Contacting Cu electrodes to $Mg_2Si_{0.3}Sn_{0.7}$: direct vs indirect resistive heating

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Abstract

Mg_2(Si,Sn)-based thermoelectric materials have been gaining interest in the past years due to their attractive properties. In this work, we present the outcome of using two different approaches to contact n- and p- type $Mg_2Si_{0.3}Sn_{0.7}$ legs with Cu electrodes to study the influence of current on the joining procedures. The first approach is a direct current heating procedure where the current runs directly through the sample, while the second approach uses the current as an indirect source of resistive heating. Results show that Cu diffuses into n- and p-type materials, creating relatively thick and complex reaction layers, both under direct and indirect resistive heating, and these layers have, respectively, an average thickness of 200 µm and 100 µm. Electrical contact resistance r_c values are also similar for both types, under both joining conditions (< 10 µΩ. cm^2). The directly and indirectly contacted samples were then annealed, and the results for all samples were similar. The reaction layers developed similarly in all cases and the contact resistances remained low (< 10 µΩ. cm^2).

Introduction

The field of thermoelectricity, which allows the conversion of waste heat into electricity, has been growing in the past decades. In fact, thermoelectricity provides an independent, renewable and environmental-friendly energy alternative that can be applied in various fields of industry (aerospace, automobile…). A large selection of thermoelectric (TE) materials is being studied and implemented into functional thermoelectric generators (TEG) such as Bi_2Te_3 or PbTe. The performance of these materials is determined by the value of their dimensionless figure of merit $zT = \sigma S^2 T / \kappa_{tot}$, where σ is the electrical

conductivity, S is the Seebeck coefficient, T is the absolute temperature and $\kappa_{tot} = \kappa_{elec} + \kappa_{lat}$ is the total thermal conductivity with κ_{elec} being its electronic component and κ_{lat} lattice component [1, 2].

To obtain a stable and efficient TEG, the optimized n- and p- type TE materials have to be contacted and assembled using metallic electrodes and bridges to form a TEG device. The interfaces resulting from these joining steps induce thermal and electrical contact resistances that vary in magnitude depending on the chosen materials. Therefore, the selection of these electrodes and joining procedures is a critical step, which has to ensure that the contact resistances are as low as possible [3, 4].

Other criteria to take into consideration while contacting metallic electrodes to TE materials are the difference in their coefficients of thermal expansion (CTE), and the joining methods. Both require experimental testing, but the latter is not as straightforward as the former, and might therefore need deeper investigations.

In this paper, we discuss the joining step of $Mg_2Si_{0.3}Sn_{0.7}$ TE materials with Cu foils as metallic electrodes under two different conditions, and we report the results for the reaction layer microstructures and the electrical contact resistances.

Magnesium silicide based materials have been selected because they possess a set of properties that make them attractive to the field of thermoelectricity.. In fact, they are non-toxic, abundant and cheap. They are also lightweight and have good thermal and mechanical stability. We study $Mg_2Si_{1-x}Sn_x$ solid solutions because these show improved TE properties compared to binary Mg_2Si [5, 6]. The specific composition of $Mg_2Si_{0.3}Sn_{0.7}$ has been selected because the material shows high zT_{max} values for both n- and p- type samples (~ 1.4 and ~ 0.55, respectively) at mid-range temperatures (350 ~ 450 °C) [7-9].

Cu has been chosen as the contacting electrode because it has a coefficient of thermal expansion (CTE) close to that of the studied TE material (Cu: $17 \cdot 10^{-6}$ K^{-1} [10] and $Mg_2Si_{0.3}Sn_{0.7}$: $17.5 \cdot 10^{-6}$ K^{-1} [11]). Cu has also been tested with the binary Mg_2Si in [12], showing good preliminary results. Cai *et al.*[12], reported that the Cu contacted samples had good adhesion and that no cracks have been observed. However, they reported a high value of electrical contact resistance r_c (~ 15 mΩ.cm^2) which was stated to decrease after doping.

The two joining conditions we used here differ in the way the samples (TE material + Cu) were heated during the sintering step. In the first case, the current from the sintering press was running through the samples and heating them up to the desired temperature. We called this procedure "*direct resistive heating*". However, in the second case, an extra layer of an electrically insulating compound was added on top and bottom of the samples to block the direct passing of current through them. Here the heating was

done indirectly through radial conduction from the sides to the inside of the samples, and we called this procedure "*indirect resistive heating*".

All samples were then annealed under the same conditions to study their thermal stability. In all cases, the reaction layers resulting from the contacting were studied with SEM/EDX, and the electrical contact resistances were resolved using electrical potential and Seebeck coefficient local mappings.

Experimental Setup

Powder batches of n-type $Mg_{2.06}Si_{0.3}Sn_{0.665}Bi_{0.035}$ and p-type $Mg_{1.97}Li_{0.03}Si_{0.3}Sn_{0.7}$ have been produced and pellets were sintered in a direct sinter press facility (DSP 510 SE from Dr. Fritsch GmbH, Fellbach, Germany)[13]. These pellets were pressed in a 15 mm die under vacuum at 700 °C, for 1200 s for n- and 600 s for p-type, with a pressure of 66 MPa and a heating rate of 1 K/s. All pressed pellets had a high relative density (≥ 97%), and were contacted with three disk shaped Cu foils on each side; each with thickness of 50 µm. The number of foils was chosen to account for the lateral resolution of the electrical contact resistance scanning measurements.

In the *direct resistive joining* procedure, n- and p-type pellets along with the Cu foils were stacked in the graphite die, then put into direct contact with the graphite pistons on top and bottom, which allows the sintering current to run directly through the electrodes and the sample.

However, in the *indirect resistive joining* procedure, the inner ends of the graphite pistons were covered with a thick layer of boron nitride (BN), and then used to press the Cu foil and pellet. The electric current, thus, flows along the walls of the graphite die and the joining reaction occurs by radial heat transfer.

To prepare for the annealing tests, cut pieces of the contacted samples were coated with a thick boron nitride layer to minimize Mg loss by evaporation. Then, they were sealed in quartz ampules under Argon gas and annealed in annealing furnaces for 7 days at 450 °C.

In the results section, eight samples will be presented. To simplify sample reference, sample names have been attributed as suggested in the table below:

Sample name	Experimental conditions
S_n_d	n- type, direct joining
S_p_d	p- type, direct joining
S_n_d_a	n- type, direct joining, annealed

S_p_d_a	p- type direct joining annealed
S_n_i	n- type indirect joining
S_p_i	p- type indirect joining
S_n_i_a	n- type indirect joining, annealed
S_p_i_a	p- type indirect joining, annealed

The results of all the above-mentioned samples were investigated under SEM/EDX (Zeiss Ultra 55 with a 15 kV acceleration voltage) to study the microstructures of the resulting reaction layers, and using a Potential & Seebeck Scanning Microprobe (PSM) [14, 15] to determine the electric contact resistances.

Results and discussion

- Microstructure

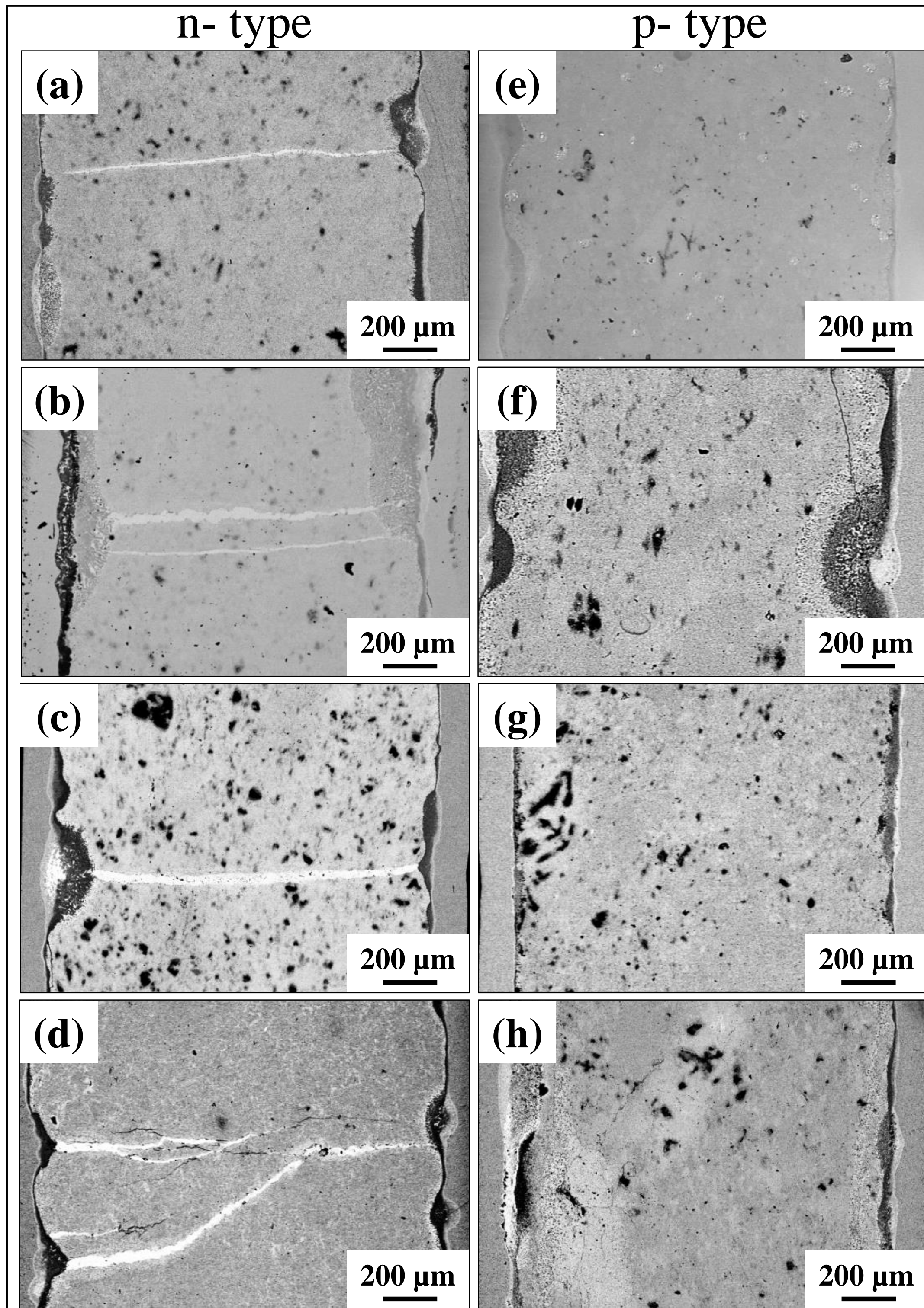

Figure 1: *Cu contacted n- and p-type $Mg_2Si_{0.3}Sn_{0.7}$ samples: (a) & (e): under direct heating, (b) & (f) under direct heating and annealed, (c) & (g): under indirect heating, (d) & (h): under indirect heating and annealed.*

Figure 1 shows the SEM/EDX results of all samples. The left column and right column contain n- and p-type samples, respectively. Starting with the directly joined samples S_n_d (***Figure 1 (a)***) and S_p_d (***Figure 1 (e)***), it is clear that both cases display thick and complex reaction layers, each containing various diffusion zones (100 ~ 200 µm thick each). These reaction layers are not single-phased; instead they are composed of several layers of different microstructures and compositions. Some of the phases contained in these layers are γ ($Cu_{1,55}MgSn_{0,45}$), τ_1 ($Cu_{1.5}MgSi_{0.5}$) which forms as Cu-rich dendrites, and Mg_2Sn. More details about the microstructure and the kinetics of the reaction layer formation are discussed in another work.

Along the TE material surface, localized darker and brighter areas can be seen. The darker areas are Si-rich $Mg_2Si_{0.3}Sn_{0.7}$ matrix, while the brighter regions are Sn-rich. In the p-type samples, Sn-rich areas are more scattered along the sample surface and appear as small agglomerations of ~ 20 µm diameter, while in n-type samples, they are seen as thin channels (Mg_2Sn-channel) running across the sample, from one Cu contacted end to the other. Such channel could be the result of Sn interdiffusion from one reaction layer to the other and Mg_2Sn formation as the channel progresses inside the TE material , So far, no exact explanation has been obtained to correctly explain why Sn in particular seems to crystalize out of the $Mg_2Si_{0.3}Sn_{0.7}$ matrix after Cu contacting.

After annealing (***Figure 1 (b) and (f)***), more Cu diffusion was observed, creating thicker diffusion zones and more Si-rich regions. It is clear here that when directly joined with $Mg_2Si_{0.3}Sn_{0.7}$, Cu diffuses easily and rapidly, and this diffusion progresses even further after just 7 days at 450 °C. As TEG often undergo continuous thermal cycling, contacting the TE materials with metallic electrodes that diffuse uncontrollably does not guarantee a constant efficiency and will cause material and generator damage.

The decision to test Cu contacting under *indirect resistive heating* conditions was to investigate any potential effect of the current on the joining and the Cu diffusion. However, as the SEM pictures on ***Figure 1 (c) and (g)*** show, indirect heating results look very similar to direct heating, for both n- and p-type samples. In fact, the inhomogeneous reaction layers with thicker diffusion zones are clearly visible, as well as the scattered Si-rich darker areas along the sample surfaces. Mg_2Sn-channels are also observed in this case, which proves that these channels are not a result of electromigration, but instead, of another diffusion mechanism. One probable explanation here could be that during contacting, micro cracks develop near the interface, and as Sn is the element with the lowest melting point, it liquefies faster and runs through them, reacting with Mg from the TE material as it diffuses. Such process causes the cracks to progress even further inside the sample, opening even more diffusion path for Sn inside the TE material.

Another interesting feature that is also observed in all SEM figures above is the demixing of the $Mg_2Si_{0.3}Sn_{0.7}$ initial matrix into what seems to two sub-matrices, one which is rich in Si and one which is

rich in Sn. This behaviour also clearly just happens after contacting under the effect of time and temperature. The electric current doesn't seem to play a big role.

After annealing, the indirectly heated samples ***(Figure 1 (d) and (h))*** didn't show any big difference from the directly heated ones. Despite the fact that the reaction layers and the diffusion zones seem to be not as thick (respectively ~ 50 µm and ~ 100 µm) as they were in the case of direct heating (respectively ~ 100 µm and ~ 200 µm), the Mg_2Sn-channels and the demixing of the initial matrix of the TE material were still observed.

As an initial conclusion, it is clear that whether $Mg_2Si_{0.3}Sn_{0.7}$ and Cu are contacted under direct or indirect heating, the resulting interfaces are similar. The diffusion of Cu inside the TE material, as well as matrix de-mixing and other observed behaviors are independent of current and mainly driven by temperature and time. The next step here would be to investigate how these complex reaction layers affect the electrical contact resistance.

- Electrical Contact Resistance

The electrical contact resistance resulting from the contacting of Cu with $Mg_2Si_{0.3}Sn_{0.7}$ is calculated through PSM measurements [14, 15]. If we have a homogeneous current density $j = {}^{I}/_{A}$ passing through the electrodes and the sample, the bulk electrical contact resistance R_c is calculated as follow:

$$R_\mathrm{c} = \frac{V_\mathrm{el} - V_\mathrm{TE}}{I} \qquad \text{(Eq.3)}$$

where V_el and V_TE are the local voltages measured on the electrode and the TE material, respectively [12, 16, 17].

However, in our case, the occurrence of a homogeneous current density is very unlikely, due to the complex interfaces and the irregularities (demixing) observed inside the TE material. Therefore, we have to assume an inhomogeneous current flow, and the value of the current density j used here can be approximated using the TE properties of the material. In this case, instead of the bulk resistance R_c defined above, we define the specific electrical contact resistance $r_\mathrm{c} = R_\mathrm{c} * A$, A being the area, as follows:

$$r_\mathrm{c} = \frac{V_\mathrm{elec} - V_\mathrm{TE}}{j}$$

with

$$j = \frac{\Delta V_{TE}}{R_{TE} * A} \quad \text{(Eq.4)}$$

$$R_{TE} = \frac{l_{TE}}{A\sigma_{TE}} \quad \text{(Eq.5)}$$

where ΔV_{TE} and R_{TE} are the voltage and the resistance across the material, l_{TE} and σ_{TE} are its length and electrical conductivity, respectively. Hence, the final specific electrical contact resistance is defined as

$$r_c = \frac{(V_{elec} - V_{TE})\, l_{TE}}{\Delta V_{TE} * \sigma_{TE}} \quad \text{(Eq.6)}$$

Furthermore, due to the demixing observed in the samples, the electrical conductivity was re-measured after contacting and after annealing, and the new values were put in (Eq. 6) to obtain correct r_c values.

Results of PSM scanning measurements as well as calculations of the electrical contact resistances are presented below.

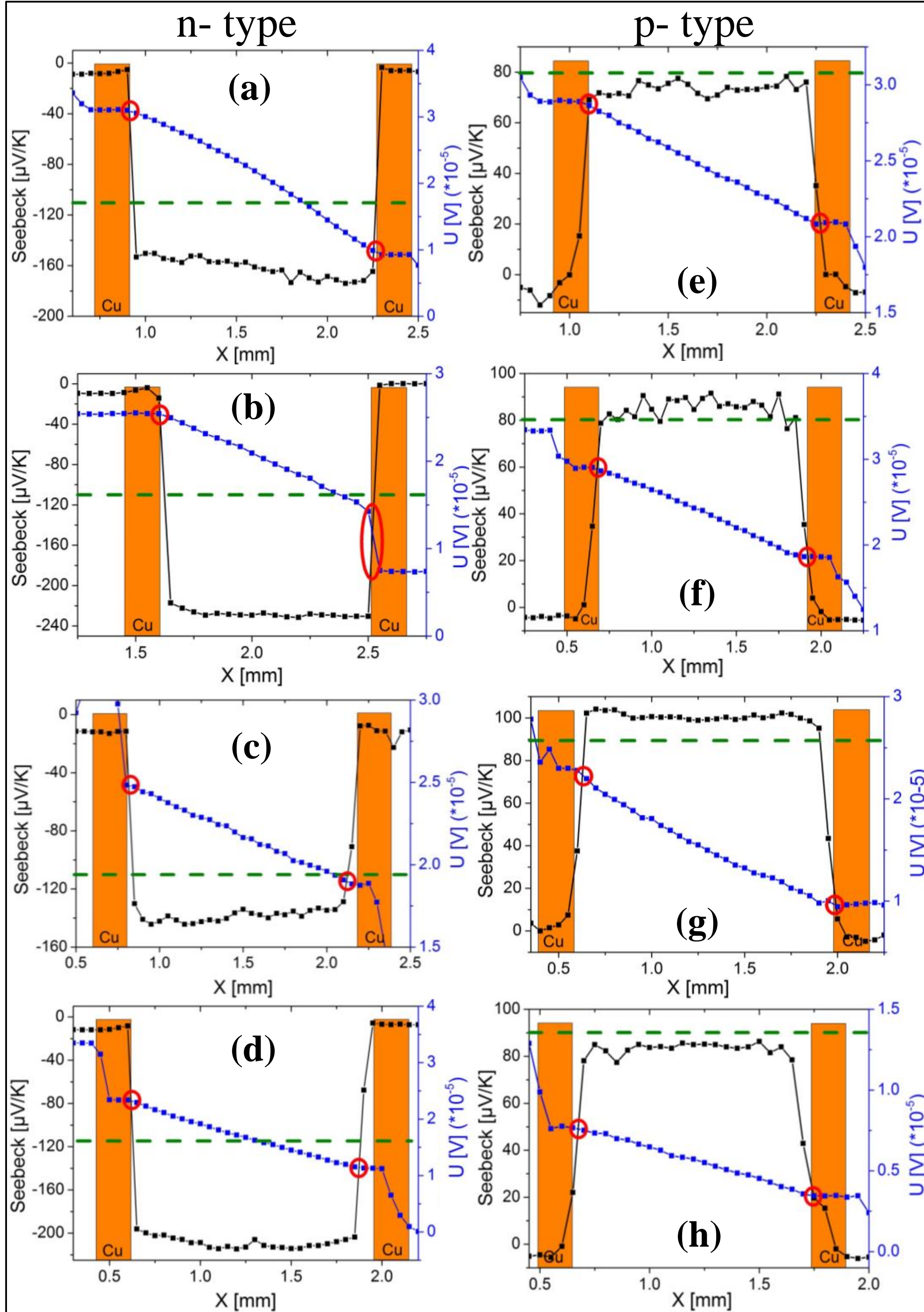

***Figure 2*:** *PSM plots of Cu contacted n- and p-type* $Mg_2Si_{0.3}Sn_{0.7}$ *samples: (a) & (e): under direct heating, (b) & (f) under direct heating and annealed, (c) & (g): under indirect heating, (d) & (h): under heating current and annealed.*

Figure 2 shows typical line scans of Seebeck and electrical potential that are used to determine the location of the interface and calculate the contact resistances. The interface locations are marked by the red circles on the graphs, and it is evident that at these positions, the U plots do not show big drops. Instead, they display a smooth transition between the metallic electrodes and the TE material, which means that there is no major resistance added from the newly grown reaction layers. One exception to this general behavior is the n-type annealed directly heated sample (***Figure 2 (b)***): the U graph shows a large drop at the right hand side interface. Further SEM/EDX investigations have shown that for that sample in particular, Mg has diffused inside the Cu layer causing the foils to delaminate, which explains the sudden increase in resistance.

The obtained r_c values for n- and p- type samples are presented in the ***Tables 1*** and ***2*** below. Equations 3 and 6 have been used to compare different potential r_c values to have a better idea of the homogeneity of the current flow across the samples.

Table 2*: Electrical contact resistance* r_c *values for n-type* $Mg_2Si_{0.3}Sn_{0.7}$ *samples contacted with Cu under direct and indirect heating, non-annealed and annealed conditions.*

Sample	$r_c\ (Eq. 6)$ / µΩ. cm^2	$r_c\ (Eq. 3)$ / µΩ. cm^2
S_n_d	6 ± 4	9 ± 6
S_n_d_a (left side)	11 ± 6	13 ± 7
S_n_d_a (right side)	155 ± 30	181 ± 30
S_n_i	7 ± 4	10 ± 7
S_n_i_a	4 ± 1	11 ± 1

Table 3*: Electrical contact resistance* r_c *values for p-type* $Mg_2Si_{0.3}Sn_{0.7}$ *samples contacted with Cu under direct and indirect heating, non-annealed and annealed conditions.*

Sample	$r_c\ (Eq. 6)$ / µΩ. cm^2	$r_c\ (Eq. 3)$ / µΩ. cm^2
S_p_d	8 ± 5	3 ± 2
S_p_d_a	7 ± 5	6 ± 4
S_p_i	7 ± 5	11 ± 7
S_p_i_a	9 ± 5	9 ± 5

As expected from the PSM graphs in Figure 2, the electrical contact resistances are very low for all samples, at all joining conditions, before and after annealing. The values of r_c obtained with Eq. 6 and Eq. 3 are also very comparable considering the measurement uncertainty, which indicates that the PSM

current runs homogeneously through all the samples. The complex interfaces as well as the demixing of the initial TE material matrix did not hinder the current flow.

One interesting behavior, however, can be seen for the Seebeck graphs in Figure 2, which is the change in S values of n-type samples a first time after contacting (~ -150 μV/K), and a second time after annealing (~ -230 μV/K). This is visible in the considerable difference between the initial S values (~ -110 μV/K) for n-type $Mg_2Si_{0.3}Sn_{0.7}$ marked with the green dashed lines on the graphs and the actual S values after contacting or annealing. Such behavior occurs independently of the heating method (direct or indirect), and is not observed for p-type samples. The change in S values indicates a change in the TE properties of the material, and the limitation of the occurrence to just one sample type suggests a dependence of the material behavior on the dominant carrier type.

So, despite the fact that r_c was low for $Mg_2Si_{0.3}Sn_{0.7}$ contacted with Cu, the change in TE properties suggests that the diffusion strongly affects the n-type TE material, which requires a certain control (e.g. diffusion barrier) in order for Cu to be a technological solution.

Finally, the way of applying the electric current during the joining step might have an influence on the final results; however it seems to be weaker than the effect of temperature and pressure, and thus cannot be clearly observed.

Conclusion

Two different contacting approaches were used in this work to understand the effect of the electric current on the contacting results and properties. When n- and p-type $Mg_2Si_{0.3}Sn_{0.7}$ were contacted with Cu electrodes, similar results were obtained, independently on the joining procedure. In all cases, the contacts had good adhesion, Cu diffused into the TE material, creating a thick and inhomogeneous reaction layer with localized thicker diffusion zones, and we obtained low r_c values. Additionally, the irregularities observed in the TE materials after joining occurred for both contacting approaches, which tells that electric current is not the only parameter to influence microstructure results. During annealing, Cu diffusion continued in all samples, though with different ratios, while values of r_c remained low ($\leq$ 10 $\mu\Omega.\ cm^2$). Thus, it is clear that the results of Cu contacting are not sensitive to the current path, and that blocking the current is not sufficient to control the metal´s diffusion.

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