Materials Letters 166 (2016) 140–144

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Multi-scale architectured thermoelectric materials in the Mg_2(Si,Sn) system

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ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form
9 December 2015
Accepted 12 December 2015
Available online 14 December 2015

Keywords:
Solidification microstructure
Thermoelectric materials
Mesostructure
Thermodynamics

ABSTRACT

Two different microstructural architectures featuring multiple length scales have been created in the thermoelectric $Mg_2(Si_xSn_{1-x})$ system. The first one combines the nano-grain microstructure, characteristic of rapid solidification, with a large-scale pseudo-periodic pattern in one direction. The second is a layered structure in which the composition and microstructural scale vary from layer to layer. The microstructural variability is obtained by two different processing methods, in the first from the consolidation of melt-spun $Mg_2(Si_xSn_{1-x})$ alloy and in the second the sequential thermal treatment of a diffusion couple between Mg_2Si and Mg_2Sn. In both cases the microstructural features are consistent with the predictions of the solidification and diffusion paths followed in each process.

1. Introduction

Thermoelectric generators (TEGs) convert heat directly into usable electric power. As huge amounts of heat are wasted or unutilized from a wide variety of sources, ranging from industrial activities to automobile engines, there is continued interest in developing TEGs. Unfortunately, at present, the energy conversion efficiencies of these devices is too low for many practical applications and so the thrust of much of the materials development is in increasing the efficiency expressed in terms of the material figure of merit, ZT. For a chemically and spatially homogeneous material, such as any of the common materials, including the magnesium silicides and its alloys, maximizing the figure of merit requires maximizing an unusual combination of properties: electrical conductivity, Seebeck coefficient as well as thermal resistivity. In recent years, much of the development of materials with enhanced values of ZT has been to create, by microstructural processing, nano-structural features that increase phonon scattering to lower the lattice thermal conductivity [1–7]. However, the presence of nanometer-scale defects such as nano-sized precipitates, affect only a portion of the phonon spectrum, typically those with small mean free paths, and phonons with longer mean free paths remain unaffected. Indeed, in many semiconductors, even phonons with mean free path above 100 nm can significantly contribute to heat conduction [8]. Consistent with this is the observation that a further reduction of the thermal conductivity can be achieved by introducing meso-scale defects to scatter the phonons with longer mean free paths [4]. Moreover, while the focus in these recent studies has been to decrease thermal conductivity, it has been implicitly assumed that the power factor is relatively unaffected. Of wider interest is the possibility that an initially homogeneous material can be converted into a deliberately architectured material of the same overall composition to not only decrease thermal conductivity by introducing phonon scattering at different length scales but also to modify other important properties, such as the fracture toughness. Inevitably, an architectured thermoelectric will be a composite thermoelectric rather than a homogeneous material and consequently ZT will be related to the phases through some mixing rules of the thermoelectric properties of the individual phases. It is also possible but not investigated in thermoelectric systems that some of the metastable compositions may have superior TE properties to those of the equilibrium solid solution phases.

Motivated by the desire to create materials with multiple microstructural length scales, we have been exploring processing

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http://dx.doi.org/10.1016/j.matlet.2015.12.056
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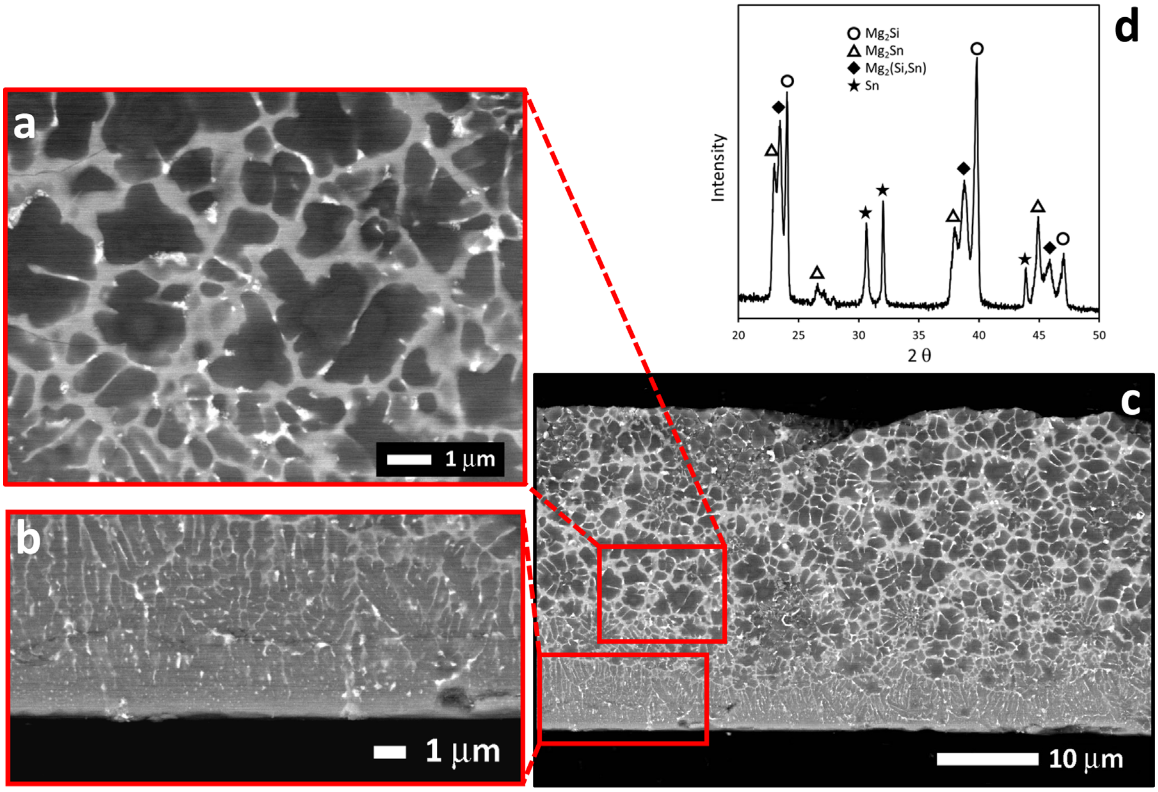

Fig. 1. (a–c) SEM-BSE images showing the graded microstructure of the $Mg_2Si_{0.65}Sn_{0.35}$ melt-spun ribbons. (d) XRD diagram of the melt-spun $Mg_2Si_{0.65}Sn_{0.35}$ ribbons.

routes to produce a variety of architectured thermoelectric materials. In the area of structural materials, Bouaziz et al. [9] have recently outlined approaches to also introduce intermediate length scales between the microstructure and the superstructures in order to provide additional degrees of freedom in manipulating property combinations hitherto unattainable [10–12]. A few examples can be found for functional materials such as Cu/Nb nanowires, which simultaneously have both high strength and high electrical conductivity [13], or segmented TE to increase the overall conversion efficiency in TEG by stacking materials with different peak temperatures of the figure of merit [14].

In the present work, we demonstrate the formation of Mg_2(Si, Sn) thermoelectric materials having two different types of microstructural architectures. The first is one that combines the nano-grain microstructure, characteristic of rapid solidification with a large-scale pseudo-periodic pattern in one direction. The second is a layered structure in which the composition and microstructural scale vary in each layer. The $Mg_2(Si_xSn_{1-x})$ alloy system was chosen for illustration because it can be cast from the melt, exhibits a range of solid solution compositions that have been shown to be promising thermoelectric materials, and the binary phases are also thermoelectric.

2. Experimental

For the formation of the first architecture, alloys having compositions of Mg_2Si and $Mg_2Si_{0.65}Sn_{0.35}$ were prepared by induction melting of magnesium (99.9%), silicon (99.999%) and tin (99.999%) sealed in a tantalum crucible under a low pressure argon atmosphere in order to minimize evaporation and oxidation. After solidifying, the ingots produced were melted in boron nitride (BN) crucibles and then melt-spun onto a copper wheel spinning at a speed of 30 m/s to form rapidly-solidified ribbons a few tens of micrometers in thickness. These ribbons were then stacked in a graphite die and consolidated by spark plasma sintering at 70 MPa, 500 °C for 5 min to form a dense, pseudo-periodic, graded microstructure. Comparison samples were produced in the same way but instead of stacking the ribbons, they were first crushed before consolidation.

An alternative architecture is a one-dimensional stepped variation in composition and structure. This was formed by creating a diffusion couple between a Mg_2Si and a Mg_2Sn pellet [15] and then annealed at successively higher temperatures. Ingots of the pure phases Mg_2Si and Mg_2Sn were prepared by induction melting as described in the previous section. After cooling, they were ground before consolidating by spark plasma sintering (SPS) to produce highly dense polycrystalline pellets of 10 mm diameter. Prior to the bonding process, the pellets faces were finely polished. Successful bonding of the two pellets occurred within 1 h at 600 °C under a moderate pressure of 60 MPa. The diffusion couples obtained this way were placed into Ta tubes, sealed under argon and then successively heated at 600, 500 and 400 °C for 3.5 h, 23 h and 109 h, respectively, conditions chosen in this particular example to develop inter-diffusion layers having different microstructures with similar thicknesses.

3. Results and discussion

The hierarchical microstructure of the melt-spun ribbons is shown in the SEM images of polished cross-sections of Fig. 1a–c. In the electron back scatter imaging mode used, the darkest phase in the images has the lowest mean atomic number and, by EDAX, is associated with Mg_2Si. The Mg_2Si ribbons consist of Mg_2Si grains surrounded by a fine eutectic structure of Mg_2Si+Si. The size and shape of the Mg_2Si grains vary across the thickness of the ribbon varying from thin grains elongated along the thermal gradient in contact with the copper wheel to equiaxed grains on the free surface of the ribbon. This gradient of microstructure indicates