion

The obtained density for pure MgB_2 was 2.065 ± 0.003 g/cm^3. As the theoretical density of MgB_2 is 2.62 g/cm^3 [7], the porosity of doped samples is in the range from 7 to 14% whereas the pure sample is around 21%. The porosity of SiC doped samples increased with an increase in the SiC content in the matrix. The sample with 5 wt.% of SiC shows the smallest value among the three samples. Thus, the 10%SiC doped sample shows the largest value. The XRD diffractograms (not included here) showed the lines that characterize MgB_2 with a honeycomb structure. Additional lines characteristic of SiC were observed for each doped sample. For both samples, traces of MgO and some traces of WC were detected, due to the ball milling process and the oxidation of Mg due to heat-treatment in air. The electrical resistivity results (not included here) showed the Tc temperature in the range from 31 to 39 K, indicating that doping was really effective in the sample. These results were supplemented by magnetic susceptibility measurements.

Figure 1 shows the internal friction and elastic modulus for pure MgB_2 measured at the driving frequency 0.2 Hz. A broad internal friction peak occurs at around 300 K. Mechanical loss measurements performed at three different frequencies are shown in Fig. 1(b). Figure 1b indicates that the broad peak is a thermally activated relaxation peak. The peak height decreases with an increase in the excitation frequency. The activation energy and pre-exponential factor of the process, obtained from the Arrhenius equation, are 1.18 eV and 6.7×10^{-16} s. These results are similar to those reported by Silva and Grandini [6]. In this case, however, this peak is associated with the motion of grain boundaries in the polycrystalline sample of MgB_2. The second internal friction peak is observed at around 240 K. This peak stems from a phase change since its height dramatically decreases with increasing frequency. The complex nature of the broad peak requires further experimental and theoretical approach for the better understanding of the 240 K peak.



(a)



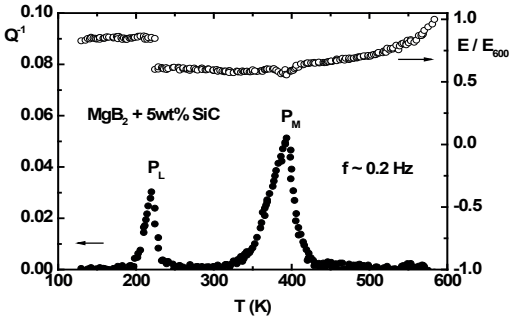
(b)

Fig. 1. Mechanical loss spectra in pure MgB_2 measured at 0.2 Hz (a), and three selected frequencies: 0.2, 2, and 20 Hz (b)

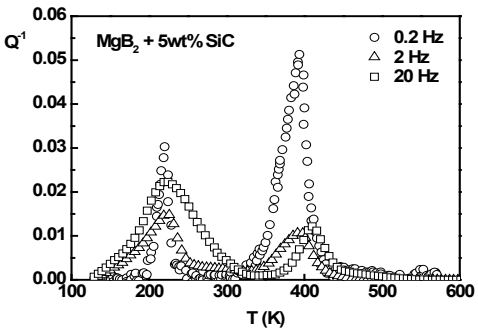
The internal friction and elastic modulus in the MgB_2 samples doped with 5wt.% of SiC measured at 0.2 Hz are shown in Fig. 2(a), where two internal friction peaks are well separated. The first peak, the so-called P_L peak, occurs at around 220 K. The second peak, P_M, occurs at around 400 K. It can also be seen as a "step" in the elastic modulus curve, characteristic of peaks associated with a relaxation process. Figure 2(b) indicates that the internal friction peaks measured at three different frequencies are thermally activated. A qualitative analysis of Fig. 2 indicates that peaks' heights are substantially higher than those observed in pure MgB_2 samples (Fig. 1), indicating that the peaks may be associated with presence of SiC. In fact, the heights of the peaks are related to the amount of the relaxing entities, in this case, SiC. The same behavior was observed in the MgB_2 samples doped with 7.5wt.% and 10wt.% of SiC. The activation energy and the pre-exponential factor of internal friction peaks are collected in Table 1 for all investigated samples. The apparent relaxation parameters listed in Table 1 are affected by side effects related to asymmetrical shape of internal friction peaks and/or broadening effect and background subtraction. It should be noted that the estimation of the effective relaxation parameters needs further scrutiny.

TABLE 1
Apparent relaxation parameters of internal friction peaks observed in MgB_2 samples doped with SiC

Sample	Peak	H (eV)	τ_0 (s)
MgB_2SiC#5	P_L	5.34	1.16×10^{-24}
	P_M	3.25	1.51×10^{-24}
MgB_2SiC#7.5	P_L	2.25	1.23×10^{-17}
	P_M	1.19	1.62×10^{-17}
MgB_2SiC#10	P_L	5.19	1.62×10^{-24}
	P_M	3.25	1.86×10^{-24}



(a)



(b)

Fig. 2. Mechanical loss spectra of MgB_2 doped with 5 wt.% of SiC measured at 0.2 Hz (a), and measured at three different frequencies (b)

The data in the literature with respect to the study of relaxation processes in MgB_2 by using mechanical spectroscopy are very scarce. In relation to SiC, Skrinkth and Gupta [14,15] demonstrated that mechanical damping (internal friction) in pure MgB_2 is higher than that in the presence of SiC, and damping increases with increasing the content of SiC particles in the magnesium matrix, a fact supplemented by the experimental results obtained in this study. To the best of our knowledge, there are no data in the literature on the diffusion of carbon or carbon compounds in Mg or MgB_2. In bcc metals, such as Fe, Nb and Ta the activation energy for diffusion of interstitial carbon is in the range from 0.87 to 1.67 eV, with the average pre-exponential factor in the range from 4.8 to 5.3×10^{-14} s [16-19]. The obtained values, except for the sample with 7.5wt.% of SiC, allow us to conclude that the incorporation of SiC can be of the interstitial form in the MgB_2 matrix [20]. The result in the case of the sample doped with 7.5wt.% SiC might be due to the sample reaching the solubility limit and forming segregates, broadening the peak and decreasing the activation energy.

4. Conclusions

Samples of pure MgB_2 with the addition of SiC were prepared by using the powder-in-tube method and were characterized by mechanical spectroscopy, density measurements, X-ray diffraction, scanning electron microscopy, electric resistivity, and magnetization. Mechanical loss measurements exhibit complex relaxation spectra composed of several constituent mechanical loss processes. For pure MgB_2, these processes were attributed mainly to the motion of grain boundaries in the polycrystalline MgB_2 sample. In the MgB_2 samples doped with SiC, the internal friction peaks were related to the presence of SiC in the MgB_2 crystalline lattice.

Acknowledgements

The authors thank the Brazilian agencies CNPq (grant No. 554.000/2008-3) and FAPESP (grant No. 2009/08811-2) for their financial support.

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Received: 20 April 2015.