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FRAUNHOFER INSTITUTE FOR MANUFACTURING TECHNOLOGY
AND ADVANCED MATERIALS IFAM, BRANCH LAB DRESDEN

ENERGY FROM WASTE-HEAT – THERMOELECTRIC MATERIALS FOR INDUSTRIAL APPLICATIONS

1 *Mg- and Mn-Silicide sinter-bodies with different diameters (1 cm, 2 cm, 4.5 cm and 6 cm) produced by high-energy ball-milling and SPS.*

One approach for the energy harvesting from waste-heat is the use of thermoelectric materials. They can directly convert heat from different sources (for example geothermal, solar heat or waste heat) into electricity. The state of the art for the conversion efficiency of the so-called thermoelectric energy-recovery lies around seven percent. Different classes of materials (Oxides, Half-Heusler, Clathrates, Silicides, Antimonides, Tellurides, etc.) are currently investigated worldwide in order to increase the thermoelectric performance. However, the high thermoelectric efficiency is not the unique criterion for applications at large scale and the requirements are very complex. For example, the thermoelectric materials should be constituted of low-price and non-toxic elements with large natural availability.

Furthermore, the electric contacts should be mechanically as well as thermally and chemically stable in the complete application temperature range. In addition, the oxidation plays an important role. Protective coatings or encapsulation of the thermoelectric generator are necessary to prevent corrosion during the operation at high temperature.

The final thermoelektric device should also possess good mechanical properties since it might be exposed to temperature oscillations that damage the mechanical stability.

Thermoelectric Materials

The research activities at Fraunhofer IFAM Dresden involve aspects of applied as well as of basic research. In the field of basic research, the effect of nanostructuring on the thermoelectric properties of bulk-nanostructured materials is investigated.

The starting nano-powders are produced by using Top-Down (Bi_2Te_3 based alloys) and Bottom-Up ($Ba_8Ga_{16}Ge_{30}$-Clathrate) approaches. In both cases, the compaction into a bulk-nanostructured material with low thermal conductivity is achieved by Spark Plasma Sintering.

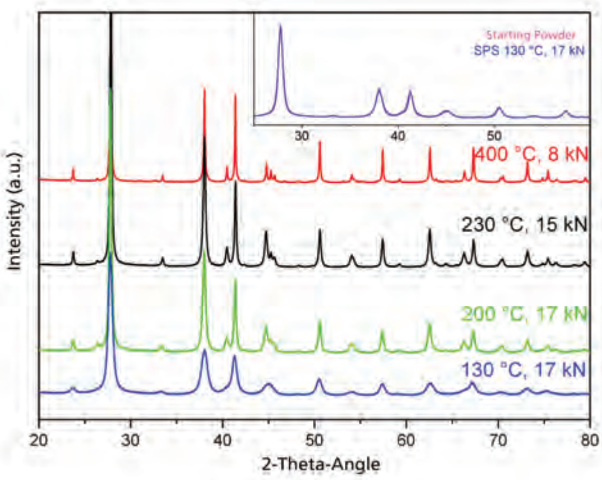
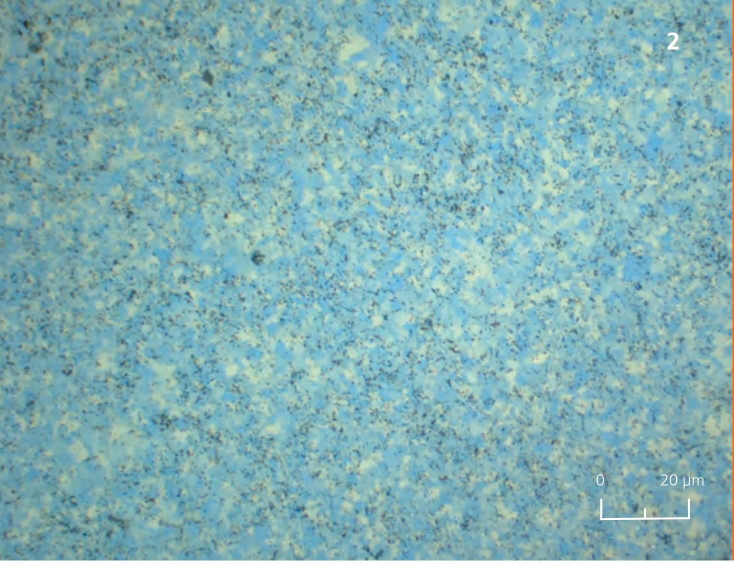


Fig. 1 Powder X-Ray diffraction patterns of n-Bi_2Te_3 sintered by Spark Plasma Sintering with different process parameters.
Inset: The X-Ray diffraction patterns of the starting powder and sintered material are identical, crystallite size = 20 nm.

In comparison to the macro-crystalline material, a significant decrease of the thermal conductivity in the nano-structured material can be reached (20 % for the Clathrate and 60 % for Bi_2Te_3). The influence of the nanostructuring on the Seebeck effect is also currently under investigation.
Concerning the applied research at the Fraunhofer IFAM, the activities focus, amongst others, on the up-scaling of the materials production by using powder metallurgical processes and on the search for low-price thermoelectric materials.



2 *Light microscopy image (polarized light) of the Mn-Silicide microstructure.*

3 *Thermoelectric legs of pre-contacted Mn-Silicide.*

Magnesium- and Manganese-silicides are constituted of inexpensive and low-toxicity elements. They show moderate efficiency (~ 5 %) in a temperature range from 300 °C to 650 °C and the efficiency can still be improved by tailoring the properties via doping.

The production of Magnesium- and Manganese-silicides in a large scale is a very challenging task due to their brittle nature. Through powder metallurgical methods it is possible to reproducibly prepare high-density samples (> 95 % of the theoretical density) with diameters of 4.5 cm and 6 cm and a grain size of around 5 µm.

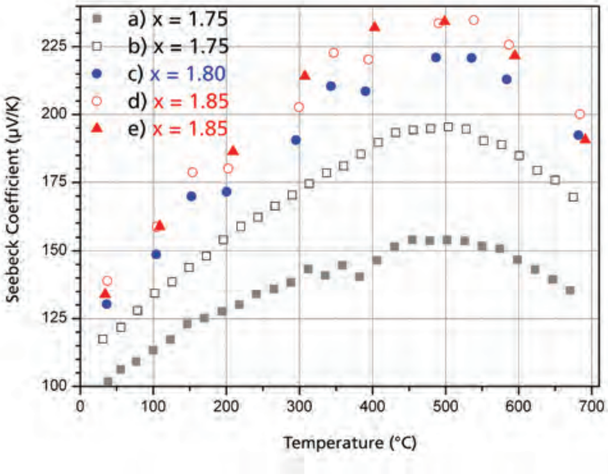


Fig. 2 Seebeck coefficient of $MnSi_x$ samples with different Silicon content.

The thermoelectric properties of these large Magnesium- and Manganese-silicide samples are in agreement with the best values in laboratory-scale specimens reported in the literature.

Module Construction

In order to create a complete production chain (from materials development to module production), the technological processes required for the electrical contacting of silicide materials and their further assembling into thermoelectric modules are under investigation. The electric pre-contacting of silicides (diffusion barriers) is achieved by using Spark Plasma Sintering in order to establish a technology for the processing of thermoelectric materials which can be transferred to an industrial scale.

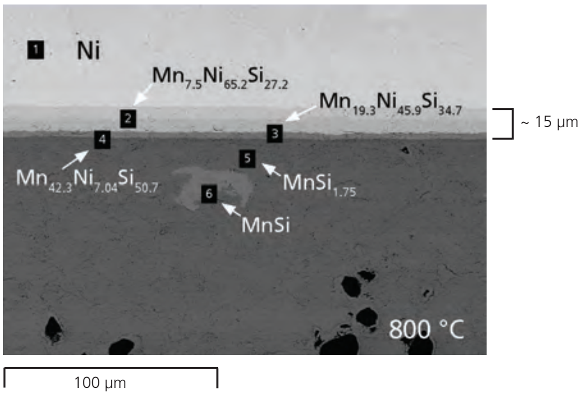
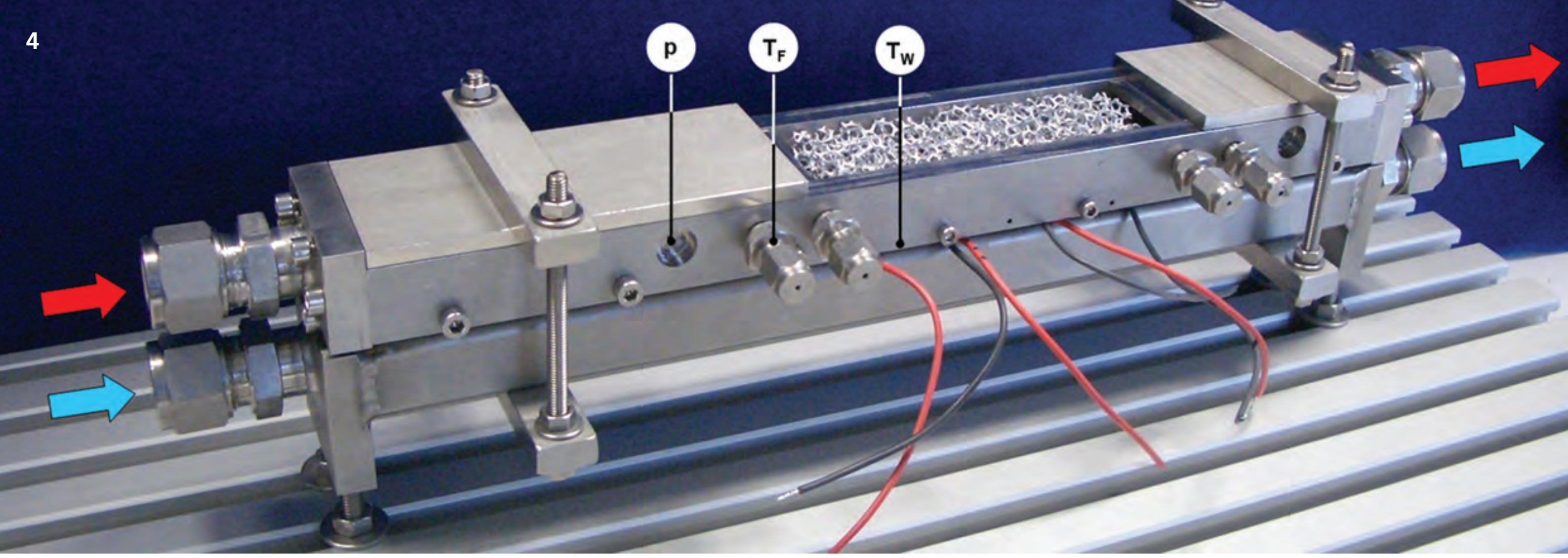


Fig. 3 SEM- Analysis of the reaction layer after the pre-contacting of Mn-Silicide with Ni-Foil by SPS at 800 °C.

A cutting process with adjusted parameters was developed at Fraunhofer IFAM for the precise dicing of the brittle pre-contacted silicides into thermoelectric legs. Furthermore, the technology and a mounting device were developed for the simultaneous brazing of the Mg- and Mn-silicide legs and final assembling of the modules.



Module characterization

The electric power output of a module strongly depends on the temperature difference between the ends of the thermoelectric legs. The temperature difference between the hot side fluid (for example combustion exhaust gas) and the cold side fluid (for example cooling water) is normally fixed. Therefore, the usable temperature difference for the Seebeck-Effect can only be maximized by minimizing the thermal resistances between the heat carrier fluids and the thermoelectric module. This includes all existing thermal contact resistances, especially the hot gas side convective heat transfer.

In the thermo-technical laboratory at Fraunhofer IFAM Dresden, a steady-state plate method is applied to measure the effective thermal conductivity of modules. This test facility allows to quantify the thermal resistance of necessary coatings or additional layers on the module even with variable contact pressures in the case of constructions screwed together.

In addition, a test flow-channel was constructed and calibrated to characterize modules thermally in their final assembled form under temperature and flow parameters close to real operating conditions. For this purpose, the modules are positioned between two flow-channels – one with a hot air flow (up to 500 °C) and one with a water flow (up to 90 °C), respectively. The flow conditions are adjusted to correspond to a channel flow model.

In the hot air channel the heat transfer can be optimized by implementing metallic structures (for example cellular metal or fin structures). Mass flow, pressure as well as fluid and wall temperatures are measured and analyzed. The thermoelectric modules are coupled to an adjustable electronic load. A detailed mathematical algorithm (validated by using measured data) considers electric, thermal and thermoelectric effects and allows for the numerical simulation of the influence of different parameters on the electric module efficiency.

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4 *Two part Model-Flow-Channel for thermal characterization of thermoelectric modules – top: hot air flow, bottom: cooling water (basic components, thermal insulation applied after completing all pipes and instruments).*

TITEL *Four-legs thermoelectric module (demonstrator) with two Mg- and Mn-Silicide legs, respectively.*