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**Oxidation Behavior and Integration into High Power Density Thermoelectric
Generators of Commercial Half-Heusler Alloys**

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Abstract

Half-Heusler (HH) alloys are among the best high-temperature thermoelectric (TE) materials able to operate above 700°C. Here, we report on a detailed experimental study of the oxidation behavior of commercial *n*- and *p*-type HH alloys, Hf_{0.6}Zr_{0.4}NiSn_{0.98}Sb_{0.02} and Hf_{0.2}Zr_{0.75}Ti_{0.05}CoSb_{0.8}Sn_{0.2}, respectively, and of their integration into high-power-density TE generators (TEGs). Oxidation behaviors were investigated from room temperature to 800°C in air on consolidated small pieces and large pellets using thermogravimetric/differential scanning calorimetry (TG/DSC). Combined with scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDXS) and powder X-ray diffraction (PXRD), these experiments enabled to identify the oxidation products and determined the oxidation pathway followed by each alloy. *n*-type HH initially slowly oxidizes upon heating to 350°C before rapidly oxidizing above this temperature, giving rise to a significant mass loss in the form of gaseous Sb₄O₆. The inward

diffusion of oxygen and outward diffusion of Sb lead to the formation of an inner core separated from an outer layer by an empty space. In spite of the higher amount of Sb in the *p*-type alloy, its oxidation behavior differs with no significant mass loss observed. In contrast, Sb reacts with Co to form oxides near the surface. A two-couple TEG was fabricated with leg's height $L = 2.0$ mm. A maximum output power density p_{max} of 7.5 W cm^{-2} was achieved under a temperature difference ΔT of 575 K. Of particular relevance, reducing L does not necessitate the insertion of mechanical buffers due to the excellent mechanical strength of these alloys. Using shortened legs allows for an increase in p_{max} at lower ΔT , thereby reaching a temperature range over which these alloys could remain stable against oxidation if further passivation optimization could be realized.

KEYWORDS: thermoelectric, half-Heusler, oxidation, thermoelectric generator, output power density

1. INTRODUCTION

Thermoelectric (TE) generators (TEGs) and Peltier coolers are all-solid-state devices that allow for a direct conversion of heat into electrical power and vice versa.¹⁻⁵ Their main advantages, which include noise- and vibration-free, lack of hazardous gas emission and long operational lifetime, have made TEGs a technology of choice for powering deep-space probes and Mars rovers for several decades. Their conversion efficiency is primarily dictated by the dimensionless thermoelectric figure of merit ZT of the active materials defined as $ZT = \alpha^2 T / \rho \kappa$ where T is the absolute temperature, α is the thermopower (or Seebeck coefficient), ρ is the electrical resistivity and κ is the total thermal conductivity.^{1,2} While several novel families of materials have emerged over the last two decades to replace state-of-the-art TE compounds,¹⁻

⁵ their integration into TEGs faces several important challenges that must be addressed for a large-scale industrial application of this technology.⁶⁻¹⁰

In addition to issues related to the chemical and thermal stability of the TE materials, these limitations are linked to the numerous interfaces between them and the metallic interconnections, yielding both additional electrical and thermal resistances that can adversely impact the overall performance of the TE device. The thermal resistances arising from the interfaces between the hot and cold thermal sources and the TEG further reduce the temperature difference ΔT across the hot and cold sides of the TE legs, exacerbating the decrease in conversion efficiency η and the maximum output power P_{max} . This last parameter is defined as $P_{max} = Ap_{max} = AN(\alpha_p - \alpha_n)\Delta T^2 / 4R_{TE}$ where A is the cross-section area of the legs, N is the number of thermocouples of the TEG, p_{max} is the output power density, $\alpha_{n,p}$ are the thermopowers of the n - and p -type TE compounds, and R_{TE} is the internal electrical resistance that must be equal to the external load impedance R_L to achieve P_{max} .¹¹⁻¹⁶ Although lowering the height of the legs decreases R_{TE} and hence, increases P_{max} , this simple strategy results in a strong increase in the thermal gradient favoring the generation of high thermomechanical stresses and impacts the conversion efficiency η due to a decrease in ΔT that originates from the numerous thermal resistances and the increasing influence of the electrical contact resistances with decreasing the height of the legs L . This approach is mainly limited by the fragility of the TE materials that often behave similarly as ceramics from a mechanical point of view. As recently demonstrated in the case of skutterudites, this issue can be overcome by using a non-conventional leg architecture through the addition of metallic composites on each side of the TE materials that act as mechanical buffers, without sacrificing the conversion efficiency.¹⁷ Alternatively, integrating materials showing superior mechanical properties is another strategy. In this regard, half-Heusler (HH) alloys are materials of choice due to their excellent mechanical properties with respect to state-of-the-art TE materials and similar TE performance. Over the

last years, the integration of these alloys in TEGs has been successfully achieved, achieving high η values of up to 11% and p_{max} of 11.5 W cm⁻² under ΔT of ~670 K for leg's height of 2 mm.¹⁸⁻⁴³

Beyond the optimization of the performance of the TE materials and the architecture of the legs, their oxidation behavior within the operating temperature range is another crucial aspect that needs to be carefully considered.⁴⁴ The presence of oxygen can be detrimental to the long-term stability of the TEG through the rapid deterioration of the output performance and mechanical integrity of the legs. Systematic oxidation studies of optimized TE materials can provide important information regarding whether passivating oxide shells can form at high temperatures or whether the application of protective layers should be considered. While such studies have been performed on several important high-temperature TE materials including the Zintl phase Yb₁₄MnSb₁₁ or skutterudites,⁴⁵⁻⁵³ only a handful of them is available for HH alloys.⁵⁴⁻⁵⁹ Furthermore, some contradictory results have been reported for *n*-type alloys, either showing no oxidation in air up to 900 K (Ref. 54) or indicating that they oxidize as their *p*-type analogs.⁵⁵

Here, we address this important aspect in detail through a systematic investigation of the high-temperature oxidation behavior of commercial *n*-type Hf_{0.6}Zr_{0.4}NiSn_{0.98}Sb_{0.02} and *p*-type Hf_{0.2}Zr_{0.75}Ti_{0.05}CoSb_{0.8}Sn_{0.2} HH alloys with optimized TE properties. We notably show that the mechanical properties of HH alloys allow them to withstand the thermomechanical stresses undergone when the height of the legs is reduced to as low as 2.0 mm, demonstrating that additional buffer layers are not required, which represents a major simplification. The high-temperature stability of both alloys was further investigated in air, showing that these alloys oxidize following two distinct pathways.

2. EXPERIMENTAL SECTION

2.1. Materials. *n*- and *p*-type HH alloys of chemical compositions $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ and $\text{Hf}_{0.2}\text{Zr}_{0.75}\text{Ti}_{0.05}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, respectively, were purchased from Isabellenhütte company. The bulk pieces received were ground into fine powders by high-energy ball milling. The powders were subsequently consolidated by spark plasma sintering (SPS) at 1223 K for 10 min under a pressure of 70 MPa. The experimental density of the cylindrical pellets was determined from their weight and geometrical dimensions and found to be higher than 96% of the theoretical density from X-ray diffraction data. Rietveld refinements of the room-temperature powder X-ray diffraction patterns are shown in Figure S1 in Supporting Information (SI), showing no obvious secondary phases within the detection limit of this technique.

2.2. Thermogravimetry and Differential Scanning Calorimetry (TG/DSC). The thermal stability and oxidation behavior of *n*- and *p*-type HH alloys were determined using TG/DSC (Setaram) with small samples cut from the consolidated pellets placed in Al_2O_3 crucibles. The samples were heated from room temperature to 800°C with heating and cooling rates of 10 K/min in a 33 mL/min (pressure of 1 bar) oxidative flow of air.

2.3. Oxidation studies. The oxidation behavior of the two alloys was further studied on small bulk pieces and on whole SPS-consolidated, cylindrical pellets with a thickness of ~2 mm. After being polished flat, the pieces or pellets were placed into an Al_2O_3 crucible, with the samples only touching the crucible on three Al_2O_3 rods. The samples were heated in a horizontal furnace in air at various temperatures between 400 and 800°C at a rate of 13 K/min, dwelt at these temperatures for 1 up to 7 days, before being cooled to room temperature. The surface of the oxidized pellets was analyzed by X-ray diffraction at 300 K.

2.4. Powder X-ray Diffraction (PXRD). Powder X-ray diffraction was performed at 300 K using a Bruker D8 Advanced diffractometer using Cu $K\alpha_1$ radiation on a zero background Si sample holder. PXRD patterns were analyzed using the FullProf software.⁶⁰

2.5. Optical Microscopy. Optical microscopy was performed using a VHX-X1 Digital Microscope (Keyence) instrument on oxidized bulk pieces to help quantify the main oxides present, based on their color.

2.6. Scanning Electron Microscopy (SEM). Scanning electron spectroscopy (SEM) was performed using a Quanta FEG650 (FEI) instrument on mirror-polished, bulk pieces. Energy dispersive X-ray spectroscopy (EDXS) was further performed to assess the spatial distribution of the elements. Analyses performed on the consolidated pellets prior to any oxidation test, shown in Figure S2 in SI, indicate that all the elements are homogeneously distributed in both alloys at the micron scale.

2.7. Transport Properties Measurements. Transport properties were measured on bulk pieces cut from the consolidated pellets in appropriate shape and dimensions using a diamond-wire saw. Electrical resistivity and thermopower were measured simultaneously between 300 and 900 K on bar-shaped samples (typical dimensions of $8 \times 2 \times 2 \text{ mm}^3$) using a ZEM-3 apparatus (Ulvac-Riko). Thermal diffusivity α was measured in the same temperature range by a laser flash technique using a LFA427 instrument (Netzsch). The thermal conductivity was calculated according to the formula $\kappa = \alpha C_p d$ where d is the experimental density, considered to be temperature independent, and C_p is the isobaric specific heat estimated by the Dulong-Petit law. The experimental uncertainties in the measurements of ρ , α and κ are estimated to be 5, 5 and 10%, respectively, resulting in an overall uncertainty of 17% in the ZT values.⁶¹ The temperature dependences of these four parameters (Figure S3 in SI) were fitted by polynomials that were used as input parameters in the numerical simulations.

2.8. Dilatometry. The thermal expansion coefficient α_T of the *n*- and *p*-type HH alloys was measured from 300 up to 973 K on bar-shaped samples of dimensions 9×2.5×2.5 mm³ using a dilatometer (DIL402, Netzsch). An alumina sample was used as a standard for these measurements.

2.9. Module Fabrication. For the *n*- and *p*-type legs, the consolidated HH pellets were carefully polished and cut into nearly-cubic-shaped bars of ~2.0 mm in length and 2×2 mm² surface area. All surfaces were polished to ensure their flatness and parallelism. The electrical connection between the TE legs was achieved using AlN plates of 0.63 mm in thickness onto which copper paths of 0.30 mm in thickness were deposited (C-Components and Curamik). The surface area of these plates was 1 cm². The legs were brazed on the Cu paths using InCuSil as the brazing alloy using a home-made brazing apparatus.

The electrical contact resistance of the legs was measured at 300 K using a commercial set-up (Quick Home) that allows for probing the resistance over the length of the legs with a resolution of 15 μ m.

2.10. Thermoelectric Performance Measurements of the Modules. The TEG was characterized with a commercial Mini-PEM apparatus (Ulvac-Riko) under primary vacuum between 300 and 773 K. The TEG was placed onto a Cu platform connected to a spring and cooled by circulating water. The hot source was provided by a resistive heater placed on the top side of the TEG. A pressure between 0.1 and 2 MPa was applied on the TEG through the spring to ensure a good thermal coupling. A thin layer of papyex (thickness of 0.1 mm) covered with thermal grease was further placed between the TEG and the hot and cold source to improve the thermal coupling. The hot-side temperature was varied between 350 and 773 K while the cold-side temperature was maintained to about 300 K. Both temperatures were continuously measured by two thermocouples attached to the respective surfaces of the TEG. The Mini-PEM system enables to determine the output electrical power of the TEG through measurements of

voltage-current curves. The efficiency can be further determined through measurements of the thermal power dissipated at the cold side.

Between 373 and 873 K, the output performance of the TEG was additionally determined using a custom-built thermoelectric generator measurement apparatus (TEGMA) at DLR. Although both measurement setups (Mini-PEM, TEGMA) are equipped with fundamentally different instrumentation, they still rely on similar measurement principles for determination of TEG properties. Past comparative measurements with both setups, which have been conducted on a prototype of a high-temperature reference TEG-module, revealed extremely low deviations of less than one percent in all electrical module properties,⁶² despite the existing differences between the two devices. Further details about the instrumentation and measurement principles of the TEGMA can be found elsewhere.^{62,63}

2.11. Numerical Simulations. 3D finite-element analyses were performed using the commercial software COMSOL Multiphysics to predict the output performances of the TEG and compare them with the experimental data. The 3D distribution of the electrical current density and heat flux, were solved using the boundary conditions of the experimental set-up (temperatures and thermal interface contact resistances) used to characterize the TEG. These simulations were conducted on model TEGs of dimensions corresponding to the fabricated devices. All the details of these calculations can be found elsewhere.¹⁷

3. RESULTS AND DISCUSSION

3.1. Oxidation of small pieces. As a starting point, a small dense piece of each alloy was measured using TG/DSC from room temperature up to 800°C in air (Figure 1a and 1b).

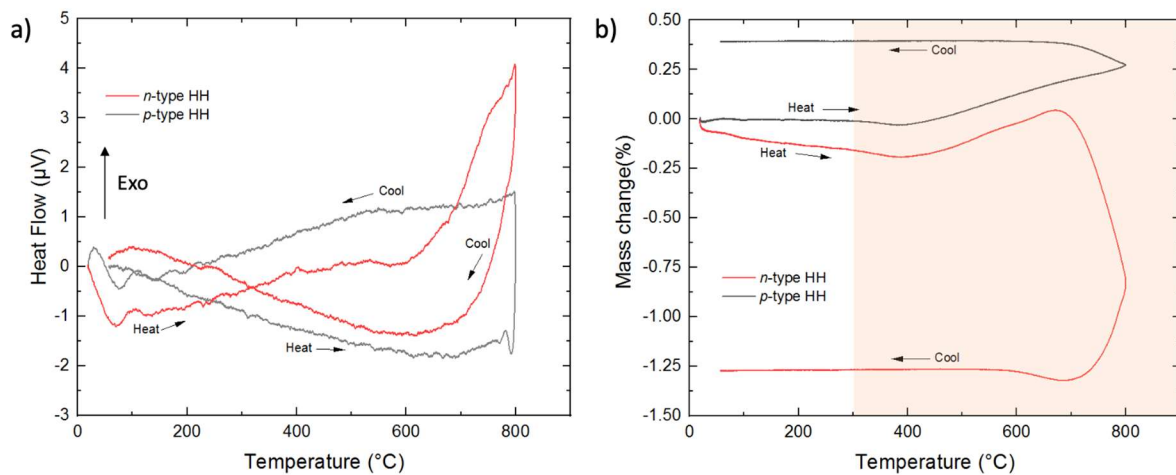


Figure 1. a) Differential scanning calorimetry (DSC) and b) thermogravimetry (TG) from room temperature up to 800°C performed on heating and cooling on two small pieces of the *n*- and *p*-type HH alloys. In panel b, the colored area represents the temperature region where oxidation starts to occur.

Upon heating, the DSC signal (Fig. 1a) of both samples shows a sweeping exotherm region near 100°C with a constant slope up to about 550°C. This behavior is attributed to the response of the sample holder to the furnace heating, yielding a non-constant base line, which is not representative of the oxidation behavior of the samples. For the *p*-type alloy, the TG signal (Fig. 1b) exhibits an upturn around 400°C followed by an increase up to 800°C that can be attributed to the oxidation process occurring at the surface of the sample. This process slightly continues upon cooling to 700°C before showing no further evolution down to room temperature. In contrast, the DSC signal of the *n*-type alloy shows a significant rise between 600 and 800°C, which correlates with the turnover observed in the TG signal indicating a significant mass loss. This process follows oxidation that starts near 400°C where an upturn in the TG signal is observed. The loss of mass further progresses upon cooling to 600°C. Below this temperature, the sample shows a steady mass, suggesting that no further oxidation and/or mass loss occurs. The overall TG signal of the *p*-type alloy indicates a weak surface oxidation that might passivate

the sample and prevent it from being further oxidized upon cooling. In contrast, a significant mass loss in addition to surface oxidation occurs for the *n*-type alloy. The results obtained for the latter are consistent with those reported by Wang *et al.*⁵⁵ on the *n*-type alloy $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{NiSn}_{0.985}\text{Sb}_{0.015}$ but differ from those of Kang *et al.*⁵⁴ obtained on the *n*-type alloy $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{NiSn}_{0.99}\text{Sb}_{0.01}$ that showed no evolution up to 900 K in air. This difference might be tied to the lower concentration of Sb in the sample of Kang *et al.* compared to the sample of Wang *et al.* and our sample, possibly indicating the existence of a possible threshold above which oxidation would occur. As this element is critical in the oxidation behavior of the *n*-type alloys, these results suggest that decreasing its concentration may help to improve their resistance against oxidation.

SEM and elemental X-ray mapping experiments were performed on the bulk pieces after TG, before being ground for additional PXRD measurements. For the *n*-type alloy (Figure 2a), these analyses suggest the presence of several oxides (SnO_2 , NiO , Sb_2O_3 , HfO_2 and ZrO_2) and the binary Ni_3Sn , in addition to the HH alloy. The presence of these various binaries confirms the results obtained by Wang *et al.* on the alloy $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{NiSn}_{0.985}\text{Sb}_{0.015}$,⁵⁵ indicating that small variations in the chemical composition do not significantly influence the oxidation behavior. For the *p*-type sample (Figure 2b), several oxides are present, identified as CoSnO_3 , TiO_2 , HfO_2 and ZrO_2 , in addition to the binary skutterudite CoSb_3 and the initial *p*-type HH alloy.

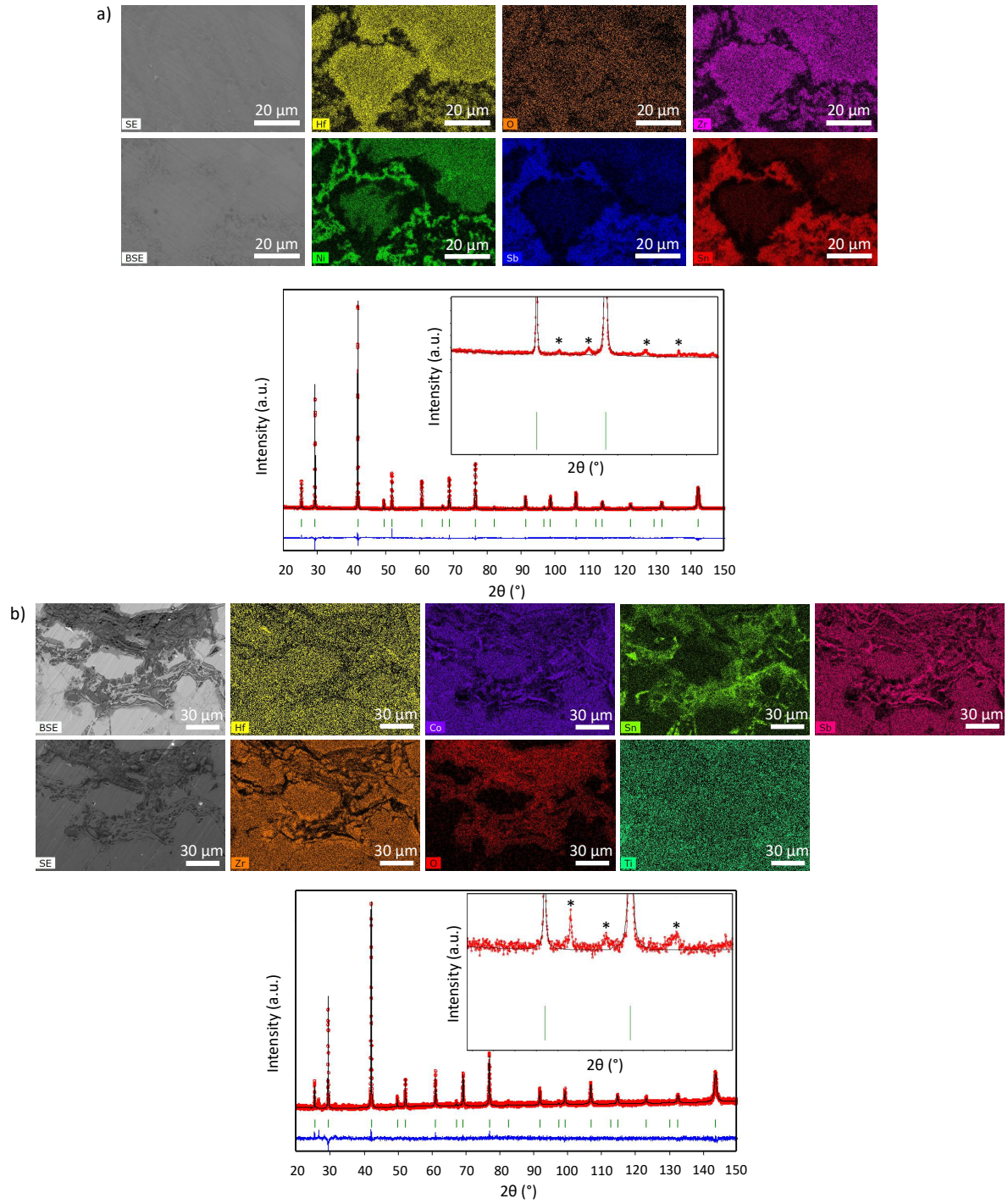


Figure 2. Backscattered electron micrographs of small pieces of the a) *n*- and b) *p*-type HH alloys after TG and corresponding PXRD patterns collected at 300 K on the ground oxidized small pieces. The additional weak reflections that can be observed between 20 and 35° (insets in both panels) besides the two main reflections of the HH phase correspond to oxides.

Ageing behavior of small pieces was further studied in argon atmosphere and air at constant temperatures of 300, 500, 580 and 680°C from 1 up to 30 days. Initial test at 300°C in air during 30 days evidence the development of only a thin oxidation layer mainly composed of SnO₂ and HfO₂ for the *p*-type alloy and SnO₂, HfO₂ and Sb₂O₃ for the *n*-type alloy (Figure S4 in SI). This agrees with the DSC/TG signals showing that oxidation starts around this temperature. Backscattered electron micrographs and elemental X-ray maps (Figure 3a and 3b), taken after 7-day annealing at 680°C under inert atmosphere, confirm the formation of Co-Sb and Co-Sn alloys and Ni-Sn phases in the *p*- and *n*-type sample, respectively. Their presence suggests that Sn and Sb diffuse in both alloys, with this process already starting at 500°C after only 1 day of annealing (Figure S5 in SI). Most importantly, in agreement with the TG signal, sublimation of Sb occurs at 680°C for both samples even under inert atmosphere, which appears as a key factor limiting the maximum temperature at which these alloys could operate in a TEG.

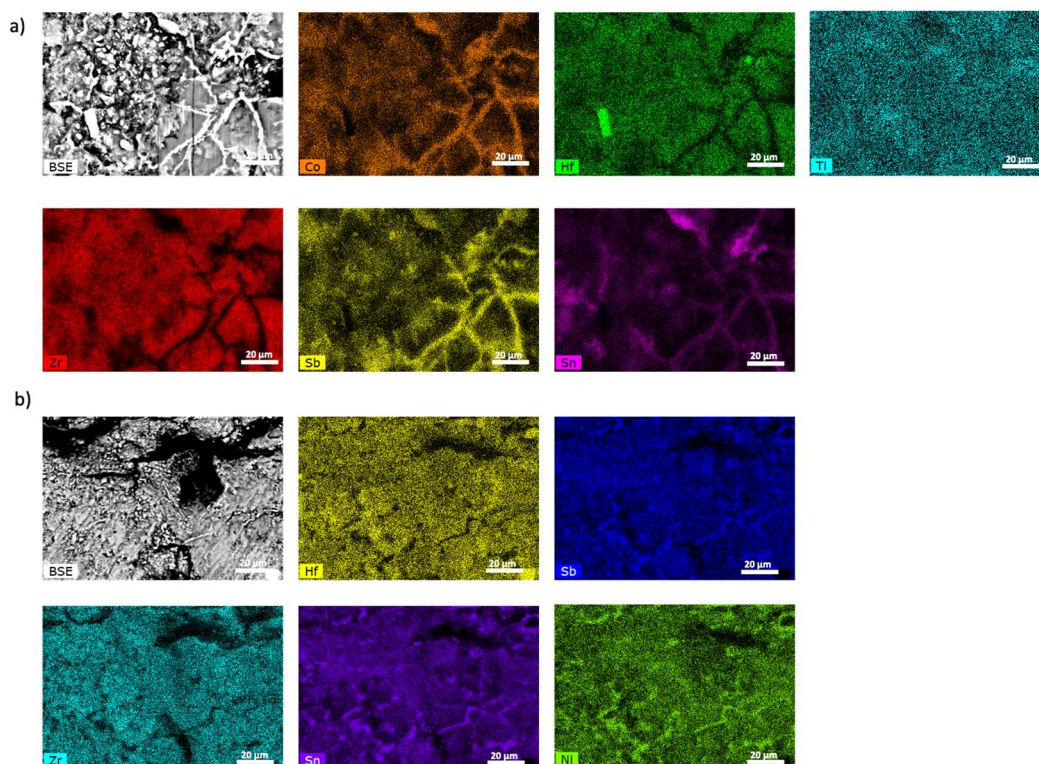


Figure 3. Backscattered electron image and corresponding energy-dispersive X-ray spectroscopy (EDXS) elemental mapping of the different elements of the a) *p*- and b) *n*-type HH alloys after annealing at 680°C for 7 days under inert atmosphere.

After 1 day at 500°C under air, the *n*-type alloy shows a continuous crust (Figure 4a), which extends about 20 μm below the surface, forming an outer layer surrounding an inner solid core. This layer tends to be separated from the non-oxidized core, likely due to the melting and evaporation of Sb as gaseous Sb_4O_6 , which is consistent with the mass loss evidenced by the TG signal. The outer layer tends to delaminate due to the difference in thermal expansion coefficients between HfO_2 ($5.9 \times 10^{-6} \text{ K}^{-1}$), ZrO_2 ($10.5 \times 10^{-6} \text{ K}^{-1}$), and the HH matrix ($\sim 10 \times 10^{-6} \text{ K}^{-1}$) in the temperature range 573 – 973 K, see Figures S6, S7 and S8 in SI). The Sb deficiency in the outer shell is confirmed by elemental X-ray mapping (Figure 4b), which further shows a homogeneous distribution of all the elements in the interior of the sample. Oxygen is mostly concentrated in the outer shell, where it oxidizes various elements during diffusion, resulting in the formation of a ZrO_2 layer.

In contrast, the oxidized *p*-type samples show a distinct microstructure characterized by the absence of an outer layer (Figure 5a). Several oxides are present at the surface of the samples (Figure 5b) after 1 day of annealing (notably TiO_2 , HfO_2 , ZrO_2), suggesting that oxygen progressively diffuses inward without a concomitant sublimation of elements, which is consistent with the TG signal showing no mass loss. This indicates that the oxidation of the *p*-type alloy follows a distinct pathway with respect to the *n*-type alloy in spite of the higher concentration of Sb. The lack of Sb sublimation is likely due to the formation of Co-Sb oxides and Co- and Sb-rich phases such as CoSb_2 , which prevents Sb from being oxidized into Sb_2O_3 and, ultimately, into gaseous Sb_4O_6 . The thickness of the outside layer formed by these oxides increases after further ageing for 7 days (Figure S9 in SI). However, in contrast to the *n*-type alloy, no cracks are observed due to the presence of a higher concentration of ZrO_2 compared to HfO_2 , mitigating differences in thermal expansion coefficients between the latter and the HH matrix.

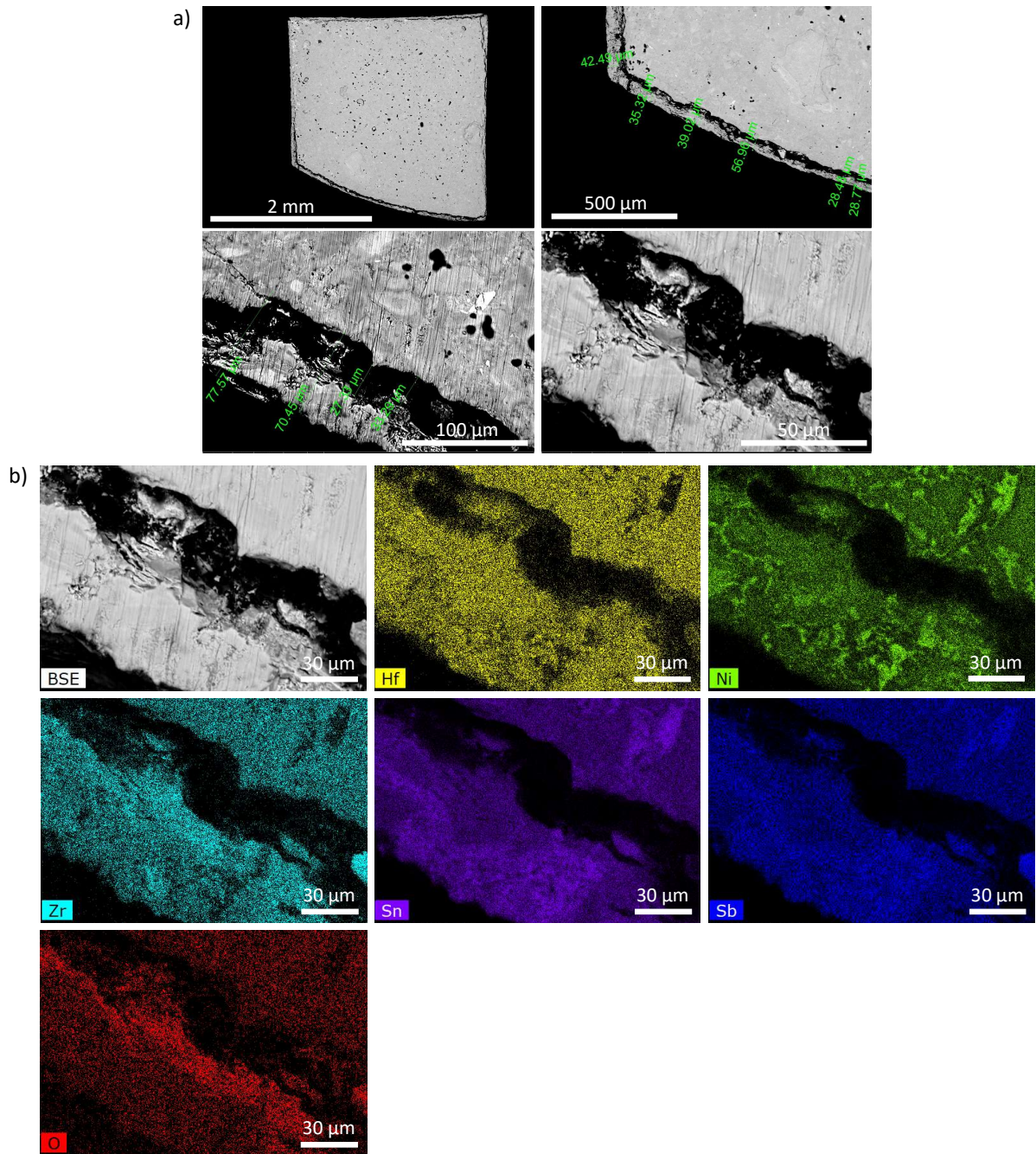


Figure 4. a) Backscattered electron images of the cross sections of small pieces of the *n*-type HH alloys after oxidation at 500°C for 1 day. b) Corresponding elemental X-ray maps.

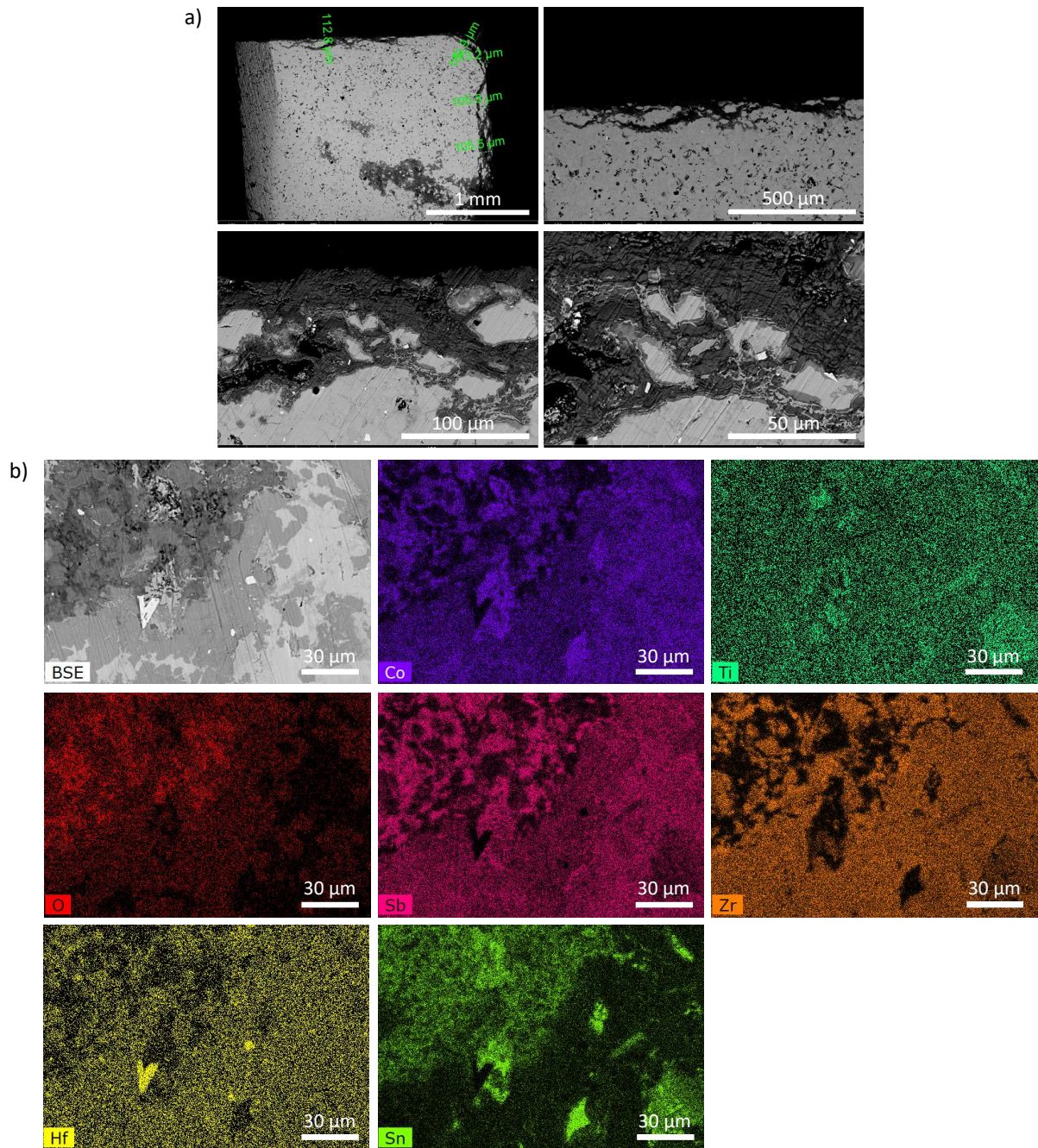


Figure 5. a) Backscattered electron images of the cross sections of small pieces of the *p*-type HH alloys after oxidation at 580°C for 1 day. b) Corresponding elemental X-ray maps.

3.2. Oxidation of large-scale pellets. To determine how oxidation evolves in larger samples, whole cylindrical dense pellets were heated and dwelt at 400, 650 and 800°C for 3h. Figures 6a to 6f show photos taken before and after oxidation at 800°C for both alloys.

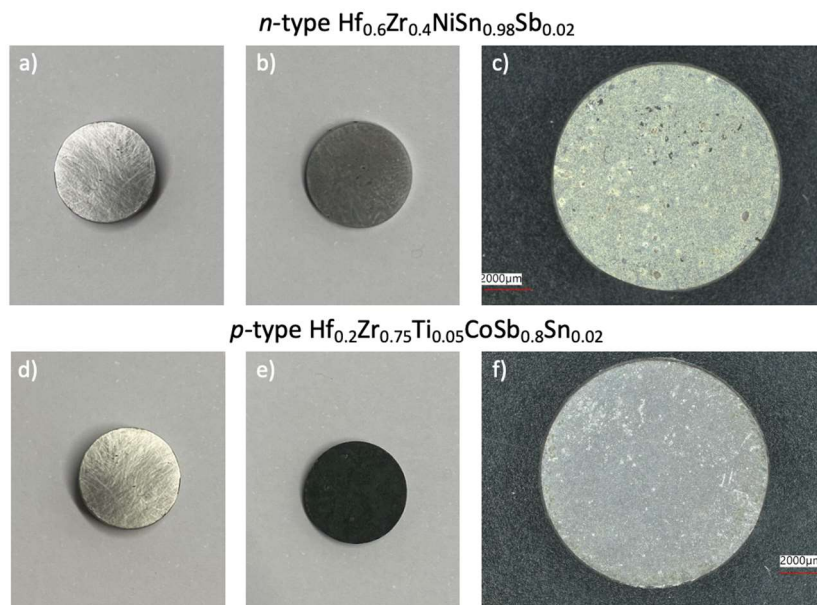


Figure 6. Photos of the pellets of *n*-type and *p*-type HH alloys before (panels a and d, respectively) and after (panels b and e, respectively) oxidation at 800°C for 3h. Panels c) and f) show the corresponding optical microscopy images for the *n*-type and *p*-type HH alloys, respectively.

Before oxidation (Fig. 6a and 6d), both samples are silver-like materials with shiny surfaces. After oxidation for 3h at 800°C, the *p*-type pellet has developed a homogeneous black coating without evident cracks (Fig. 6e). In contrast, the *n*-type alloy, subjected to similar experimental conditions, developed a continuous, gray-like tan outer layer covering the entire surface of the pellet (Fig. 6b). Closer inspection of the oxidized surfaces by optical microscopy suggests that the dominant greenish and black colors of the *n*- and *p*-type alloys, respectively, correspond to the NiO and Co₃O₄ oxides (Fig. 6c and 6f).

PXRD patterns were collected on the oxidized pellets after annealing at 400, 650 and 800°C to follow the successive oxidation reactions occurring in both alloys. These results were complemented by elemental X-ray maps and line profiles taken from the oxidized surface towards the HH matrix on cross-cut pellets after oxidation at 800°C (Figures 7a and 7b and 8a and 8b for the *n*- and *p*-type sample, respectively).

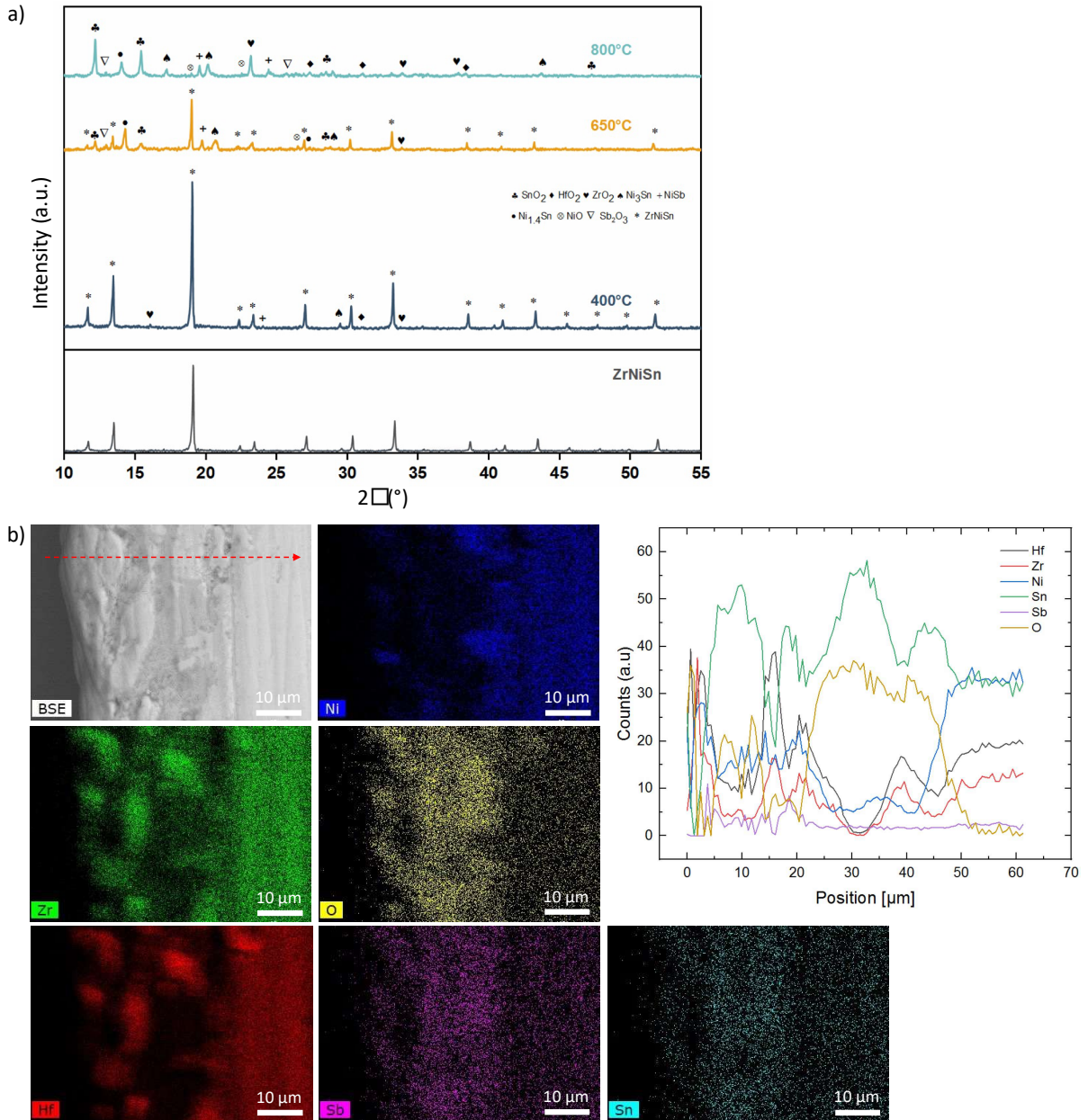
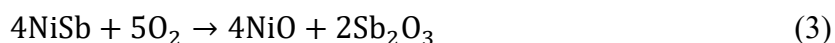
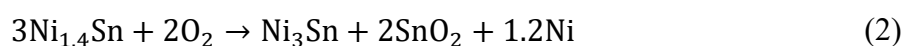
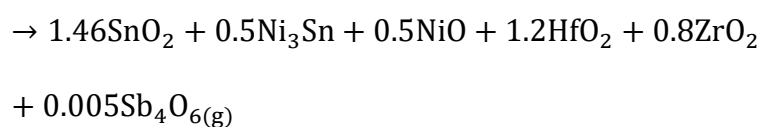
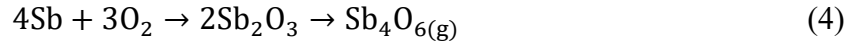


Figure 7. a) PXRD patterns obtained on ground pieces of the large pellets after oxidation at 400, 650 and 800°C for the *n*-type HH alloy. The main reflections of the various oxides and intermetallic phases are indicated. For comparison, the PXRD pattern of the non-oxidized alloy

has been added. b) SEM image in BSE mode and the corresponding elemental X-ray maps. Elemental line profiles from the oxidized surface towards the interior of the sample, represented by the red arrow in the BSE image, are also shown.

For the *n*-type sample (Fig. 7a), the pattern at 400°C shows the formation of the binary Ni_{1.4}Sn and of the oxides SnO₂ and NiO, which agrees with the TG curves showing that oxidation begins above 350°C. At 650°C, formation of oxides HfO₂, ZrO₂, and Sb₂O₃ is observed in addition to the binary Ni₃Sn. Their formation is in agreement with the Ni-Sn phase diagram indicating that the binary Ni_{1.4}Sn decomposes above 480°C.⁶⁴ Further increasing the temperature to 800°C leads to the presence of the four oxides SnO₂, NiO, HfO₂ and ZrO₂ and the binary Ni₃Sn, which is stable up to about 1189°C. Sb₂O₃ likely sublimates, explaining the significant mass loss observed in the TG curve above 600°C. Equations 1 to 4 provide a possible pathway for these successive reactions initiated above 350°C with the transformation of Ni_{1.4}Sn into Ni₃Sn above 480°C, which may result in elemental Ni at 650°C that would further react with molten Sb (melting point of 630.6°C) to form the binary NiSb. This binary, stable up to 1147°C,⁶⁵ would then oxidize to form NiO and Sb₂O₃ that eventually sublimates upon heating in the form of gaseous Sb₄O₆. The sublimation of Sb₂O₃ explains the formation of the outer layer in the oxidized small pieces and whole pellet, protecting the inner core from oxidation.





For the *p*-type sample (Fig. 8a), the pattern collected at 400°C reveals the formation of the ternary oxides CoSnO₃, Sn_{0.9}Sb_{0.1}O₂ in addition to the binaries TiO₂, HfO₂ and ZrO₂, in agreement with the TG/DSC measurement showing that oxidation begins above 350°C as in the *n*-type alloy. At 650°C, CoSb₂ is observed in addition to the above-mentioned oxides. In contrast to the *n*-type alloy, only Co-Sb oxides are present with no obvious sign of the presence of Sb₂O₃, which is consistent with what has been observed on small pieces. Upon heating to 800°C, no additional compounds are formed, which agrees with the TG signal showing no significant evolution between 350 and 800°C and, in particular, no mass loss due to the absence of Sb₂O₃.

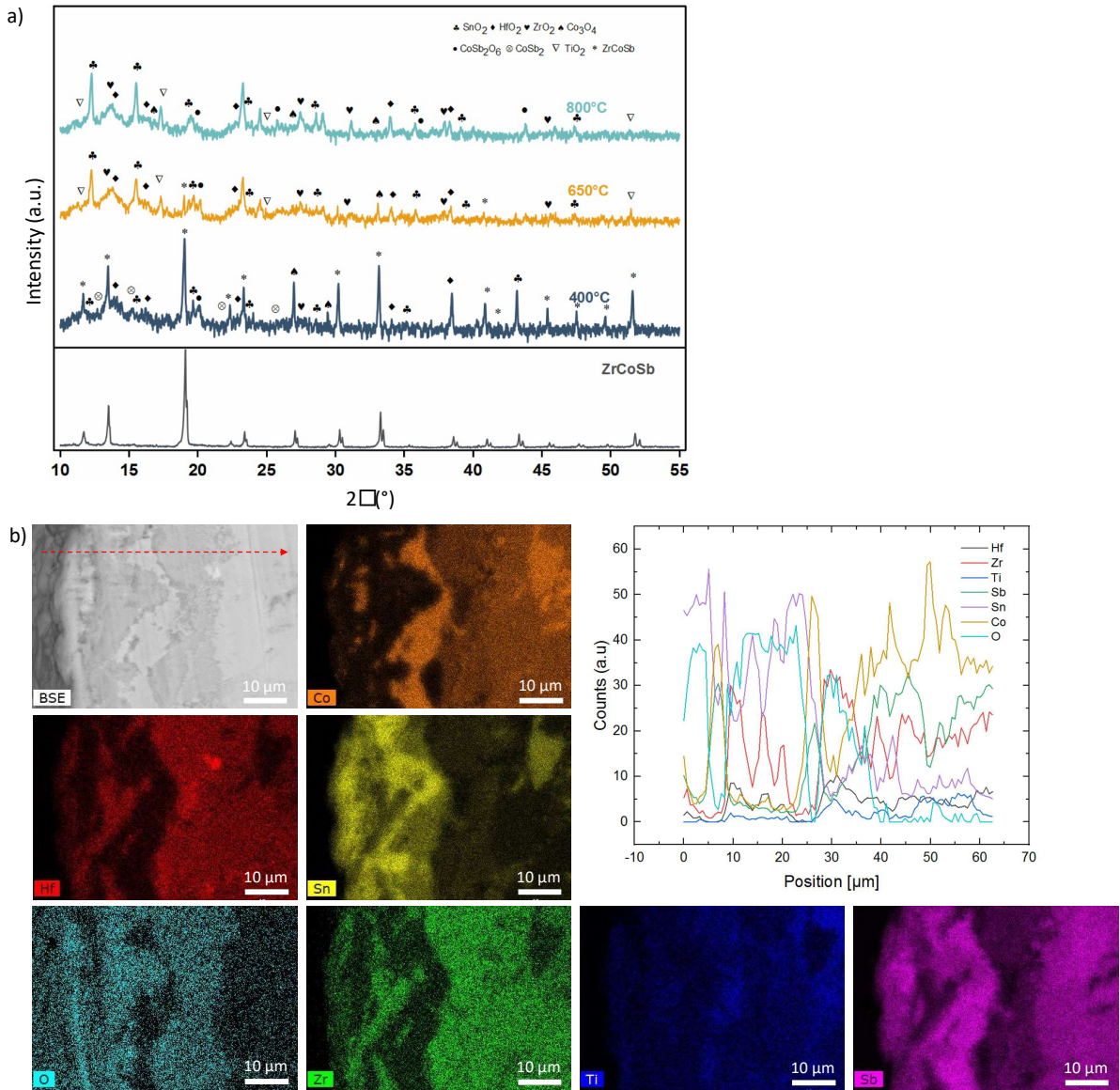
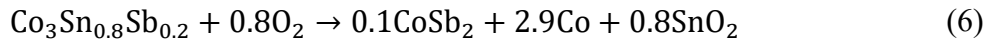
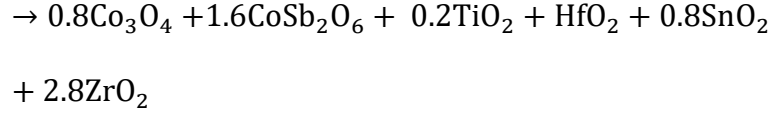


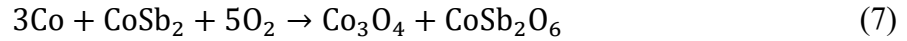
Figure 8. a) PXR D patterns obtained on ground pieces of the large pellets after oxidation at 400, 650 and 800°C for the p -type HH alloy. The main reflections of the various oxides and intermetallic phases are indicated. For comparison, the PXR D pattern of the non-oxidized alloy has been added. b) SEM images in BSE mode and the corresponding elemental X-ray maps. Elemental line profiles from the oxidized surface towards the interior of the sample, represented by the red arrow in the BSE image, are also shown.

Equations 5 and 6 give a possible oxidation pathway for the p -type HH alloy. According to this reaction scheme, oxidation is initiated by the formation of the ternary and binary oxides. The

formation of SnO₂ is initiated by the decomposition of the ternary compound Co₃Sn_{0.8}Sb_{0.2} that also leads to the presence of CoSb₂ and elemental Co.



Other phases begin to appear as the temperature increases and oxygen reacts with Co and CoSb₂, leading to the formation of the oxides Co₃O₄ and CoSb₂O₆ according to Equation 7



In comparison with the *n*-type alloy, the initial formation of dense Co- and Sb-containing oxides likely yields a passivation barrier that explains the lack of further oxidation observed in the TG cooling curve. Although distinct from the *n*-type alloy, this mechanism leads to a similar oxidation behavior, suggesting that pre-oxidation might be effective in protecting the *p*-type alloy from oxidation in air. However, this pre-process should be performed at 800°C to avoid the formation of Ti, Hf and Zr oxides at lower temperatures that yield numerous cracks due to the significant differences between their thermal expansion coefficients and that of the HH alloy. Finally, the combination the BSE images and concentration profiles after annealing at 800°C enables to obtain estimates of the growth rate of the oxidized layer for both alloys, yielding ~0.1 and ~0.3 μm h⁻¹ for the *n*- and *p*-type HH alloy, respectively. For the former, this estimate is in good agreement with the ageing tests performed by Wang *et al.*⁵⁵ on the *n*-type alloy Zr_{0.5}Hf_{0.5}NiSn_{0.985}Sb_{0.015}.

3.3. Thermoelectric Generator Performance. After the brazing step, the good quality of the interfaces between the legs and the In-Cu-Ag braze is confirmed by SEM images (Figure 9a and 9b for the *n*- and *p*-type HH sample, respectively). An interlayer structure that extends to about 20 μm is typical of the eutectic Ag-Cu-In, with an Ag-rich phase, into which both Cu and In are dissolved, coexisting with a Cu-rich phase containing Ag and In. Both intermetallic phases and reaction layers are formed during the brazing step of the *n*- and *p*-type legs. Interestingly, Ti diffuses and forms a uniform and thick intermetallic layer on both HH materials, providing a natural diffusion barrier. For both alloys, Ti accumulates at the interface with the HH and probably reacts with Zr, Hf and Sb, ensuring strong bonding at the interfaces. Although the evolution of this intermetallic layer over prolonged high-temperature operation remains to be determined, it appears likely that the growth kinetics is very slow, if any, up to about 600°C. A first experimental hint pointing to its inertness is provided by the thermoelectric performance of the TEG, which showed no evolution over 10 days of measurements (see below). Overall, the direct brazing process, without the use of a diffusion barrier, results in stable bonding with minimal reactions at the interfaces. Due to the relatively low operating temperature on the hot side of the TEG (maximum of around 600°C), interdiffusion of Ti, present in the braze and among the elements of the HH matrix, is limited, preserving the structural integrity of the brazing layer and HH alloys. Notably, no diffusion of Cu from the electrodes or the braze into the HH matrix is observed, despite the high brazing temperature of 720°C, due to the short duration time of this step (few minutes).

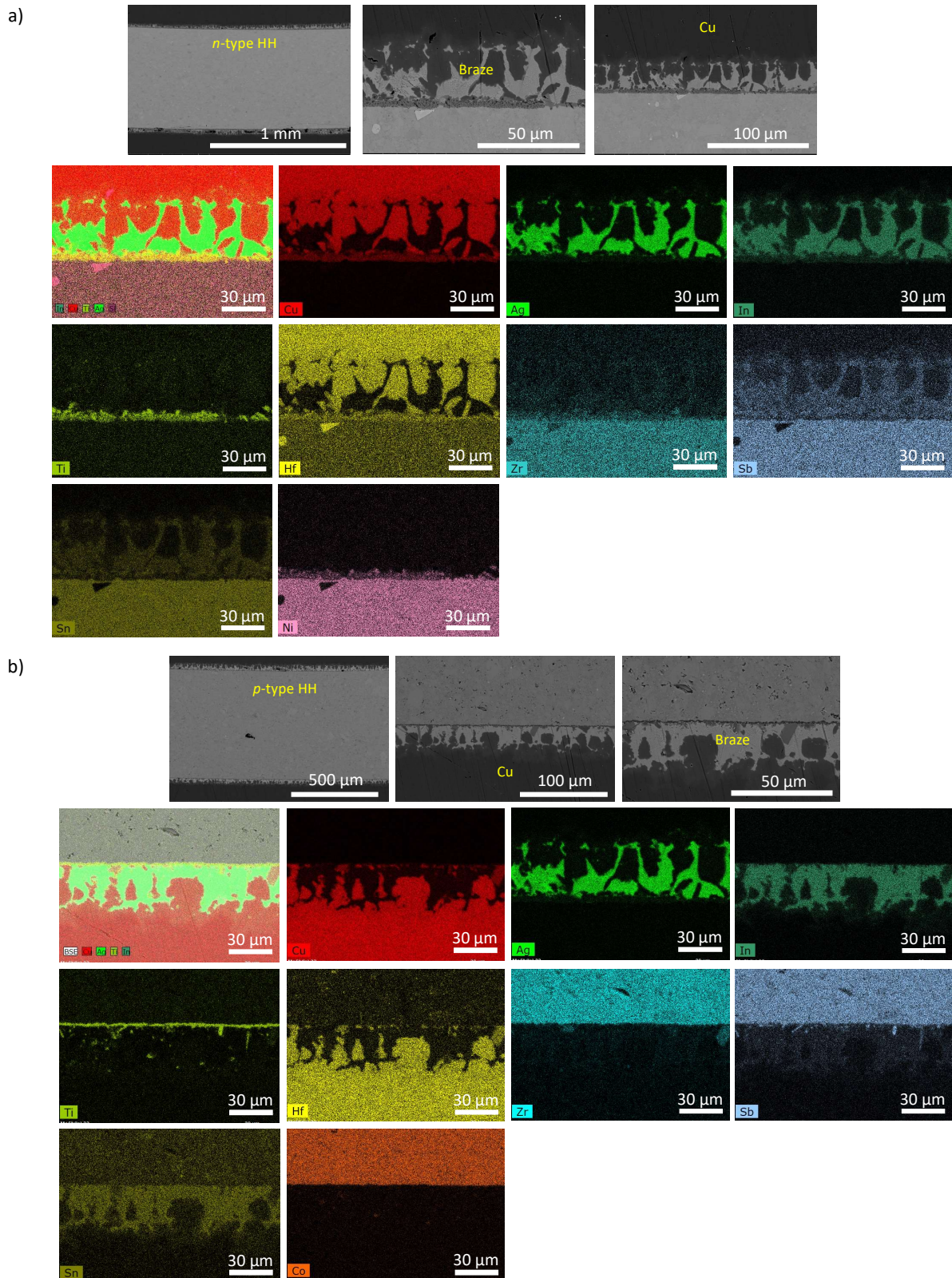


Figure 9. BSE images and elemental X-ray maps of the interface layer between the braze and the a) *n*-type HH and b) *p*-type HH alloy. The first panels correspond to overlaid images of several X-ray maps as indicated by the legend (left bottom).

In order to verify that the growth of the Ti layer during the brazing step does not induce significant electrical contact resistance ρ_c at the interface, the variations in the resistance R were measured at 300 K over the length of the legs x . The $R(x)$ profiles, shown in Figure 10a and 10b, are characteristic of low ρ_c values, being as low as 2.7 and 14 $\mu\Omega \text{ cm}^2$ for the n - and p -type leg, respectively. These low values are comparable with those achieved in prior studies.¹⁸⁻⁴³ The absence of steps at the interface between the Ti layer and HH alloys indicates that the low thickness of this layer remains below the resolution of these measurements. As mentioned above, the likely slow growth kinetics of this layer below 600°C should prevent any additional increase in the contact resistance between this layer and the HH alloys. The slopes of the $R(x)$ curves correspond to room-temperature electrical resistivity values of 5.9 and 120 $\mu\Omega \text{ m}$ for the n - and p -type alloy, respectively, that are in good agreement with those measured on bulk samples (see Figure S3 in SI).

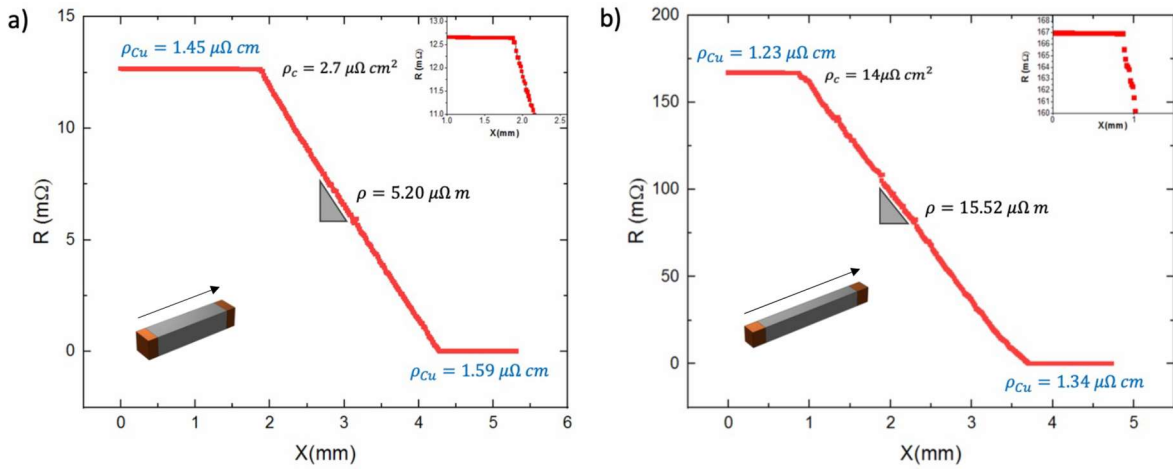


Figure 10. Electrical contact resistance ρ_c determined from local contact resistance profiles measured on the a) n -type and b) p -type HH legs after formation of Ti layers during the brazing step. The profiles do not show any obvious drop at the interfaces between the HH alloys and the metallic contacts. The slopes of the two linear lines (multiplied by the section area of the samples) are consistent with the electrical resistivities of the alloys. The insets show a

magnification of the ρ_c drop, evidencing good quality contacts. The schematic views of the legs (bottom left) are accompanied by arrows indicating the x-direction used in these measurements.

A two-couple TEG was fabricated and tested. The lowered height of the active HH legs to 2.0 mm and the low ρ_c values yield a p_{max} of 7.5 W cm^{-2} at a temperature difference of 575 K (Figure 11). Similar values were measured on both measurement systems, demonstrating the good reproducibility of these results and the stability of the module properties over the duration of these measurements. The experimental temperature dependence of p_{max} is well reproduced by numerical simulations, which confirms the validity of supposed boundary conditions and material properties during pre-processing steps of the simulations and likewise a good control of the different experimental steps of the fabrication process. Of note, p_{max} could be further enhanced by decreasing the leg's height below 2.0 mm,⁶⁶ provided that the temperature difference over the legs can be maintained. Indeed, the reduction in the leg's height would decrease the thermal resistance of the module compared to the thermal resistances at the cold and hot source/module interfaces. In other words, the temperature difference ΔT across the TE elements would represent a smaller fraction of the applied temperature difference, which will effectively decrease efficiency and output power. These detrimental effects could be mitigated by reducing the leg area of the active elements to some extent and/or by increasing the heat transfer at the two interfaces.

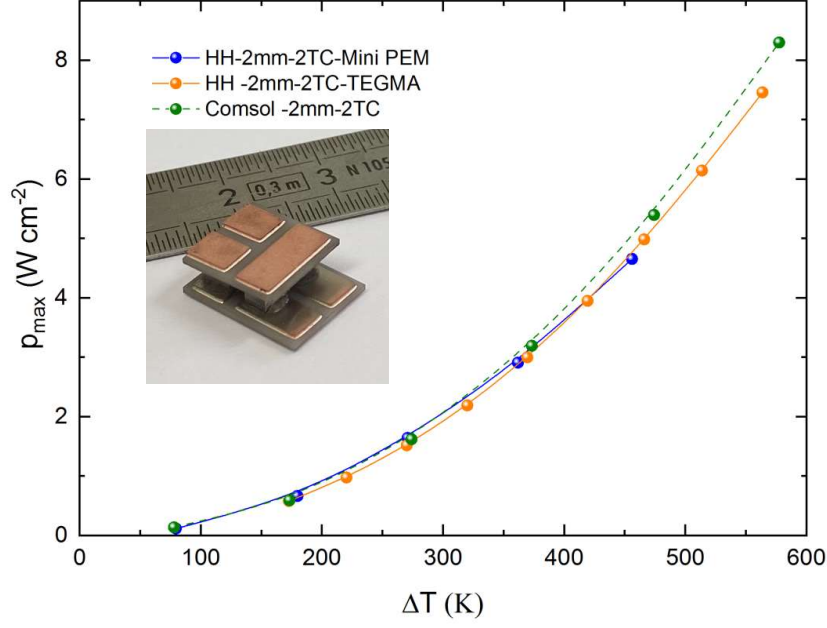


Figure 11. Output power density p_{max} as a function of the temperature difference ΔT applied between the hot and cold side of a TEG composed of 2 couples (TC) with leg's height of 2.0 mm. The experimental data, measured with the Mini-PEM and TEGMA set-up, are compared to the results of numerical simulations. The inset shows a photograph of the TEG.

A comparison of these values with those obtained in prior studies show that controlling the height of the active HH layers can yield a significant enhancement in p_{max} , notably for intermediate temperature differences. The values of p_{max} and respective heat flow data give access to a maximum TEG conversion efficiency η of 4.6%. This value is consistent with those obtained for non-segmented, HH-based TEGs that range between 5 and 10.7% for leg's height varying between 1.93 and 3 mm and between 3.2 and 10.5% for leg's height ranging from 5 up to 10 mm (see Table S1 in SI for further details).^{18,21,23,24,27,35,36,38,39,42} Further increase in η could be achieved by considering segmented legs, as demonstrated in several studies.⁶⁷⁻⁶⁹ Furthermore, measurements performed upon a total of 4 cycles of heating/cooling under inert atmosphere (1 on the Mini-PEM system and 3 on the TEGMA system equivalent to 10 days, see Figure S10 in SI) did not evidence any degradation of the output performance (Figure S11

in SI), confirming the good mechanical and thermal stability of the TEG. The lack of cracks in the legs after these measurements is notably due to the excellent mechanical properties of the HH alloys, which demonstrates that buffer layers are not necessary in the present case, in contrast to skutterudites that are more fragile.¹⁷ Finally, the oxidation behavior of both alloys suggests that this TEG could operate below $\sim 300^{\circ}\text{C}$, where the oxidation kinetics seems to be slow enough. In this regard, further measurements in air will be helpful in providing direct insights into its stability against oxidation over time.

4. CONCLUSIONS

Both small- and large-scale oxidation experiments on commercial *n*- and *p*-type HH alloys have evidenced that oxidation onsets near $\sim 300^{\circ}\text{C}$, following two distinct pathways. The *n*-type alloy $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ experiences a mass loss above $\sim 600^{\circ}\text{C}$ due to the sublimation of oxidized Sb in the form of gaseous Sb_4O_6 . All the elements form oxides that are contained in an outer layer, creating a void region separating it from the inner solid core. In contrast, this mechanism is absent in the *p*-type alloy $\text{Hf}_{0.2}\text{Zr}_{0.75}\text{Ti}_{0.05}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, in spite of its higher Sb content. Several intermetallic compounds and oxides form at high temperatures, including notably two Sb-containing compounds that prevent the oxidation of Sb and hence, its sublimation away from the surface. The formation of these compounds yields a good level of protection against oxidation, indicating that both HH alloys could be used up to $\sim 300^{\circ}\text{C}$ in air without significant degradation.

The remarkable mechanical properties of these alloys enable a continuous decrease in the height of the TE legs in TEGs from the typical value of 10 mm to 2.0 mm without compromising their mechanical integrity. These unique properties among TE materials offer the possibility to significantly increase the output power density, as demonstrated by measurements performed

on a two-couple TEG fabricated with these alloys. One of the main advantages of this approach is that high output power densities are achieved for lower temperature differences, which fall in an intermediate temperature range that encompasses temperatures found in many industrial environments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi>

Rietveld refinements of the PXRD patterns of the *n*- and *p*-type HH alloys, SEM images and corresponding elemental X-ray maps of the *n*- and *p*-type HH alloys, temperature dependence of the thermoelectric properties of the *n*- and *p*-type HH alloys, SEM images and corresponding elemental X-ray maps of the *n*- and *p*-type HH alloys annealed at 300°C in air for 30 days, SEM images and corresponding elemental X-ray maps of the *p*-type HH alloys annealed for 1 day at 500°C under inert atmosphere, temperature dependence of the thermal expansion coefficient of the *n*- and *p*-type HH alloys, comparison of SEM micrographs of a small piece of the *n*-type HH alloy annealed under O₂ at 500°C for 1 and 7 days, cycling measurements of the maximum output power P_{max} and internal resistance R_i of the TEG, list of output parameters of various HH-based TEGs reported in the literature.

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Notes

The authors declare no competing financial interest.

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