Interfacial Reactivity of the Filled Skutterudite Sm$_y$(Fe$_x$Ni$_{1-x}$)$_4$Sb$_{12}$ in Contact with Liquid In-Based Alloys and Sn

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Abstract: The study of the wettability of thermoelectric materials, as well as the search for the most proper brazing alloys, is of the maximum importance to get one step closer to the realization of a thermoelectric device. In this work, a wettability study of the filled skutterudite Sm$_y$(Fe$_x$Ni$_{1-x}$)$_4$Sb$_{12}$ by Sn and In-based alloys is presented. Samples, having both $p$- and $n$- characters were prepared by the conventional melting-quenching-annealing technique and subsequently densified by spark plasma sintering (SPS). Afterward, wettability tests were performed by the sessile drop method at 773 K for 20 min. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analyses performed on the cross-section of the solidified drops suggest quite a complicated scenario due to the coexistence and the interaction of a large number of different elements in each analyzed system. Indeed, the indication of a strong reaction of In-based alloys with skutterudite, accompanied by the formation of the InSb intermetallic compound, is clear; on the contrary, Sn exhibits a milder reactivity, and thus, a more promising behavior, being its appreciable wettability, whilst coupled to a limited reactivity.

Keywords: thermoelectricity; skutterudites; wettability; sessile drop; electron microscopy; intermetallic compounds

1. Introduction

Nowadays, the general lack of energy and its always increasing demand leads us to explore different fields and technologies with the aim of searching for new energy sources or energy-saving pathways. As a response, thermoelectricity is an attractive effect based on the ability of materials to directly convert thermal energy into electrical power. The thermoelectric approach can be employed in different fields dealing with fundamental problems of sustainability and eco-environmental compatibility. Thermoelectric generators (TEGs) can be used in every circumstance where it is essential to produce energy in small volumes and with neither moving parts nor working fluids [1]; alternatively, they can be coupled to traditional energy production technologies in order to recover waste heat where there is a lack of conversion efficiency [2,3]. Moreover, energy harvesting is of the primary importance for the development of the Internet of Things [4,5].
Following the idea behind the PGEC (Phonon Glass Electron Crystal) concept [6], which states that a good thermoelectric material should ideally conduct heat like a glass and electricity like a crystal, the experimental approach aiming at filling structural cavities of the host structure with ions of the proper size is commonly pursued in order to insert scattering centers able to depress phonon thermal conductivity without virtually affecting electrical conductivity [7]. Some examples of such currently studied materials are Heusler [8,9] and half-Heusler phases [10–13], clathrates [14,15], and filled skutterudites [16–21].

Filled skutterudites \( R_xM_yX_{12} \), in particular, are of significance due to the high \( ZT \) values of some of them, reaching a peak of ~1.7 for the \( n \)-type \((Sr,Ba,Yb)Co_4Sb_{12}\) [22]. Moreover, the electronic content of this family of compounds can be easily tuned by employing, in place of Co, other transition metals or mixtures of them, giving rise to a lot of different compounds, such as Ni- [23], Fe/Ni- [6,24,25] and Fe/Co-based ones [26–28].

A TEG device is composed of \( n \)- and \( p \)-conducting legs made of thermoelectric material, electrically coupled in series and thermally in parallel. One step closer to the design of a thermoelectric device is the availability of reliable joining methods linking thermoelectric material to metal electrodes; this can be done by different techniques, such as mechanical [29] or chemical [30] methods. Brazing is included within the latter techniques. When the assembly of skutterudite-based modules is taken into account, the issue related to the joining of the thermoelectric material to electrodes is particularly challenging, mainly due to the difficulties posed by the presence of a large amount of Sb, which tends to form stable and brittle intermetallic compounds at the interface, negatively affecting the reliability of the joint [30–35] and the integrity of the thermoelectric material itself. For this reason, the metallization of the thermoelectric material is often attempted, in order to interpose a diffusion barrier between skutterudite and electrode, and possibly to enhance the wettability of the thermoelectric material by the braze; to this purpose, metals such as Ni [36,37], Mo [38], Co [30], Ti [39], Pd [40], Au [39] and Pt [39] are commonly employed. Ag-Cu alloys are by far the most diffusely used brazes to join CoSb\(_3\) [30,41], due to the relatively low eutectic temperature (1052 K [42]) and to the good wettability of Ni, which is often used as a metallization layer.

In this work, the wettability of the filled skutterudite \( Sm_{y}(Fe_xNi_{1−x})_4Sb_{12}\) was studied by employing two different brazes. The cited composition was chosen due to its promising thermoelectric properties [43–45], as described in previous works of the present research group, where also the structural [46–48], mechanical [47,49] and electrochemical [50,51] features of the material were investigated. The temperature of a joint process involving \( Sm_y(Fe_xNi_{1−x})_4Sb_{12}\) has to be carefully chosen since it is restricted to a limited range by the operating temperature of the thermoelectric device (the studied skutterudite system shows the maximum \( ZT \) value at ~700 K) and by the peritectic decomposition temperature of the material (~873 K [52]). Due to the lack of reliable soldering/brazing alloys in this temperature range, new methods had to be sought: the partial transient liquid phase bonding (PTLPB) applied to non-metallic materials allows to overcome the issue of producing a joint without affecting the skutterudite integrity as a consequence of high process temperatures [53–55]. This technique exploits metallic interlayers which melt, thus ensuring the contact and adhesion of the adjoining surfaces, and form new phases with higher melting temperatures by means of diffusion phenomena. In a typical PTLPB setup for non-metallic materials, a low-melting layer is interposed between the adjoining material and a thick high-melting layer; if the setup is properly designed, the low-melting layer melts, wets the surfaces assuring adhesion and diffuses into the high-melting layer leaving behind a phase with higher melting temperature than that used in the process. It follows that the first step to undertake is to test wetting and interfacial phenomena of the metallic liquid interlayers in contact with the materials to be joined. To the authors’ knowledge, no papers or patents can be found in the literature regarding the wettability of the \( Sm_y(Fe_xNi_{1−x})_4Sb_{12}\) skutterudite. To the purpose of exploring the possibility of producing joint by PTLP bonding using Sn- and In-based low-melting fillers [56,57], in this work, both wetting and interfacial reactivity of \( Sm_y(Fe_xNi_{1−x})_4Sb_{12}\) were studied for the first time using pure Sn and an In-based alloy in the wetting tests performed at 773 K for 20 min.
by the sessile drop method. Wettability tests were carried out on squared samples obtained after densification by SPS.

2. Materials and Methods

2.1. Synthesis and Compositional Characterization of Substrates

Four compositions belonging to the Sm_y(Fe_{x}Ni_{1-x})_4Sb_12 system (x = 0.50, 0.63, 0.80, 1; y = 0.12, 0.33, 0.53, 0.75) were synthesized by the conventional melting-quenching-annealing technique. Small pieces of pure elements Fe (Alfa-Aesar, Kandel, Germany, 99.99 wt. %), Ni (Alfa-Aesar, Kandel, Germany, 99.99 wt. %), Sm (NewMet, Waltham Abbey, UK, 99.9 wt. %) and Sb (Mateck, Jülich, Germany, 99.99 wt. %) were polished with the purpose of removing any surface oxide layer; they were weighed in stoichiometric amounts and placed into a quartz tube subsequently closed under vacuum, in order to limit oxidation and hinder the possible occurrence of undesired reactions. The elements mixture was then reacted at 1223 K for 1 h and rapidly cooled in order to prevent the crystal growth of extra phases. The maximum Sm amount that can be hosted by the skutterudite was calculated by considering the results obtained by Artini et al. [48]. Sb was used in slight excess (~1%), with the aim to compensate for the partial loss caused by its non-negligible vapor pressure (~10^{-1} Pa at 873 K [58]). As-cast samples were then annealed in the same quartz tube at 873 K for seven days; samples were named FeXX_ann, where XX stands for the Fe % amount in regard to the total (Fe + Ni) amount.

With the purpose of obtaining homogeneous substrates for wettability tests, samples were ground by ball milling and subsequently densified using the SPS machine CSP-KIT-02121 by S.S. Alloy Corporation, Tokyo, Japan, in the laboratory of the Toyota Technological Institute in Nagoya (Japan). Powders were densified heating samples at a rate of 30 K/min up to 773 K; a pressure of 50 MPa and a current of 200 A was applied for 20 min. Four discs of 2 cm of diameter were obtained, and samples were named FeXX SPS, where XX stands, as before, for the Fe % amount.

Both powders and dense discs were analyzed by scanning electron microscopy coupled to energy dispersive system (SEM-EDS) by means of a Zeiss EVO 40 microscope (Carl Zeiss AG, Oberkochen, Germany), with Oxford Instruments Pentafet Link (Oxford Instruments, Abington, UK), software package: Oxford-INCA v. 4.09 (Oxford Instruments, Abington, UK), standard: Co, acceleration voltage: 20 kV, working distance: 8.5 mm, live time: 40 s. Samples were micrographically polished and coated with a graphite layer prior to be analyzed.

2.2. Preparation of the Brazing Alloys

Wettability of skutterudites was tested using two different alloys—an In-based alloy (80% In and 20% eutectic alloy Ag_{0.62}Cu_{0.38}, hereafter named AgCuIn), and pure Sn (melting point = 504.9 K, purity: 99.9999%, Goodfellow, Huntingdon, UK). Before the wetting tests, the AgCuIn alloy was prepared by combining appropriate amounts of In (purity: 99.9999%, Goodfellow, Huntingdon, UK) and eutectic AgCu (purity: 99.95%) and melting them in an arc melting furnace. The alloy was melted five times in order to ensure compositional homogeneity. Arc melting was carried out under an Ar atmosphere; before this procedure, a small drop of Zr was melted with the purpose of pick-up any residual oxygen. A weight loss of 0.001–0.002 g was quantified after the preparation, which indicates that evaporation of the molten alloy can be neglected. Both substrates and brazing alloys were carefully cleaned in ethanol using an ultrasonic machine before wetting tests.

2.3. Sessile Drop Experiments

Sessile drop wetting tests were carried out in a tubular alumina furnace (T_{max}~1800 K), fully described in [59], equipped with the ad hoc designed ASTRAView image analysis software (version 2006, running on NI-Labview environment, developed at CNR-ICMATE, Genoa, Italy), which allows obtaining contact angles and drop dimensions during each experimental run. Temperature is read by a type S thermocouple, located just underneath the test sample, which was previously calibrated using
were extracted from the hot region, moved to the cold sector, and cooled down to room temperature. The weight loss during the wetting tests resulted in being below 1%. The substrate significant pore reduction, which reflects in a density value exceeding 92% for all the compositions [44].

Moreover, the small amounts of extra phases recognizable in annealed samples [Sb, (Fe,Ni)SmSb3, SmSb2, FeSb2] cannot be detected in dense samples, meaning that the SPS treatment also contributes in improving phase homogeneity. SEM microphotographs taken on Fe100 skutterudites before and after SPS are reported in Figure 1, as representative examples. The densification treatment also induces a significant pore reduction, which reflects in a density value exceeding 92% for all the compositions [44].

Table 1 reports an overview of the experimental compositions of skutterudites as obtained from EDS analyses; all the samples present a composition which is very close to the nominal one [44]. Moreover, the small amounts of extra phases recognizable in annealed samples [Sb, (Fe,Ni)SmSb3, SmSb2, FeSb2] cannot be detected in dense samples, meaning that the SPS treatment also contributes in improving phase homogeneity. SEM microphotographs taken on Fe100 skutterudites before and after SPS are reported in Figure 1, as representative examples. The densification treatment also induces a significant pore reduction, which reflects in a density value exceeding 92% for all the compositions [44].

### Table 1. Experimental composition and extra phases in FeXX ann samples.

| Sample  | Experimental Composition | Additional Phases (before SPS) |
|---------|--------------------------|--------------------------------|
| Fe100   | Sm0.75(3)(Fe0.95(1))4Sb12 | Sb, SmSb2, FeSb2               |
| Fe80    | Sm0.53(4)(Fe0.74(1)Ni0.20(1))4Sb12 | Sb, SmSb2                     |
| Fe63    | Sm0.33(5)(Fe0.60(1)Ni0.34(1))4Sb12 | -                             |
| Fe50    | Sm0.12(5)(Fe0.47(1)Ni0.47(1))4Sb12 | Sb, (Fe,Ni)SmSb3              |

**Figure 1.** SEM microphotographs taken by backscattered electrons (BSE) on (a) Fe100_ann and (b) Fe100_SPS, respectively.
3.2. Wettability Study

3.2.1. AgCuIn Alloy

The In-based alloy in contact with skutterudites started upon melting to wet and spread over the surface (see Figure 2); a strong reactivity between the alloy and the substrate could be detected. The occurrence of remarkable amounts of solid phases during the test made it impossible to report a final contact angle. The strong interaction can be easily observed in Figure 2d, where the skutterudite substrate appears even deformed due to intense reactivity. This behavior is roughly the same whatever the Fe amount in the skutterudite.

![Figure 2](image-url) Drop profiles of Fe50 in contact with AgCuIn at (a) 0 s from the start of melting, (b) 100 s, (c) 600 s, and (d) 1200 s.

Figure 3 shows the SEM pictures of the solidified drops deriving from wetting tests performed with AgCuIn. It can be easily recognized that reactivity was strong, because the classical shape of a solidified drop is not recognizable, and substrates appear heavily damaged.

![Figure 3](image-url) Top view of the drops for samples (a) Fe63_SPS and (b) Fe50_SPS in contact with the AgCuIn alloy.

Figures 4 and 5 show the cross-section of the Fe100_SPS and Fe50_SPS samples after interaction with the AgCuIn alloy, respectively. Substrates did not retain a flat surface due to the remarkable interaction with the liquid, and large reaction zones are recognizable.

Coming to microchemistry, as shown in Table 2, the scenario is quite complicated by the presence of a considerable number of elements; the most relevant feature is the formation of the InSb phase, which was found all over the drop interspersed in a solidified phase formed of Fe, Sb, Sm, Ag, Cu, In. At the skutterudite/solidified drop interface, an infiltrated zone was observed, which was formed of the same phases. Similar reactive microstructures were observed for all the skutterudites in contact with AgCuIn with an increasing reactivity taking place with decreasing the Fe amount (Figure 5).
that wetting is guided by interfacial phenomena. Asymmetry of the drop profile, resulting in different spreading kinetics lasting several minutes from melting was observed, indicating the contact angle, was observed for the Sn drops, and the formation of solid phases on the drops during tests was limited, as can be seen in Figure 6.

3.2.2. Sn

When skutterudites were put in contact with pure Sn, the melting process proceeded with a significantly reduced reactivity in comparison to the previous case: drops appear considerably more rounded, and the formation of solid phases on the drops during tests was limited, as can be seen in Figure 6.

For this reason, it was possible to obtain the plots of contact angle vs. time (see Figure 7) and to measure contact angles (see Table 3). An increased wettability, corresponding to a lower value of the contact angle, was observed for the n-composition Fe50_SPS with respect to other samples. For all the Sn drops, spreading kinetics lasting several minutes from melting was observed, indicating that wetting is guided by interfacial phenomena. Asymmetry of the drop profile, resulting in different

![Figure 4. (a) SEM-EDS micrograph (BSE) of the cross-section of Fe100_SPS after interaction with AgCuIn. (b) and (c) SEM-EDS (BSE) magnifications of two selected areas indicated by rectangles in (a)](image)

![Figure 5. (a) SEM-EDS micrograph (BSE) of the cross-section of Fe50_SPS after interaction with AgCuIn. (b) SEM-EDS (BSE) magnification of a selected area indicated by rectangle in (a)](image)

| Sample          | Region | Fe | Ni | Sb | Sm | Ag | Cu | In  | Possible Phase |
|-----------------|--------|----|----|----|----|----|----|-----|----------------|
| Fe100-AgCuIn    | A      |    |    | 50.0 | 0.1 |    |    | 49.9 | InSb           |
|                 | B      | 3.5 |    | 15.0 | 1.0 | 6.2 | 3.2 | 71.1 |                |
| Fe50-AgCuIn     | C      |    |    | 50.3 |    |    |    | 49.7 | InSb           |
|                 | D      | 20.3 | 13.1 | 65.8 | 0.4 |    | 0.4 |     |                |

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values of the right and left contact angles, was also observed, due to the pinning of the liquid at the triple line (i.e., the line of coexistence of the liquid, solid and vapor phases) as a consequence of porosities and asperities of the surface.

Figure 6. Drop profiles of Fe50_SPS in contact with pure Sn at (a) 0 s, (b) 100 s, (c) 600 s, and (d) 1200 s from melting.

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Figure 7. Trend of the contact angle as a function of time of pure Sn on (a) Fe50_SPS, (b) Fe630_SPS, (c) Fe80_SPS, and (d) Fe100_SPS.

Table 3. Summary of the contact angles measured for pure Sn on skutterudites.

| Sample    | Left Angle | Right Angle |
|-----------|------------|-------------|
| Fe50_SPS  | 55°        | 55°         |
| Fe63_SPS  | 70°        | 50°         |
| Fe80_SPS  | 80°        | 80°         |
| Fe100_SPS | 80°        | 105°        |

At variance with the In-based alloy, Sn exhibited a reduced reactivity towards skutterudites, and the shape of the solidified drops are better recognizable (see Figure 8).
As shown in Figure 9, due to the reduced reactivity, the overall integrity of the substrate was preserved, and the skutterudite surface remained flat, while a large infiltration zone of the liquid into the solid was observed, as observable in Figure 10. The microstructural scenario was consequently quite simpler, as can be seen in Table 4: the EDS analysis revealed the formation of the Sb2Sn3 intermetallic both in the drop bulk and in the infiltration zone. The interfacial behavior and the final microchemistry were similar for all the skutterudite compositions; also, for these systems, a more intense reactivity was observed at lower Fe amounts, accounting for the increased wettability.

**Figure 8.** Top view of the drops for samples (a) Fe100_SPS and (b) Fe80_SPS in contact with pure Sn.

**Figure 9.** (a) SEM-EDS micrograph (BSE) of the cross-section of Fe100_SPS after interaction with pure Sn at 773 K; (b) SEM-EDS (BSE) magnification of a selected area indicated by rectangle in (a).

**Figure 10.** (a) SEM-EDS micrograph (BSE) of the cross-section of Fe50_SPS after interaction with pure Sn at 773 K; (b) SEM-EDS (BSE) magnification of a selected area indicated by rectangle in (a).

| Sample      | Fe  | Ni  | Sb  | Sm | Sn          | Possible phase                  |
|-------------|-----|-----|-----|----|-------------|---------------------------------|
| Fe100_SPS   | 0.6 | 19.7| 0.2 | 86.9| Sn(Sb) + Sb | FeSn2                            |
| Fe50_SPS    | 0.1 | 0.1 | 43.3| - 56.5| Sb2Sn3        |                                 |
| Fe80_SPS    | 0.1 | 0.1 | 60.7| - 39.3| FeSn          |                                 |
| In-based    | 0.1 | 0.1 | 43.3| - 56.5| FeSn          |                                 |
| AgCuIn      | 0.1 | 0.1 | 43.3| - 56.5| FeSn          |                                 |
| Fe100_SPS   | 0.6 | 19.7| 0.2 | 86.9| Sn(Sb) + Sb | FeSn2                            |
| Fe50_SPS    | 0.1 | 0.1 | 43.3| - 56.5| Sb2Sn3        |                                 |
| Fe80_SPS    | 0.1 | 0.1 | 60.7| - 39.3| FeSn          |                                 |
| In-based    | 0.1 | 0.1 | 43.3| - 56.5| FeSn          |                                 |
| Fe100_SPS   | 0.6 | 19.7| 0.2 | 86.9| Sn(Sb) + Sb | FeSn2                            |
| Fe50_SPS    | 0.1 | 0.1 | 43.3| - 56.5| Sb2Sn3        |                                 |
| Fe80_SPS    | 0.1 | 0.1 | 60.7| - 39.3| FeSn          |                                 |
| In-based    | 0.1 | 0.1 | 43.3| - 56.5| FeSn          |                                 |

**Table 3.** Summary of the contact angles measured for pure Sn on skutterudites.

As observed from microstructures, the main feature of the interfacial phenomena during the process due to the strong reactivity with skutterudites, which led to the destruction of the starting substrates. On the other hand, the weaker reactivity of Sn with skutterudites, accompanied with the shape of the solidified drops are better recognizable (see Figure 8).

Regarding the tests with AgCuIn, the InSb formation was accompanied by the solidification of the In-based melt without forming any other interfacial compound, and they were found as indicated in Figure 9 (regions A and B) and 10 (regions C and D); at least five spots were observed, and liquid drops maintained their shape during the high-temperature experiments.
Table 4. EDS chemical analysis (at. %) of different regions identified in the wetting samples tested with Sn and indicated in Figure 9 (regions A and B) and 10 (regions C and D); at least five spots were analyzed for each phase.

| Sample  | Region | Fe   | Ni   | Sb   | Sm   | Sn   | Possible Phase                  |
|---------|--------|------|------|------|------|------|----------------------------------|
| Fe100-Sn| A      | 0.6  | -    | 19.7 | 0.2  | 86.9 | Sn(Sb) + Sb_2Sn_3               |
|         | B      | 32.3 | -    | 6.7  | 0.3  | 60.7 | FeSn_2                           |
| Fe50-Sn | C      | 0.1  | 0.1  | 43.3 | -    | 56.5 | Sb_2Sn_3                        |
|         | D      | 16.2 | 16.2 | 56.3 | 0.4  | 10.9 | (Fe, Ni)Sb(Sn)_2                |

4. Discussion

As observed from microstructures, the main feature of the interfacial phenomena during wetting tests was the skutterudite dissolution with the formation of new compounds, namely InSb and Sb_2Sn_3, formed of Sb from the skutterudites, and from the base metal in the alloy.

Regarding the tests with AgCuIn, the InSb formation was accompanied by the solidification of the drop at the testing temperature of 773 K. Looking at the binary In-Sb phase diagram [60], one can see that InSb exhibits congruent melting at 800 K; this means that the liquid In alloy dissolves the skutterudite, and the solid InSb compound is rapidly formed—it was observed as the solid phase in our experiments. The presence of other elements, namely Ag and Cu in the alloy, and Fe and Ni in the skutterudite, does not change this reasoning to a great extent; these elements were dissolved in the In-based melt without forming any other interfacial compound, and they were found as solidification phase in the microstructure (phases B and D in Figures 4 and 5).

When moving to liquid Sn in contact with skutterudites, the situation is quite different. In fact, while a slight dissolution and interfacial reactivity were still present, no solidification phenomena were observed, and liquid drops maintained their shape during the high-temperature experiments. The process of spreading lasted several minutes (Figure 7) with kinetics, which are typical of dissolutive spreading processes [61], thus demonstrating that wetting and infiltration of the liquid into the solid substrate were guided by the dissolution of the substrate. Looking at the binary Sb-Sn phase diagram [62], it results that no solid intermetallic compounds can be formed at the testing temperature; for this reason, the interfacial compound Sb_2Sn_3, that undergoes peritectic reaction at 596 K, was formed upon cooling. The fact that the β-SbSn phase was not found suggests that the liquid composition remains rich in Sn (X_Sn > 0.82), indicating that the dissolution of the skutterudite happens just to a slight extent. According to microstructures, Fe released from skutterudite and introduced into the liquid reacted with Sn to form FeSn_2, while, for the skutterudites containing Fe and Ni, the phase (Fe, Ni)Sb_2 with Sn partially substituting Sb was detected.

To summarize, from the wetting tests, it has been shown that In is unfeasible for any joining process due to the strong reactivity with skutterudites, which led to the destruction of the starting substrates. On the other hand, the weaker reactivity of Sn with skutterudites, accompanied with good wettability, was more promising, provided that appropriate solutes were added to Sn in order to reduce the interfacial reactivity while maintaining the overall adhesion properties.

Therefore, further studies aimed at obtaining reliable joints through the transient liquid phase diffusion bonding (TLPB) technique should focus on the selection of the most proper interlayer compositions and thicknesses, as well as of process parameters (temperature, time, thermal cycles) in order to preserve the integrity of the skutterudite, and to assure good adhesion between the adjoining materials.

5. Conclusions

In this work, a wettability study of the filled skutterudite Sm_y(Fe_xNi_{1-x})_4Sb_12 system by Sn and In-based alloys was performed by the sessile drop method in order to find a proper brazing alloy able to connect the thermoelectric material to the device. The temperature range of a possible joining
method is limited by the operating temperature of the thermoelectric device (~773 K) and by the temperature at which Sm\textsubscript{(Fe\textsubscript{x}Ni\textsubscript{1-x})\textsubscript{4}Sb\textsubscript{12} under}goes the peritectic decomposition (873 K).

Due to the lack of reliable soldering/brazing alloys in the cited temperature range, the transient liquid phase bonding approach was attempted by using pure Sn and an In-based alloy as brazes. SEM-EDS analyses carried out on the cross-section of the solidified drops suggest a quite complicated scenario in both cases, due to the coexistence and the interaction of a large number of different elements in each analyzed system. Indeed, the clear indication of strong reactivity of the In-based alloys with skutterudite, accompanied by the formation of the InSb intermetallic compound, leads to consider In as inappropriate, and to exclude In-based alloys from further studies; on the contrary, Sn exhibits a more promising behavior, being its reactivity limited while coupled to good wettability and to an appreciable adhesion to the skutterudite substrate.

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