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Structure, microstructure and microhardness of rapidly solidified $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ ($x = 0.45, 0.50, 0.70, 1$) thermoelectric compounds

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ABSTRACT

Skutterudites are interesting compounds for thermoelectric applications. The main drawback in the synthesis of skutterudites by solidification of the melt is the occurrence of two peritectic reactions requiring long annealing times to form a single phase. Aim of this work is to investigate an alternative route for synthesis, based on rapid solidification by planar flow casting. The effect of cooling rate on phases formation and composition, as well as on structure, microstructure and mechanical properties of the filled $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ ($x = 0.45, 0.50, 0.70, 1$) skutterudites was studied. Conversely to slowly cooled ingots, rapidly quenched ribbons show skutterudite as the main phase, suggesting that deep undercooling of the liquid prevents the nucleation of high temperature phases, such as (Fe,Ni)Sb and $(Fe,Ni)Sb_2$. In as-quenched samples, a slightly out of equilibrium Sm content is revealed, which does not alter the position of the *p*/*n* boundary; nevertheless, it exerts an influence on crystallographic properties, such as the cell parameter and the shape of the Sb_4 rings in the structure. As-quenched ribbons show a fine microstructure of the skutterudite phase (grain size of 2–20 μm), which only moderately coarsens after annealing at 873 K for 4 days. Vickers microhardness values (350–400 HV) of the skutterudite phase in as-quenched ribbons are affected by the presence of softer phases (*i.e.* Sb), which are homogeneously and finely dispersed within the sample. The skutterudite hardens after annealing as a consequence of a moderate grain growth, which limits the matrix effect due to the presence of additional phases.

1. Introduction

The current effort in searching materials to be profitably employed in thermoelectric devices is directed toward classes of compounds such as clathrates [1], half-Heusler phases [2], tetrahedrites [3] and paracostibite [4,5]. In addition to these compounds, filled skutterudites play a key role due to the relatively easy tunability of their electronic properties through suitable doping [6–8].

Skutterudites MX_3 (M ≡ Co, Rh, Ir and X ≡ P, As, Sb) are known since the first study performed by Oftedal in 1928 [9]. They crystallize in a body-centred cubic cell (Pearson symbol *cI*32, isotypic crystal: $CoAs_3$) belonging to the $Im\bar{3}$ space group, characterized by two atomic positions, namely the 8*c* (¼, ¼, ¼) and the 24g (0, *y*, *z*), which are occupied by M and X, respectively. As a consequence of this atomic arrangement, an X_{12} icosahedral cage forms around the 2*a* site located in (0, 0, 0), which can host atoms of proper size, such as alkaline-earths or lanthanides. In the case of complete filling of all the available cavities by a rare earth (RE), the stoichiometry REM_4X_{12} occurs. Filling the cages by the aforementioned atoms results particularly advantageous for efficient thermoelectric materials, since it is generally expected to reduce the phonon mean free path, λ_{ph}, and thus to enhance the figure of merit *ZT* [10]. This prediction is indirectly confirmed in many cases by the high values of the RE displacement parameter [11–14], which point at the occurrence of a rattling movement of the guest atom within the cavity.

From the electronic point of view, the insertion of a foreign atom into the cell alters the electronic count of the skutterudite. $CoSb_3$, for instance, if treated within the Zintl's concept [15], is expected to be a

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diamagnetic semiconductor [6], as experimentally confirmed; for this reason it cannot accept the injection of electrons from a foreign atom, which would perturb its electronic stability. On the contrary, if Co is substituted by a lighter transition metal (*e.g.* Fe) or by a Fe/Ni mixture, filling by a cation is needed to compensate the electronic deficiency. In $CeFe_4P_{12}$, for example, Ce^{4+} provides the missing electrons necessary to reproduce the electronic count of a diamagnetic semiconductor [16]. In general, a linear correlation is observed between the amount of each transition metal M and the content of the filler atom [17]. Nevertheless, since the exact compensation of the electron deficiency by filling is generally not possible, *p*- and *n*-type skutterudites occur, depending on the excess of electrons or holes with respect to the fully compensated diamagnetic semiconductor parent compound. It has been often observed that the amount of filler atom able to enter the structure is dependent on its oxidation state and essentially independent of its chemical identity [7,14], thus implying that even the position of the *p*/*n* crossover is strictly related to the valence state of the filler. In Fe/Ni-based skutterudites, such as in $Sm_y(Fe_{1-x}Ni_x)_4Sb_{12}$ [13,18] and in $DD_y(Fe_{1-x}Ni_x)_4Sb_{12}$ (where DD is didymium, a mixture of Pr and Nd) [19], the *p*/*n* transition is located at *x* ranging between 0.63 and 0.65.

Several methods have been suggested for an effective synthetic procedure of filled skutterudites [20,21] and the most commonly used are derived from the one proposed by Sales et al. [22,23]. They consist in a melting process of all the starting elements, followed by a quenching in water or in air, and by a subsequent long annealing in vacuum, which is needed because the two peritectic reactions occurring on solidification are never completed upon cooling. An important issue dealing with the preparation of these compounds in a form suitable for the measurement of transport properties concerns the need for dense bulk samples: this goal is generally achieved by grinding and subsequently densifying the obtained powder by means of techniques such as spark plasma sintering (SPS) [24], hot pressing [12,19,25], cold pressing [17] or open die pressing (ODP) [26,27]. Rapid solidification methods, such as melt spinning [28], are useful to obtain fragile samples, which can be easily crushed and powdered before sintering [26,29]. Moreover, a partial amorphization of the structure can be expected too, which could result in a reduction of the phononic mean free path [30]. In addition, a possible effect of rapid solidification on the appearance or disappearance of small amounts of additional phases, on structural parameters relevant for the electronic properties of the material, as well as on microstructure, cannot be *a priori* excluded.

Aim of this work is to investigate the effects of a processing route based on planar flow casting on the synthesis and properties of skutterudites, since rapid solidification is considered responsible for a significant reduction in the preparation length [31,32]. $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ ($x = 0.45,\ 0.50,\ 0.70,\ 1,\ y = 0.15,\ 0.20,\ 0.45,\ 0.70$) samples underwent rapid solidification followed by an annealing process in vacuum at 873 K. Composition, structural, microstructural and microhardness properties of specimens were investigated, both prior and after the annealing process, and compared to the ones of as sintered samples [13,33], in order to reveal the effect of the rapid solidification and the subsequent thermal treatment on relevant parameters for thermoelectric applications. The results obtained suggest that rapid solidification of $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ alloys is a promising processing route to obtain single phase precursor materials to be used in the sintering of dense thermoelectric skutterudites.

2. Materials and methods

2.1. Synthesis

Samples belonging to the $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ system were prepared with nominal $x = 0.45$, 0.50, 0.70, 1.00 and $y = 0.15$, 0.20, 0.45, 0.70 by direct reaction of pure elements Fe (Alfa-Aesar, 99.99 wt%), Ni (Alfa-Aesar, 99.99 wt%), Sm (NewMet, 99.9 wt%) and Sb (Mateck, 99.99 wt%). The Sm amount to be added to each starting mixture was chosen relying on the results reported in Ref. [13]; a slight excess of Sb compared to the stoichiometric content was employed to counterbalance possible losses due to its high vapor pressure. Pure elements were mixed as small pieces, put into Ar-filled silica ampoules, subsequently sealed under an Ar flow, and heated up to 1223 K for 3 h. Quenching in an iced water bath followed. The obtained samples were then annealed in vacuum at 873 K for 4 days (as-sintered samples, AS series [13]).

Rapidly solidified (RS) samples were obtained in the form of fragmented ribbons by a planar flow casting apparatus (Edmund Bühler GmbH). Each alloy obtained after the aforementioned quenching was induction melted under Ar atmosphere in a BN crucible and ejected by an Ar overpressure (0.2 bar) on a copper wheel rotating at 20 m s^{-1}. The so obtained ribbons (thickness: 20–30 μm) is called RS, and samples are hereafter named Fe40_rs, Fe50_rs and so on, according to the nominal % Fe content with respect to the total (Fe + Ni) amount.

Rapidly solidified samples were subsequently annealed in vacuum at 873 K for 5 days in order to investigate the effect of the thermal process on the structural and microstructural features of the material. The so prepared series is called ANN, and samples are named Fe40_ann, Fe50_ann and so on.

The described samples (RS and ANN series) are compared in terms of structure, microstructure and microhardness to as-sintered samples (AS series), *i.e.* to samples which did not undergo the rapid solidification process; data of the latter are taken from Ref. [13].

2.2. SEM-EDS

The overall microstructure, as well as the possible presence of additional phases, the Fe/Ni elemental ratio and the Sm content, were analyzed by scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) (Zeiss EVO 40, with Oxford Instruments Pentafet Link, software package: Oxford-INCA v. 4.07, standard: Co, acceleration voltage: 20 kV, working distance: 12 mm, live time: 40 s). In each ribbon the side cooled in contact with the copper wheel (wheel side) can always be distinguished from the free side (air side). Analyses of unpolished and unetched ribbons were performed both on the wheel and air sides, as well as on the cross sections. Microphotographs were taken by backscattered and secondary electrons, and EDS analyses were carried out on at least eight points or areas for each sample.

2.3. X-ray diffraction

Powders of both rapidly solidified and annealed samples were sieved through a 44 μm sieve, and analyzed by powder x-ray diffraction making use of a Bragg-Brentano powder diffractometer (PANalytical X'pert Pro, Co Kα radiation). Samples were placed on a zero-background Si sample-holder; acquisitions were performed in the angular range 10°–120°, with step 0.02° and time per step 17 s. Diffraction patterns were then refined by the Rietveld method employing the FullProf software [34]. For all the diffractograms, the background was optimized by linearly interpolating a set of ~70 points taken from the experimental pattern, and peak profiles were fitted by the pseudo-Voigt function. In order to obtain accurate values of the lattice parameter, diffraction patterns of each sample were also acquired by using Ge as an internal standard.