Technological Problems in Fabrication of Mg-Based Thermoelectric Materials by Conventional Casting Methods

A. Gryc*, M. Malczewska, T. Rzychoń and A. Kiełbus

Institute of Materials Engineering, Silesian University of Technology, Politechnika Śląska,
Z. Krasińskiego 8, 40-019 Katowice, Poland

In the paper the potential of conventional casting technology in fabrication of modern magnesium-based thermoelectric materials was evaluated. Although these materials are considered as potential environmental-friendly alternative for commercially used thermoelectric materials based on heavy metals, fabrication of bulk Mg-based thermoelectric materials with simple and cost-effective technologies is still challenging. In the present work it was found that it is possible to obtain Mg-based thermoelectric materials with conventional gravity casting technology. The following technological problems were identified: high reactivity and vapor pressure of magnesium, large difference in melting point and density of the components, high fragility, high synthesis temperature and significant solidification volume shrinkage. The application of solutions and adjustments to the conventional gravity casting method, comprising the usage of non-reactive crucible and mold materials, inert atmosphere of argon, intensive mechanical stirring, and decrease of cooling rate of solidifying ingots led to fabrication of relatively pure (98%) bulk Mg_2Sn thermoelectric compound.

1. Introduction

Presently used technologies of energy production are based mainly on fossil fuels and are known to have a negative impact on the environment and living conditions of humans. Simultaneously the global energy demand is increasing constantly, while the existing technologies for converting the alternative energy sources into desired energy forms are far from being competitive with conventional technologies [1]. The fossil fuels depletion and global efforts to overcome this problem by developing and implementing renewable energy sources are crucial factors determining the significant growth in the field of thermoelectric materials and their applications. Their ability of converting the waste heat directly to electrical energy without any intermediate step is considered as one of the promising strategies in this field of interest. On the other hand, the low efficiency of commercial thermoelectric materials limits their usage to niche specialized devices, such as laboratory chillers and thermoelectric generators for space probes and military equipment [2]. Nevertheless, the concept devices, such as thermoelectric generator for conversion of the waste heat of car exhaust to electrical energy, justifies the importance and necessity of further exploration of new high-efficient thermoelectric materials.

The efficiency of thermoelectric material is described by dimensionless thermoelectric figure of merit ZT ($ZT = S^2\sigma\kappa^{-1}T$, where S represents the Seebeck coefficient, σ — electrical conductivity, κ — thermal conductivity and T — the absolute temperature). The main commercial thermoelectric generator material is bismuth telluride, which has a high enough dimensionless thermoelectric figure of merit (ZT $\approx$ 1) at room temperature to be practical for energy generation applications. In recent years, the price of tellurium, a key component in the best-performing thermoelectric materials, has increased significantly, hence their application in thermoelectric generators on commercial scale is questionable [3]. The other materials used at higher operating temperatures are PbTe and GeTe. However, all of the described materials are expensive and contain toxic elements, such as lead or tellurium. Therefore, it is necessary to find alternative materials with comparable or higher figure of merit, which do not contain toxic elements and can be obtained by cost-effective technologies.

One of the most promising candidates, fulfilling the mentioned requirements, are Mg_2X (X = Si, Sn, Ge) intermetallic phases. These materials do not contain toxic elements, are environmental-friendly, possess a low density ($\rho \approx$ 2.0–3.6 g/cm^3) and incorporate highly available elements [4]. These compounds and their solid solutions have received extensive attention as potential high-performance thermoelectric materials since the 1950s, and numerous investigations have been carried out regarding the electrical, optical, and thermal properties, particularly in case of Mg_2X phases [5–10]. However, later the interest to these compounds has been almost vanished until the last decade. A new wave of research activity on Mg-based thermoelectric materials was initiated by information about high figure of merit achieved in Mg_2Si–Mg_2Sn solid solutions and growing interest to

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*corresponding author

environmental-friendly materials for thermoelectric energy conversion [11]. Zaitsev et al. [12] reported the high ZT of up to 1.3 in some of these materials, obtained by several research groups [13–17]. The increase of ZT by doping with other elements and formation of solid solutions of different Mg_2X (X = Si, Sn, Ge) phases has been reported by Du et al. [18], Zwolenski et al. [19] and Ihou-Mouko et al. [20]. It is believed that this success is based on combination of two approaches to maximize the thermoelectric performance: the band structure engineering and the alloying.

A number of fabrication technologies of Mg-based thermoelectric materials have been studied, e.g. direct co-melting [21], mechanical alloying [22–24], solid-state reactions [25–28], spark plasma sintering [28–30] and the Bridgman method [31–33]. Among them, the material with one of the highest reported ZT values has been obtained by Zaitsev et al. by direct co-melting followed by long annealing [12]. However, the majority of aforementioned technologies is relatively expensive and allow to obtain only small amounts of the material, while fabrication of bulk Mg-based thermoelectric materials with low cost technologies is still challenging.

In the paper the potential of conventional gravity casting technology in fabrication of Mg-based thermoelectric materials was evaluated. The major technological problems were identified and their analysis provide a basis to propose potential solutions, improving the designed process as cost-effective and simple synthesis method of Mg_2X (X = Si, Sn, Ge) thermoelectric materials.

2. Research material and methods

Mg_2Sn intermetallic phase was selected as the research material. The samples were fabricated by direct co-melting method. Ingots of elemental magnesium (99.95%) and tin pellets (99.99%) were used as starting materials and were melted in stoichiometric ratios in an electric resistance furnace at 850 °C under protective atmosphere of argon, using graphite crucible. The melt was homogenised for 30 min at the same temperature, mechanically stirred for 15 min, and subsequently poured into the graphite casting molds.

Macrophotographies of obtained samples were registered using Canon EOS 1200D camera. Metallographic specimens were prepared by grinding on waterproof abrasive papers (P220, P320, P500, P1200) and polishing using water suspensions of polycrystalline diamond with grain size of 6, 3, and 1 μm. Microstructural investigation was performed by means of light microscopy (Olympus GX71, equipped with Olympus DP70 12Mpix digital camera and Olympus AnalySIS FIVE software) and scanning electron microscopy (SEM), using Hitachi S-3400N scanning electron microscope equipped with Thermo Noran System 7 energy dispersive spectrometer (EDS).

X-ray diffraction (XRD) patterns were collected using X'Pert[3] powder diffractometer equipped with curved graphite monochromator on diffracted beam and with the

following slits (in the sequence form Cu tube counter): Soller (2°), divergence (1/2°), antiscatter (1/2°) and receiving (0.15 mm). The X-ray data collection was performed for 10–150°2θ range. XRD investigations were performed on the powder samples received from as-cast material. After identification of all the phases in alloy, the Rietveld refinement was performed, following the turn-on sequence of parameters suggested by Young. The Rietveld analysis was performed applying X'Pert Highscore Plus v. 3.0a program. The pseudo-Voigt function was used in the describing of diffraction line profiles at the Rietveld refinement. The R_{wp} (weighted-pattern factor) and S (goodness-of-fit) parameters were used as numerical criteria of the quality of the fit of calculated to experimental diffraction data. The quantitative phase analysis was performed using the relation proposed by Hill and Howard

$$W_p = \frac{S_p(ZMV)}{\sum\limits_{i=1}^{n} S_i(ZMV)} \times 100\%, \qquad (1)$$

where W_p — the relative weight fraction of phase p in the mixture of n phases (wt%), S — the Rietveld scale factor, Z — the number of formula unit per units cell, M — the mass of the formula unit (in atomic mass units), and V — the unit cell volume.

3. Results and discussion

3.1. Design of the fabrication process

The first stage of process design comprised identification and elimination of the most common problems in fabrication of materials containing magnesium — high reactivity and flammability of this element. To overcome these problems it was necessary to use the possibly non-reactive crucible and mold materials and perform the casting process under the inert atmosphere to prevent the contact of the liquid magnesium with air. Therefore, graphite was chosen for the crucible and mold material and the protective atmosphere of Ar (12 dm^3/min) was applied. The liquid melt was covered with flux powder immediately after pouring it into the casting mold to prevent ignition of casted ingots. Additionally, the problem of high evaporation of magnesium was identified, especially at temperature exceeding 750 °C, while the investigated materials were obtained at 850 °C. The intensive evaporation of magnesium resulted in deficiency of this element and presence of non-reacted components in the structure of obtained materials — apart from Mg_2Sn and Sn phases, small amounts of MgO magnesium oxide were found (Fig. 1). The Mg_2Sn phase is dominant compound in obtained materials (Table I).

The further studies on evaporation of magnesium in Mg_2Sn phase revealed that approximately 10 wt% surplus of magnesium compensates the evaporation of this element and enables obtaining Mg_2Sn phase characterised by higher purity. The identification of the phase composition using XRD analysis revealed two crystalline
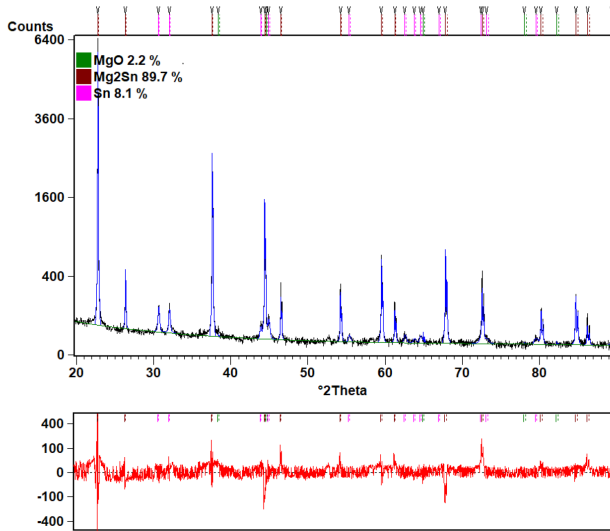
Fig. 1. X-ray diffraction pattern fitting by Rietveld method for as-cast Mg_2Sn compound in stoichiometric ratio ($R_{exp} = 14.1\%$, $R_{wp} = 19.8\%$, $S = 1.95$).

Fig. 2. X-ray diffraction pattern fitting by Rietveld method for as-cast Mg_2Sn material with 10 wt% surplus of magnesium ($R_{exp} = 16.9\%$, $R_{wp} = 20.7\%$, $S = 1.49$).

TABLE I

Phase contents and their lattice parameters in as-cast Mg_2Sn compound in stoichiometric ratio, determined from the Rietveld method.

Phase	Space group	Contents [wt%]	Lattice parameters [nm]	
			Rietveld	ICDD
MgO	cubic, $Fm\text{-}3m$ (225)	21.8(4)	$a_0 = 0.4057$	$a_0 = 0.4058$
Mg_2Sn	cubic, $Fm\text{-}3m$ (225)	70.8(4)	$a_0 = 0.6763$	$a_0 = 0.6765$
Sn	tetragonal, $I41/amd$ (141)	7.4(2)	$a_0 = 0.5833$ $c_0 = 0.3180$	$a_0 = 0.5820$ $c_0 = 0.3175$

TABLE II

Phase contents and their lattice parameters in as-cast material with 10 wt% surplus of magnesium, determined from the Rietveld method.

Phase	Space group	Contents [wt%]	Lattice parameters [nm]	
			Rietveld	ICDD
Mg_2Sn	cubic, $Fm\text{-}3m$ (225)	98.0(4)	$a_0 = 0.6762$	$a_0 = 0.6765$
Sn	tetragonal, $I41/amd$ (141)	2.0(3)	$a_0 = 0.5834$ $c_0 = 0.3180$	$a_0 = 0.5820$ $c_0 = 0.3175$

phases: Mg_2Sn (cubic crystal structure) and Sn (tetragonal crystal structure). The Rietveld refinement plot of the powder sample obtained from the as-cast specimen is presented in Fig. 2. The S (goodness of fit) parameter has reached the value of 1.49 and it can be considered as a satisfactory value for determining the phase content and lattice parameters (Table II).

Additionally, the problem of high evaporation of magnesium may be solved by reduction of melting time through replacement of resistance heating by induction heating. Moreover, in case of induction heating the material is intensively mixed with eddy currents, which has a beneficial influence on homogeneity of fabricated ingots.

The second stage of process design was focused on identification of specific problems, occurring in fabrication of Mg_2X (X = Si, Sn, Ge) intermetallic phases. Numerous problems were identified during solidification of molten phases, due to their high volume shrinkage and low thermal conductivity, which makes the material prone to cracking. The first attempts to cast the ingots of $Mg_2S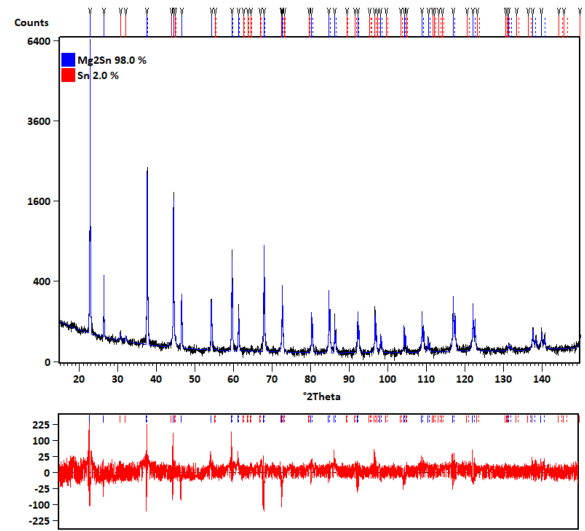n$ phase comprised pouring the molten phase into the graphite casting mold with diameter of 20 mm and resulted in disintegration of the obtained ingot after around 48 h (Fig. 3a). In the second technological test the mold was preheated to 400 °C. As a result the ingot of Mg_2Sn phase with diameter of 20 mm and height of 50 mm was obtained. The macrostructural investigation of the ingot revealed the presence of cracks in the entire longitudinal section (Fig. 3b). The grain structure consists of a wide zone of columnar grains with narrow zone of equiaxed grains in the middle of the ingot. Although the equiaxed structure is desired, knowledge on obtaining the columnar structure might be useful in the further research, particularly in case of potential anisotropy of thermoelectric properties. In the last technological test the diameter of the ingot was increased to 40 mm. The molten phase was casted into the graphite casting mold preheated to 400 °C and cooled with furnace with cooling rate of 10 °C/h. The obtained ingot with a diameter of 40 mm and height of 100 mm was characterised by columnar grain structure with some cracks (Fig. 3c). Nevertheless, neither disintegration, nor the increase of the number of cracks were observed in comparison to the ingot with diameter of 20 mm. It is believed that

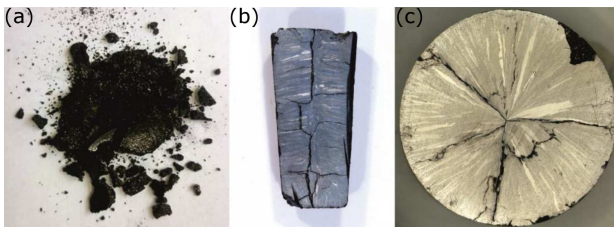Fig. 3. Fabricated ingots of Mg_2Sn phase: (a) ingot casted to non-preheated graphite mold, (b) ingot casted to graphite mold preheated to $400\,°C$, (c) ingot casted to graphite mold preheated to $400\,°C$ and cooled with furnace with cooling rate of $10\,°C/h$.
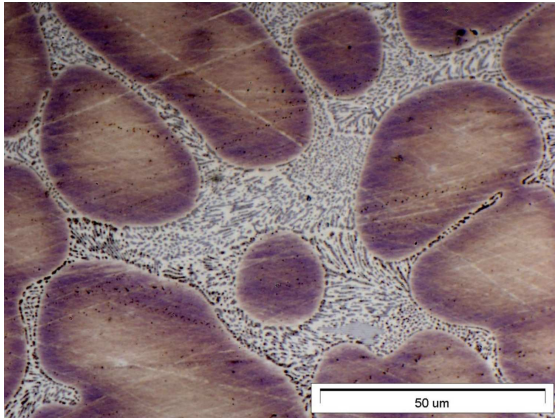

Fig. 4. Microstructure of the top part of Mg_2Sn ingot with eutectic compounds resulting from segregation of tin (LM, 100×).

the further decrease of cooling rate or using the molding material with lower thermal conductivity may result in fabrication of crack-free bulk ingots of Mg_2X (X= Si, Sn, Ge) phases.

The last identified technological problem was the significant difference in density of components, resulting in inhomogeneity of fabricated ingots. Tin, characterised by higher density than magnesium tends to sediment to the bottom part of the melt, which influenced the microstructure of a part of the casted ingots (Fig. 4). In consequence in the top part of the ingots the mixture of eutectic compounds was observed instead of homogeneous one-phase structure. However the problem of inhomogeneity was solved by application of intensive mechanical stirring preceding the casting.

3.2. Microstructure of obtained Mg_2Sn ingots

Identification of technological problems and application of proposed solutions led to fabrication of bulk ingot of Mg_2Sn phase with diameter of 40 mm and height of 100 mm. The ingot was casted to graphite mold preheated to $400\,°C$ and cooled with furnace with cooling rate of $10\,°C/h$. SEM investigation of fabricated ingot revealed the homogeneous one-phase structure of the material composed of tin and magnesium (Fig. 5, Table III).
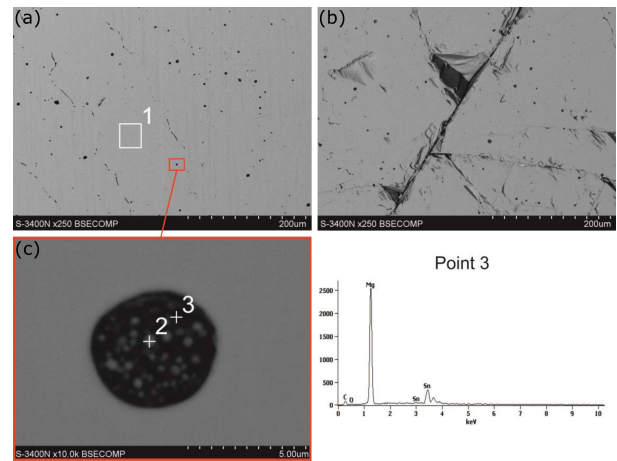

Fig. 5. Microstructure of Mg_2Sn ingot casted to preheated mold and cooled with furnace: (a) Mg_2Sn matrix with inclusions, (b) brittle cracks observed within the matrix, (c) inclusion.

TABLE III

Results of EDS analysis of areas and points indicated in Fig. 5 (at.%).

	Mg	Sn
area 1	52.6	47.4
point 2	86.1	13.9
point 3	88.4	11.6

A number of small inclusions, distributed uniformly in Mg_2Sn matrix was observed (Fig. 5c). The mentioned inclusions contain islands of Mg_2Sn phase surrounded by Mg-rich areas. The EDS analysis of point 3 revealed also presence of carbon and oxygen. Therefore, the identified inclusions may be particles of magnesium oxide and crucible material (graphite), introduced to the liquid phase during the mechanical stirring before casting. Additionally, in some areas of the investigated samples brittle cracks were observed (Fig. 5b). Their presence confirms the susceptibility of material to cracking and may be justified by occurrence of significant tensile stresses caused by high volume shrinkage during the solidification process.

4. Summary and conclusion

The conducted technological tests lead to development of promising one-step method of fabrication of Mg-based thermoelectric materials. Identified technological problems and purposed solutions resulted in fabrication of bulk, homogeneous ingot of Mg_2Sn phase. Although the designed method is not free from imperfections, concerning mainly the cracking of material, the reduction of cooling rate during the solidification process let to decrease the number of cracks even in case of ingot with increased diameter. Hence, it is believed that the further development of presented technology may enable fabrication of

bulk, defect-free ingots of Mg-based thermoelectric materials. Basing on the conducted research, the following conclusions were drawn:

- The main technological problems, identified in fabrication of Mg-based thermoelectric materials by conventional casting methods are: high reactivity, flammability and evaporation of magnesium, significant difference in density of components, as well as susceptibility of the material to cracking caused by high volume shrinkage and low thermal conductivity. The mentioned problems may be eliminated by application of inert atmosphere, introduction of mechanical or electromagnetic stirring before casting and reduction of cooling rate.

- Mg_2Sn ingot, fabricated by designed technology is characterised by homogeneous structure and consists of Mg_2Sn phase (98%). Tin (2%) and some inclusions, composed probably of graphite and magnesium oxide, were introduced to the molten phase during the mechanical stirring. The presence of cracks in the structure of ingot reveals the necessity of further decrease of cooling rate.

Acknowledgments

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