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Synthesis and structural characterization of dense polycrystalline Mg_9Sn_5, a metastable Mg–Sn phase

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ABSTRACT

We present a method for synthesizing bulk dense polycrystalline Mg_9Sn_5, a phase that is related to the familiar Mg_2Sn phase but is metastable at ambient pressure and temperature. Our procedure requires significantly lower temperatures and pressures, which are in the 100 MPa range compared to the previously reported methods that required pressures in the GPa range. We used a combination of high energy ball milling and current activated pressure assisted densification (CAPAD) to synthesize and retain the high pressure phase in a bulk (low porosity) form. We show the effect of CAPAD processing temperature and pressure on the density and phase composition of the material. We also present the first neutron diffraction study to confirm phase identity and refine the structure of Mg_9Sn_5.

1. Introduction

The controllable production of metastable materials is one of the most exciting challenges in processing science today [1]. The allure is that metastable phases can have radically different properties compared with their more stable brethren and thus potentially be used in new applications. Mg_2Sn is the only intermetallic phase found on the familiar Mg–Sn binary phase diagram, making it the only thermodynamically stable phase at ambient conditions [2]. Here we present the synthesis of Mg_9Sn_5—a related phase that is not found on the Mg–Sn temperature–composition phase diagram and is therefore metastable at room temperature and pressure.

We used a combination of high energy planetary ball milling and Current Activated Pressure Assisted Densification (CAPAD) [3] to produce a bulk material that has previously only been synthesized in dense form at high pressures (in the Giga Pascal range). Moreover, to the best of our knowledge, this is the first time this metastable Mg–Sn phase has been made in a polycrystalline dense (low porosity) form. The stable phase, Mg_2Sn is a well-studied semiconducting material with applications in thermoelectric energy generation [4]. By contrast, the transport properties of Mg_9Sn_5 are relatively unknown, since reports of the preparation of bulk, dense Mg_9Sn_5 are limited. Therefore our processing procedure presents an opportunity to further the understanding of Mg_9Sn_5 transport properties, which is currently an active area of research in our laboratories. While it is known that Mg_9Sn_5 is a semiconductor, a study of its transport properties, both thermal and electrical, will determine its utility as a thermoelectric material.

The crystal structure of this resulting phase has been refined via Rietveld analysis of powder neutron diffraction data. We expect the processing procedures presented here to be translatable to other alloy systems, opening the door for the production of other metastable alloys that are difficult to produce by other methods.

The semiconducting material, Mg_2Sn crystallizes in the cubic antifluorite structure under ambient pressures and temperatures. A metastable phase forms when subjected to high temperatures and pressures and persists upon returning to ambient conditions. This “dense” phase of Mg_2Sn was first synthesized at pressures and temperatures ranging from 2.5 to 5.5 GPa and 600–1200 °C, respectively, by Cannon and Conlin in 1964 and is described as having a hexagonal crystal structure [5]. Seifert also synthesized the high pressure metastable phase by applying 6–6.5 GPa and 600–1000 °C in 1967. Its crystal structure was described as being orthorhombic with a Ni_2Si-type structure [6]. In 1972 & 1995 [7], Dyuzheva grew single crystals from a melt and investigated the effect of high pressures and temperatures of 4–8 GPa and 50–1100 °C on phase relations of the Mg_2Sn system. This study also

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showed in depth X-ray diffraction investigations of the polymorphism of the system [8]. A crystal structure refinement was carried out in 1996 by Range et al. using single crystal samples synthesized at 5 GPa and 1400 °C. The resulting structural refinements concluded that the composition of this high pressure phase is in fact Mg_9Sn_5 which contains an excess of Sn compared to the thermodynamically stable Mg_2Sn [9].

The formation of the metastable phase has also been observed using ball milling methods. Schilz et al. used a planetary ball milling setup to produce the metastable and stable phases from a mixture of Mg, Si, and Sn and milling times up to 130 h [10]. In 2002, Urretavizcaya et al. synthesized the metastable phase using mechanical alloying for 150 h in different gases (H_2 and Ar) at gas pressures of 0.1 MPa and 0.5 MPa, respectively [11]. It is worth emphasizing that both of these ball milling treatments [8,9] produced a polycrystalline powder and not a bulk dense material.

2. Experimental procedure

2.1. Powder synthesis and consolidation

Planetary ball milling (PBM) is a useful mechanical alloying technique used to react multiple powders at room temperature conditions. The high frequency and repetition of ball-powder collisions fracture and cold weld the starting materials over the course of the entire process. The method allows for grain size reduction and, in extreme cases, phase amorphization [12]. Elemental magnesium and tin powders (Alfa Aesar, 99 + % metal purity) with stoichiometric ratio of 19:10 and 9:5 were planetary ball milled (Fritsch Pulverisette 7) at 450 RPM using stainless steel jars and balls for a total of 48 h at room temperature. Due to its ductility, 200–300 mg of magnesium powder was added incrementally every 2 h until reaching the targeted stoichiometric proportions to avoid agglomeration of the magnesium on the walls of the jars [13]. The final ball to powder weight ratio was 10:1. All powders and milling media were handled under an argon atmosphere.

CAPAD (also referred to as Spark Plasma Sintering (SPS)) is a well-known method for powder consolidation. Graphite die and punch sets are loaded with the powder and a heating current is applied to the system under a mechanical load. This technique has been highly successful in producing bulk materials with unique microstructures. A custom built CAPAD device was used to consolidate the powder into bulk samples [14]. Graphite plunger and die sets similar to the high pressure setup described by Anselmi-Tamburini et al. [15] were used to produce 9.52 mm diameter disks. All samples were processed under vacuum with an applied mechanical pressure of 0 or 112 MPa and temperatures up to 600 °C with a heating rate of 200 °C/min. One plunger was removed in the 0 MPa case in order to ensure that no load (and therefore no pressure) was transferred to the powder. The maximum heating currents were varied between 400 and 1200 A. All samples were processed within 20 min. XRD phase characterization was performed with a PANalytical Empyrean diffractometer using a Cu Kα X-ray source ($\lambda_{K\alpha 1} = 1.54056$ Å and $\lambda_{K\alpha 2} = 1.54440$ Å). Densities of the CAPAD processed samples were measured using the Archimedes method. Samples densified from the 9:5 ratio ball milled powder were analyzed using neutron diffraction.

2.2. Neutron diffraction

Time-of-flight neutron diffraction experiments were performed at the NPDF (Neutron Powder Diffractometer) beamline of the Manuel Lujan, Jr. Neutron Scattering Center, Los Alamos National Laboratory [16]. The CAPAD synthesized/densified bulk Mg_9Sn_5 sample (processed as described in Section 2.1 from a 9:5 Mg:Sn PBM powder) was crushed into a fine powder in an argon-filled glove-box. The resulting powder was then sealed in a low background vanadium can measuring 0.63 cm in diameter. The sample was then mounted on the neutron diffractometer for room temperature data collection. High-resolution data were collected for about 14.5 h simultaneously using four groups of detector banks with nominal diffraction angles of ± 46°, ±90°, ±119° and ±148°. The mass of powder used was 2.5 g.

The obtained neutron data were analyzed using the Rietveld method with the General Structure Analysis System (GSAS) program of Larson and Von Dreele [17]. The starting structural parameters were taken from the single-crystal X-ray diffraction study of Range et al. (space group: $R3$ (No. 146), $a = 13.222$ Å, $c = 13.150$ Å) [9]. Since the sample contains a small portion of MgO, we included periclase as a secondary phase in the analysis (space group: $Fm\text{-}3m$ (225), $a = 4.217$ Å). All four datasets from the detectors at $2\theta = \pm 46°, \pm 90°, \pm 119°$ and $\pm 148°$ were simultaneously analyzed. The refinements proceeded as follows: after the scale factor and four background terms (Shifted Chebyshev function) for each histogram had converged, lattice parameters and phase fractions were added and optimized. Eight or fourteen additional background terms were then added for each histogram, and the peak profiles were fitted to a TOF profile function [18]. On convergence of the preceding parameters), atomic coordinates and atomic displacement parameters (constrained to be equivalent on all six Mg sites and, separately, all Sn sites) were refined, yielding an R_{wp} value of 2.13%.

2.3. SEM/EDS

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy images and measurements were made using a JEOL JSM 6360LV microscope at an accelerating voltage of 15–20 keV coupled to an Oxford Instruments EDS detector for elemental mapping experiments. A CAPAD processed Mg_9Sn_5 sample was mechanically cleaved and was immediately introduced into the vacuum chamber. The sample was mounted on copper tape with no need for further sputter treatment.

3. Results and discussion

3.1. Synthesis and densification

Fig. 1 presents XRD phase analysis of the two starting elemental powders (Mg and Sn) and the planetary ball milled powders with 19:10 and 9:5 Mg:Sn stoichiometric ratios. The two ball milled powders both show the presence of two phases, Mg_2Sn and Mg_9Sn_5, after 48 h of milling. No crystalline Mg and Sn peaks can be detected. The integral peak intensities of the highest intensity Mg_2Sn peaks (111) are one third of the highest Mg_9Sn_5 peaks (300) in each of the two powders. The metastable phase is formed after the planetary ball milling due to the repeated impact, fracturing, and cold welding of the powder. These powders were dull blue/grey color in appearance. Similar results were reported by Urretavizcaya et al. [11] where they produced Mg_9Sn_5 after 150 h using a magnetic field assisted high energy ball milling approach.

Fig. 2 is the XRD analysis of two samples processed using CAPAD from the 9:5 ratio batch of powder. The samples were processed using 0 and 112 MPa of applied pressure at 600 °C. The sample processed at 112 MPa shows only the presence of the Mg_9Sn_5 phase while the sample processed at 0 MPa still shows both Mg_2Sn and Mg_9Sn_5, indicating an effect of pressure on the formation of the metastable phase. It is not surprising that the pressure plays a significant role since as mentioned earlier, the phase is usually synthesized under high pressures. It is worth emphasizing however, that 112 MPa is significantly lower pressure than previously reported. It is also noteworthy that the peaks in the ball milled powder are considerably broader than those of the CAPAD processed samples. This is likely due to residual stress and/or fine crystal size of the PBM powder.

In order to find the optimum processing conditions for producing bulk dense Mg_9Sn_5, seven samples from the 19:10 ratio powder

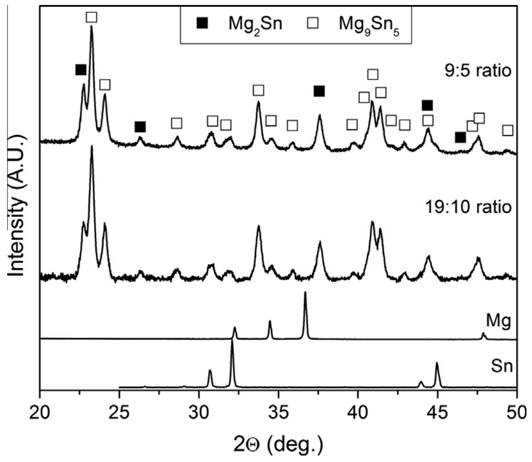

Fig. 1. XRD powder patterns of the starting elemental powders and planetary ball milled powders with Mg:Sn stoichiometric ratios of 9:5 and 19:10. Dark squares represent the Mg_2Sn phase. Open squares represent the Mg_9Sn_5 phase.