Journal of Ceramic Processing Research. Vol. 10, No. 6, pp. 840~843 (2009)

JOURNAL OF
Ceramic
Processing Research

An upgrade recycling from Mg alloy chips toward superconducting MgB_2 via powder processing

Makoto Nanko[a,*], Daisuke Maruoka[a], Hitoshi Ozawa[a], Shigeharu Kamado[a], Hiroya Abe[b], Akira Kondo[b] and Makio Naito[b]
[a]*Nagaoka University of Technology, Nagaoka, Niigata 940-2188, JAPAN*
[b]*Joining & Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, JAPAN*

A recycling process of Mg alloy chips to obtain superconducting MgB_2 is proposed. In the present process, mechanical milling was used to mix and grind AZ31 chips and boron powder. Fine AZ31/boron powder mixture can be fabricated via a mechanical milling process. Mechanical milling can reduce the process time to synthesize MgB_2 powder. An AZ31/boron mixture via mechanical milling can be reacted completely to MgB_2 by heating at 700 °C for 3 h. Sintered MgB_2 bodies produced by a pulsed electric current sintering technique showed approximately 30 K as the superconducting critical temperature.

Key words: Magnesium alloys, AZ31, MgB_2, Recycle, Powder Processing.

Introduction

Magnesium alloys are new structural light metallic materials with high specific strengths. However the recycling processes of Mg alloy chips made by machining processes have not been established as yet. Because Mg alloy chips are easily oxidized, it is difficult to use them in castings without oxidation. One of the other routes for the recycling of Mg alloy chips is to produce valuable Mg compounds from them.

On the other hand, MgB_2 is a superconducting compound with 39 K as the critical temperature, which is the highest value for the metallic compounds [1]. Generally MgB_2 bulk bodies or wires are fabricated via sintering of MgB_2 powder or its raw materials [2-6].

In this report, a production process of MgB_2 from Mg alloy chips is proposed as a new upgraded recycling technique for Mg alloy chips. The proposed process was developed by using a mechanical milling process reported by Abe and his coworkers [7]. They studied a powder processing route for the low-temperature formation of MgB_2 powder from Mg and B powder using a mechanical milling technique [7]. They applied an attrition type device without a milling media such as ceramic or steel balls [8]. With this milling system it is easy to handle the powder materials and to collect the powder after processing. Low contamination is also one of the advantages of this milling process.

Experimental Procedure

The Mg alloy, AZ31 was selected in this study. The nominal chemical composition of AZ31 is 3 mass% (2.7 mol%) Al and 1 mass% (0.4 mol%) Zn, 0.15 mass% (0.01 mol%) Mn and the balance Mg. AZ31 chips produced by a machining process were selected as a starting material. Because AZ31 chips were contaminated by machine oil, they were washed ultrasonically in alcohol for 5 min and dried at 80 °C for 4 h. Those AZ31 chips were mixed with commercial amorphous boron powder. Fig. 1 shows

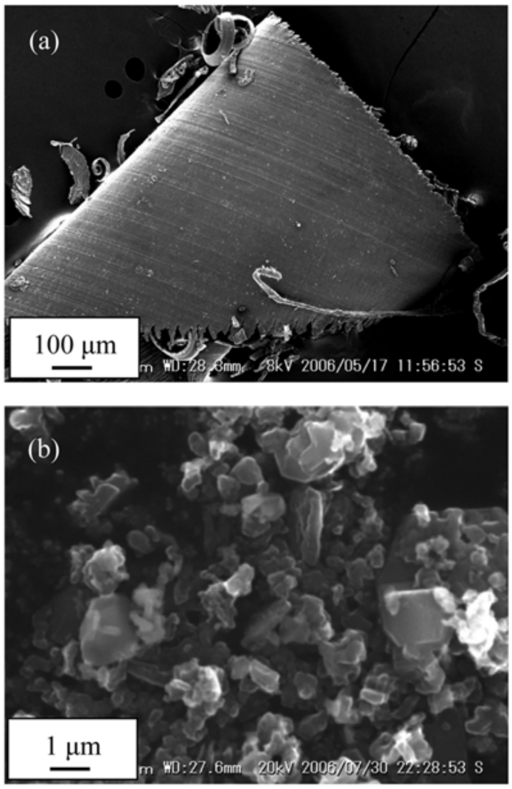

Fig. 1. SEM images of (a) AZ31 chips and (b) boron powder.

*Corresponding author:
Tel : +81 258 479709
Fax: +81 258 479770
E-mail: nanko@mech.nagaokaut.ac.jp

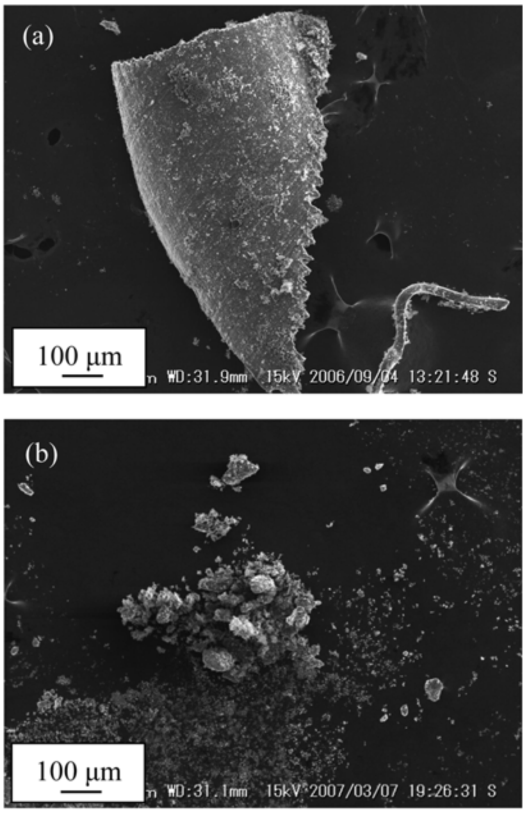

Fig. 2. SEM images of AZ31/boron mixture. (a) a hand-shaken mixture and (b) a mechanically- milled one.

scanning electron microscope (SEM) images of (a) AZ31 chips and (b) boron powder. Two different routes were investigated. One was a mixture of the AZ31 chips and the boron powder by shaking in a plastic bottle for 5 min (hand-shaking). Another one was to use a mechanical milling process with the Mechanofusion system [8]. A mixture of AZ31 chips and boron powder was mechanically milled at 4,000 min^{-1} for 10 min and then 2,000 min^{-1} for 60 min in vacuum.

Powder mixtures were heated at 700 °C for several hours in Ar at 0.02 MPa. After pounding with a mortar, the reacted powder was consolidated using the pulsed electric current sintering (PECS) technique at a die temperature of 1,000 °C for 5 min under a pressure of 75 MPa in a vacuum.

The phase identification of powder products and sintered bodies was conducted by X-ray diffraction (XRD) with CuKα. The bulk density and porosity of sintered bodies were measured by the fluid replacement method with toluene. The microstructure of sintered bodies was observed using SEM. DC 4-probe resistance measurements were conducted in order to evaluate the superconductivity of the sintered bodies.

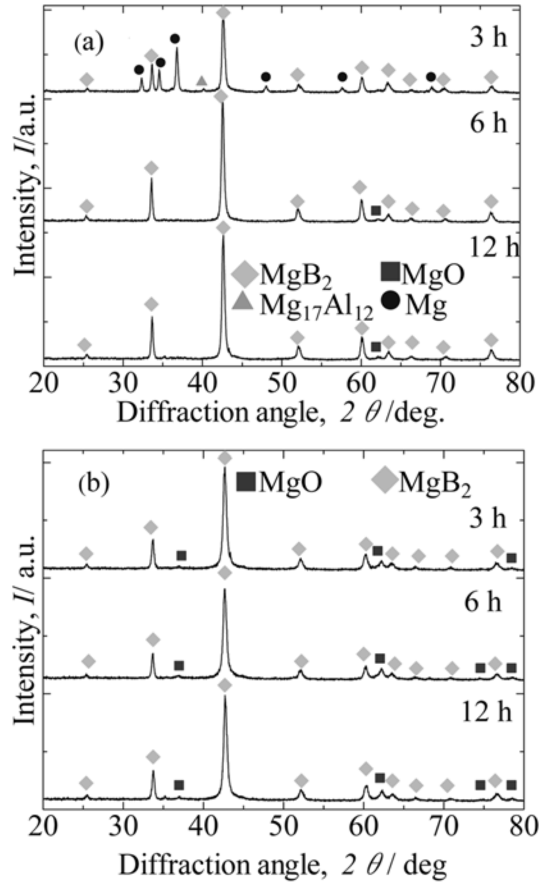

Fig. 3. XRD patters of the AZ31 chips and boron powder mixture processed at 700 °C in Ar at 0.02 MPa. (a) a hand-shaken mixture and (b) a mechanically- milled one.

Results and Discussion

Figure. 2 shows SEM images of AZ31/boron powder mixtures with different mixing processes. Using a

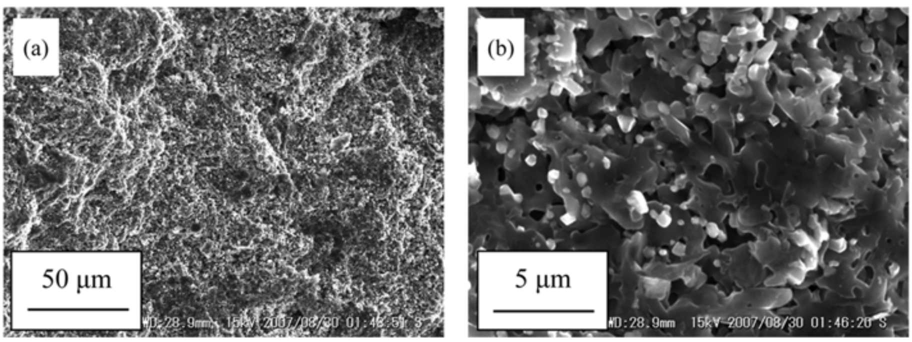

Fig. 4. SEM images of a fractured surface of sintered MgB_2 via mechanical milling. (a) low magnification and (b) high magnification.

mechanical milling process, large Mg chips were fractured to less than 50 μm. Fig. 3 shows XRD results of powder mixtures after reaction at 700 °C using different mixing processes. MgB_2 was formed at 700 °C after 3 h by the mechanical milling technique, compared with 6 h by hand-shaking. A small amount of MgO was identified. Mechanical milling can reduce the heat treatment time to obtain MgB_2 from AZ31 chips.

Figure 4 shows the SEM images of the fracture surface of a sintered body. The bulk density of the sintered bodies was 2.7 Mgm^{-3}, which is 80% of the theoretical value of MgB_2. The sintered MgB_2 consisted of fine grains and a small amount of fine pores. Large voids, which were likely formed as openings among AZ31 chips, were also observed. Fig. 5 shows XRD patters of sintered MgB_2. A small amount of MgB_4 was identified by XRD. MgB_4 was formed for evaporation and/or oxidation of Mg during the PECS process. With an increase in the sintering temperature, the bulk density was increased. The amount of MgB_4 was, however, also increased.

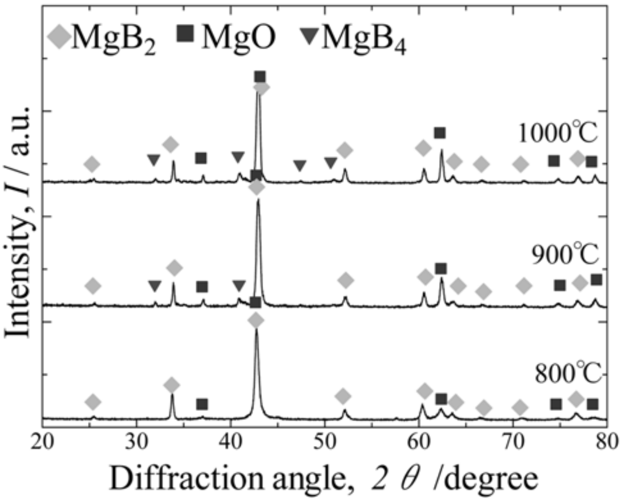

Fig. 5. XRD patterns of AZ31/boron powder mixtures sintered by the PECS process at different sintering temperatures.

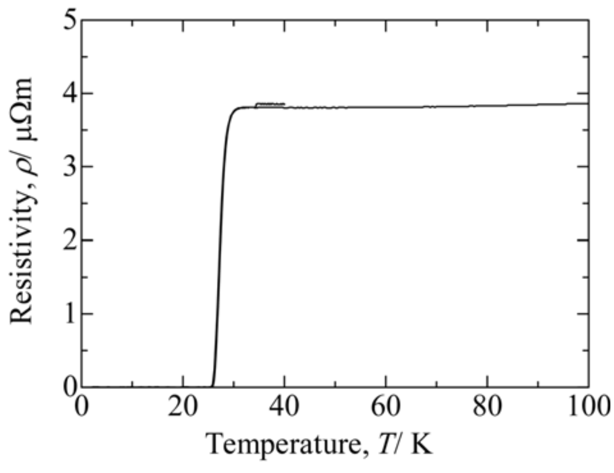

Fig. 6. Relationship between resistivity and temperature on a sintered MgB_2 body prepared from AZ31 chips and boron powder via mechanical milling.

Figure 6 shows a typical resistance-temperature plot of a sintered MgB_2 body obtained in the present study. Resistance of the sample falls around 30 K and was zero at 27 K. The value of the critical temperature of this sample was lower than the critical temperature of MgB_2 prepared from high purity materials [1] and from AZ31 with boron powder [3]. According to Matsuzaki et al.[3], use of AZ31 as an Mg source decreased the critical temperature to 34 K. Muranaka and Akimitsu investigated the doping effects of metallic elements into MgB_2 [9]. The influence of the level of Al, Zn and Mn in AZ31 on the critical temperature was not significant. Our result may be due to the contamination by oxygen and/or carbon during the machining process and/or the milling process. The value of T_c can be improved by applying better washing processes to AZ31 chips and optimizing the experimental conditions.

Summary

An upgraded recycling process for Mg alloy chips to obtain superconducting MgB_2 was proposed via mechanical milling. A fine AZ31/boron powder mixture was fabricated from AZ31 chips and commercial boron powder via a mechanical milling process. The AZ31/boron powder mixture was reacted completely to MgB_2 by heating at 700 °C for 3 h, compared with 6 h for a hand-shaken AZ31/boron powder mixture. Sintered MgB_2 bodies produced by PECS showed approximately 30 K as the superconducting critical temperature.

Acknowledgements

The present mechanical milling process was conducted at JWRI Osaka University with the Joint Research Program. The authors thank Dr. T. Aida in Toyama University for evaluating the temperature dependence of resistance of sintered bodies. The authors also wish to express their gratitude to the Japanese government for partially supporting the present work through the 21st Century Center of Excellence (COE) Program and Cooperation of Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, Nature 410 (2001) 63-64.
2. S.Y. Lee, S.I. Yoo, Y.W. Kim, N.M. Hwang and D.Y. Kim, J. Am. Ceram. Soc. 86[10] (2003) 1800-1802.
3. K. Matsuzaki, K. Hanada, K. Htsukano, T. Shimizu, S. Suzuki and S. Huchisawa, J. Jpn. Powder Powder Metall. 49[10] (2002) 851-855.
4. K. Matsuzaki, K. Hanada, K. Htsukano, T. Shimizu, S. Suzuki and S. Huchisawa, J. Jpn. Powder Powder Metall. 50[4] (2003) 310-313.

5. K. Matsuzaki, K. Hanada, K. Htsukano, T. Shimizu, S. Suzuki and S. Huchisawa, J. Jpn. Powder Powder Metall. 50[9] (2003) 717-720.
6. A. Yamamoto, J. Shimoyama, S. Ueda, Y. Karsura, I. Iwayama, S. Horii and K. Kishio, Appl. Phys. Lett. 86 (2005) 212502.
7. H. Abe, M. Naito, K. Nogi, M. Matsuda, M. Miyake, S. Ohara, A. Kondo and T. Fukui, Phys. C 391[2] (2003) 211-216.
8. M. Naito, A. Kondo and T. Tokoyama, Iron Steel Inst. Jpn. Int. 33[9] (1993) 915-924.
9. T. Muranaka and J. Akimitsu, Materia Japan 44[9] (2005) 722-728.