Local mechanical properties of advanced skutterudites processed by various routes

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Abstract. Skutterudites are an important class of thermoelectric p- and n-type materials and they have already achieved fair efficiencies for the conversion of heat to electricity. Nevertheless researchers try to further enhance the figure of merit, ZT, by various ways. In this work we compare the microstructure and mechanical properties of an industrial p-type DD<sub>3</sub>Fe<sub>3</sub>CoSb<sub>12</sub> skutterudite powder processed by several routes containing various combinations of ball milling, hot pressing, cold pressing and high pressure torsion. Details of the resulting microstructure are studied by means of analytical electron microscopy as well as by means of local mechanical testing.

1. Introduction

Skutterudites are known as excellent thermoelectric (TE) materials and have already achieved good efficiencies for the conversion of heat to electricity. Researchers try to further enhance the figure of merit, ZT, by various ways [1-4]. Among several groups of state-of-the-art TE materials, filled skutterudites continue to draw much scientific interest and have also been identified as one of the top candidates for real-life thermoelectric applications, particularly in the 300–800 K range. Didymium (DD) represents a natural double-filler composed of about 5 wt. % Pr + 95 wt. % Nd, being cheaper than rare earth elements. The TE performance may be enhanced by nanostructuring procedures resulting in submicron crystallites.

In this work we compare the microstructure and mechanical properties of an industrial p-type DD<sub>3</sub>Fe<sub>3</sub>CoSb<sub>12</sub> skutterudite powder processed by several routes of thermomechanical processing leading to compacting and nanostructuring of the material. Overall characterization of these materials including measurements of temperature dependent electrical resistivity, Seebeck coefficient, power factor, and figure of merit as well as measurements of hardness and elastic moduli was completed and is summarized in [5].

2. Materials and experiments

The material studied was a commercially produced p-type DD<sub>3</sub>Fe<sub>3</sub>CoSb<sub>12</sub> skutterudite powder (Treibacher Industries AG, TIAG, Austria). It was further either (i) hot pressed (Ar atmosphere, 700 °C, 56 MPa, 30 min, HP), or (ii) cold pressed (resulting in pellets 1 cm in diameter and about 1 mm in height, CP) followed by high pressure torsion (Ar atmosphere, 375 °C, applying 4 GPa and 1 revolution, HPT), or (iii) ball milled (BM) followed by HP and HPT; for details see [5].
Thin cross sectional lamellae were prepared by focussed ion beam (FIB) in a Tescan LYRA 3XMU SEM×FIB scanning electron microscope (SEM). A Philips CM12 STEM transmission electron microscope (TEM) and a FEI Titan Themis 60-300 cubed high resolution TEM with high sensitivity EDX system (0.7 rad solid angle) were then used to study details of the microstructure.

The mechanical properties were studied using nanoindentation techniques by means of a Hysitron TI950 (Bruker) triboindenter. The nanoindentation tests were carried out using a Berkovich diamond tip with a diameter less than 50 nm. A nanoscale measuring head with resolution of 1 nN and load noise floor less than 30 nN was used for this study. Two testing modes were employed in the range of indentation loads from 0.1 to 10 mN, namely quasi-static nanoindentation and quasistatic tests with several unloading segments. The quasistatic indentation tests were carried out in a load controlled regime at a constant loading rate of 0.2 mN/s. Both the partial unload regime and the nanodynamical analysis were carried out in a constant strain rate regime. The standard procedure proposed by Oliver and Pharr [6] was used for the evaluation of the hardness and elastic modulus. The hardness and effective elastic modulus maps were obtained on areas of 5×5 μm². The effective elastic modulus can be expressed as

\[ E_{\text{eff}} = \frac{E_s}{1 - \nu^2} \frac{E_{\text{ind}}}{E_{\text{ind}} - E_r} \left(1 - \nu_{\text{ind}}^2 \right), \]

where \( E_s, \nu, E_{\text{ind}} \) = 1141 GPa and \( \nu_{\text{ind}} = 0.07 \) are the Young’s moduli and Poisson ratio values of samples and the diamond indenter, respectively. \( E_r \) is the reduced modulus value.

Moreover, nanodynamic mechanical analysis (nanoDMA) in the range from 0.1 to 300 Hz served to study the local mechanical properties of the samples prepared. The modulus mapping capability was applied on areas 5×5 μm² and 1×1 μm² to obtain quantitative maps of the storage and loss stiffness and the storage and loss modulus. A sharp CubeCorner diamond tip with diameter less than 40 nm was used for the modulus mapping studies.

3. Results and discussion
According to the SEM observations the HP, BM-HP-HPT, CP-HPT and the annealed CP-HPT samples showed substantial differences in their grain size. The HP sample consisted of grains in the size of 10μm. The BM-HP-HPT sample exhibited a bimodal structure (mixture of coarse grains with diameter ≤10 μm and fine grains) similarly to the CP-HPT sample which also showed grains in the size of almost 10 μm mixed with fine and nano-sized grains. The annealed CP-HPT sample exhibited a relatively homogeneous grain structure.

Mechanical properties of DD₃Fe₂CoSb₁₂, prepared by different technological procedures, were studied using both quasistatic nanoindentation with a maximum load of 5mN and quasistatic nanoindentation with 20 unloading segments and a maximum load of 10mN. The results obtained with these techniques were in good accordance.

**Table 1.** Summary of mechanical properties of DD₃Fe₂CoSb₁₂ samples. HV is the Vickers hardness, \( E_{\text{MI}} \) is the Young’s modulus received from microindentation tests (maximum load of 1 N, loading rate of 0.1 N/s and a loading time of 10 s) and \( \nu \) is Poisson’s ratio as reported in ref. [5]. \( H_{\text{IT}} \) is the indentation hardness and \( E_r \) is the reduced elastic modulus, \( E_{\text{eff}} \) is the effective elastic modulus and \( E_{\text{NI}} \) is the Young’s modulus determined on the basis of the nanoindentation tests.

| DD₃Fe₂CoSb₁₂ processing | HV [GPa] | \( E_{\text{MI}} \) [GPa] | \( \nu \) | \( H_{\text{IT}} \) [GPa] | \( E_r \) [GPa] | \( E_{\text{eff}} \) [GPa] | \( E_{\text{NI}} \) [GPa] |
|-------------------------|---------|-------------------|------|-------------|-------------|----------------|----------------|
| CP-HPT                  | 525 [5] | 140 [5]           | -    | 7±2         | 134±9       | 140±10         | -              |
| CP-HPT-ann.             | 506 [5] | 136 [5]           | -    | 8±3         | 140±9       | 160±10         | -              |
| BM-HP-HPT               | 522 [5] | 0.23 [5]          | 7±3  | 130±8       | 147±9       | 139±8          | -              |
| HP                      | 510 [5] | 0.225 [5]         | 7.4±0.3 | 142±4       | 162±5       | 154±4          | -              |

It was found that the bimodal grain size distribution of the samples also manifested itself in the local mechanical properties. In each sample it was possible to find areas with relatively high hardness (around 9 GPa) and regions with a lower hardness (around 6 GPa). The CP-HPT sample exhibited a low amount of soft grains with hardness \( H_{\text{IT}} \) of 5.5 GPa and effective elastic modulus \( E_{\text{eff}} \) of 120 GPa. The
remaining part of the CP-HPT sample was characterized by $H_{IT}$ of up to 8.5 GPa and $E_{eff}$ of 155 GPa. The annealed CP-HPT sample exhibited grains with $H_{IT}$ of up to 10 GPa and $E_{eff}$ up to 170 GPa together with softer grains ($H_{IT} \sim 6.5$ GPa and $E_{eff} \sim 150$ GPa). In case of the BM-HP-HPT sample, $H_{IT}$ values were around 8 and 6.5 GPa and the $E_{eff}$ values were around 160 and 135 GPa in harder and softer regions, respectively. The HP sample exhibited relatively homogeneous mechanical properties ($H_{IT} \sim 7.4$ GPa and $E_{eff} \sim 160$ GPa). Moreover, soft particles ($\sim 1.5$ GPa and $E_{eff} \sim 40$ GPa) with a size up to 100 nm were found in the samples studied.

Mechanical properties of DD$_3$Fe$_3$CoSb$_{12}$ prepared by different technological procedures using both micro- and nanoindentation methods are compared in table 1. The microindentation results were obtained at a maximum load of 1N [5]. The nanoindentation results were obtained by means of quasistatic nanoindentation tests using a sharp Berkovich indenter (tip radius $R<50$ nm). The indentation hardness $H_{IT}$ and the reduced elastic modulus $E_r$ were calculated according to the Oliver&Pharr method [6]. Results obtained from 25 indentation tests from an area of $50\times50$ µm$^2$ were averaged. The effective elastic modulus was calculated according to formula (1). $E_{NI}$ is the Young's modulus, estimated from nanoindentation tests as $E_{NI}=E_r(1-v^2)$, where $v$ was used from ref. [5]. The microindentation and nanoindentation data show some differences because nanoindentation gave localized data from different grains whereas microindentation provided the average hardness over a larger area containing several grains.

In the further study thin lamellae were prepared by FIB for TEM observations of fine details of the microstructure. Long term high magnification EDX maps were collected in TEM to see at least qualitatively the elements’ distribution. As it can be seen on EDX maps in figure 1, precipitates of (Nd+Pr)-rich phases were often found both inside the skutterudite grains and at the grain boundaries. Possibly a small amount of the fillers was squeezed out of the icosahedral Sb-cage during HPT processing under a pressure of 4 GPa and formed rare earth oxides and antimonides.

The modulus mapping capability was applied to obtain quantitative maps of the storage and loss modulus. In figure 2 examples of storage modulus maps obtained at an oscillation frequency of 300 Hz and oscillation amplitude of 2 µN are shown. The loss modulus was negligible for both samples studied. In modulus maps the (Nd+Pr)-rich phases were observed as nanometre sized areas with a low elastic modulus around 50-80 GPa.

**Figure 1.** EDX maps showing (Nd+Pr)-rich precipitates in the grain interior.
Figure 2. Storage modulus mapping results obtained on an area of 1×1 µm² of DD₃Fe₃CoSb₁₂ samples prepared using CP-HPT (a), annealed CP-HPT (b), BM-HP-HPT (c) and HP (d).

4. Conclusions
The processing route influenced both the microstructure and the local mechanical properties of DD₃Fe₃CoSb₁₂ samples. Samples which underwent high pressure torsion showed a bimodal grain structure and mechanical properties. According to nanoindentation and EDX results, the samples contained soft (Nd+Pr)-rich precipitates inside the grains and at the grain boundaries.

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