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Design, assembly and characterization of silicide-based thermoelectric modules

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ABSTRACT

Silicides have attracted considerable attention for use in thermoelectric generators due mainly to low cost, low toxicity and light weight, in contrast to conventional materials such as bismuth and lead telluride. Most reported work has focused on optimizing the materials properties while little has been done on module testing. In this work we have designed and tested modules based on N-type magnesium silicide $Mg_2(Si–Sn)$, abbreviated MGS, and P-type Higher Manganese Silicide, abbreviated HMS. The main novelty of our module design is the use of spring loaded contacts on the cold side which mitigate the effect of thermal expansion mismatch between the MGS and the HMS. We report tests carried out on three modules at different temperatures and electric loads. At a hot side temperature of 405 °C we obtained a maximum power of 1.04 W and at 735 °C we obtained 3.24 W. The power per thermoelectric material cross section area ranged from 1 to 3 $W\,cm^{-2}$. We used the modeling tool COMSOL to estimate efficiencies at 405 and 735 °C and obtained values of 3.7% and 5.3% respectively – to our knowledge the highest reported value to date for silicide based modules. Post-test examination showed significant degradation of the N-type (MGS) legs at the higher hot side temperatures. Further work is underway to improve the lifetime and degradation issues.

1. Introduction

Silicides are among the most promising materials for thermoelectric generators (TEG) exploiting medium temperature waste heat recovery sources such as exhaust gas heat from internal combustion engines. Recent studies on novel thermoelectric material have shown that silicides offer considerable advantages over conventional materials for mass production and scale up due to their low cost, relatively high abundance and availability of raw materials and high thermoelectric efficiency [1–3]. However, module manufactures have had very limited experience with silicide based materials thus creating a paucity in performance data for modules based on silicides. Today the highest performing silicide thermoelectrics are based on $Mg_2(Si–Sn)$ solid solutions and are all N-type with peak zT values up to 1.5 [4–7]. Typically, the efficiency improves with increasing Sn-content in $Mg_2Si_xSn_{1-x}$ to a peak value with x between 0.4 and 0.6, but will simultaneously reduce the stability to the extent that lower hot side temperatures must be used [8]. Decomposition due to fast oxidation of Mg is especially of concern [9,10]. In contrast to N-type silicides, there are few examples of P-type silicides and of these the Higher Manganese Silicides (HMS) exhibits the best performance with peak zT values in the range 0.6 to 0.8 [11]. One problem with combining both N-type and P-type materials as unicouples in a module construction is caused by their relative difference in coefficients of thermal expansion (CTE). Generally, N-type silicides have CTE in the range $16–18 \cdot 10^{-6}\,K^{-1}$ for $Mg_2(Si–Sn)$ whereas P-type HMS materials exhibit CTE's in the range of $9\text{-}13 \cdot 10^{-6}\,K^{-1}$ [6,12–14]. This inevitably leads to stress build up as a result of the large

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temperature gradient between the hot and cold sides of the module. This in turn can cause degradation of the legs and a reduction in performance over time. This effect is particularly observed with the N-type legs on the hot side of the module. Attempts by Nemoto et al. have been made to overcome this problem by constructing unileg modules based on N-type Mg_2Si only [15–17]. These modules shows very good stability and reliability but still have quite low efficiency, with power per module area of around 0.22 W/cm^2 at a temperature difference of 500 °C.

A very important consideration in module design is minimizing degradation of thermoelectric properties during long periods of time. This is especially the case for the hot side where interdiffusion and material loss is more prevalent. The general approach is to introduce functional layers between the thermoelectric leg material and the current collecting plate. This process is collectively referred to as "Metallization". These include a diffusion barrier layer, a contact layer, an adhesion layer and a compliant layer [18]. In order for these layers to function reliably there needs to be some interdiffusion between them but not a persistent amount that would otherwise spoil their effect. This requires careful selection of material and method of application. In the case of contact layers, one promising option is the use of other silicides such as $TiSi_2$, $CrSi_2$, CoSi and MnSi. The latter has been combined with HMS and exhibits low contact resistances in the order of 10^{-6}–10^{-5} $\Omega\,cm^2$ [19–22]. Another approach is to use pure metals such as Ni to form contacts. With HMS a diffusion barrier needs to be inserted between the leg and the contact layer in order to hinder reaction and crack formation. A thin layer of chromium seems to be a good option for this function mainly because it has a very close matching CTE ($\sim 10 \cdot 10^{-6}\,K^{-1}$) and relatively low contact resistance in the order of 10^{-5} $\Omega\,cm^2$ [23–25]. The Iida group in Japan [22] has investigated the direct sintering of nickel powder on top of Mg_2Si giving a good contact layer, but even better contact can be achieved by pressing a thin nickel foil onto the surface of the leg instead of using nickel powder. In such experiments contact resistances in the region of 10^{-6} $\Omega\,cm^2$ have been observed and this approach seems promising for long term stability [26]. Both these methods have been shown to work well within the ThermoMag project. However, concern has been raised on how stable the direct contact of Ni on Mg_2Si is due to the formation of NiSi, and whether or not a diffusion barrier is also needed in this case. In the case of Mg_2(Si–Sn), we are not aware of any published work on contacts, but we assume that similar approaches used for other silicides and especially pure Mg_2Si could be used. However as stated previously in this article there is concern about the higher CTE of Mg_2(Si–Sn) compared with Mg_2Si. The goal of the design presented in this article was to facilitate a versatile and simple test-module that could be easily fabricated, incorporating different N- and P-type materials with different CTE values. Several methods of metallization were also used as described in the experimental section.

2. Experimental

2.1. Material preparation

The thermoelectric material used within this work is a result of the effort of several partners within the ThermoMag project [27]. Details of the synthesis of the thermoelectric material can therefore be found in the references to the respective partners work and are not given in details in this report. General powder-compaction techniques where used to prepare cylindrical pellets ($\varnothing$ = 10–50 mm). These were then cut into legs of the size $3 \times 3 \times 4$ mm^3 at Fraunhofer IPM. The material composition and thermoelectric properties of the materials used for the modules are listed in Table 1.

2.2. Module design

The construction of the module is shown in Fig. 1. The left illustration shows two legs (N and P) sandwiched between a copper block and a molybdenum plate both acting as current collectors (electrodes). The copper block is a structural element and also has recessed cavities into which springs are located; these provide compression to the legs to maintain contact while at the same time provide some compliance to mitigate the effect of thermal expansion mismatch between the N- and P-type material. The metallized legs are attached to the cold side by use of lead based solder foil as described in the module assembly. The right hand side of Fig. 1 shows the complete module with two rows of 3 pairs of unicouples containing 12 thermoelectric legs in total. The unicouples are held in position on the cold side by an anodized aluminum block of size 11.7×32.8 mm^2. Heat transfer is effected through from the *side* of the copper blocks to the anodized aluminum, while the springs press the blocks up (~1 mm) from the bottom. The current collection on the hot side was made using copper (module #1) and molybdenum (modules #2 and #3). The hot side was electrically isolated from the heating source using thin sheets of mica plates. The normal use of substrates attached to the hot side was considered unnecessary in this test setup.

2.3. Module assembly

The "as received" thermoelectric legs were subjected to a quality control involving matching of physical dimensions and checking of thermo power, electrical conductivity and evidence of cracking or chipping. Particular attention was given to select legs of equal height as this affects the quality of the electrical and thermal contact– only the closest matching legs were selected for module construction. The metallization was carried out by sputtering one or more metal layers onto the selected legs. Prior to this however there was a pretreatment stage in which the faces of the legs were polished and cleaned to remove any traces of surface oxidation and grease. Both N- and P-type materials were given the same metallization treatment and both hot and cold sides were metallized. After metallization the legs were placed in the correct orientation and soldered onto the cold side of the copper blocks using foils of a lead based solder allow. The solder operation was carried out in a vacuum tube back filled with argon at 450 °C. The hot side bonding was accomplished through diffusion bonding at the beginning of the performance testing.

2.4. Performance testing

The modules were tested in an evacuated chamber back filled with argon. The module was first placed onto a water cooled aluminum plate to maintain the cold side. An insulating sheet of mica was placed between the hot side of the module and a heater element. The whole setup was then clamped together using a spring loaded plate. The hot side temperature was measured with thermocouples placed both on the surface of the heater and on the surface of the hot side of the module. The cold side temperature of the module was not directly measured, but estimated from V_{OC} and the temperature of cooling water flow. Copper wires were soldered onto the two cold side current collecting electrodes for performance measurements of module voltage and current. Two test regimes were used – either the hot side was heated up to a fixed temperature while monitoring module behavior or the module was thermally cycled while measuring the performance. The measured open circuit voltage (V_{OC}) was compared with the theoretical value calculated from the integral of the Seebeck coefficients of the N- and P-type thermoelectric materials according to Eq. (1). The