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Surface aluminization for enhancing oxidation resistance of $\text{Nb}_{0.86}\text{Hf}_{0.14}\text{FeSb}$ thermoelectric element

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NbFeSb-based half-Heuslers (HHs) exhibit exceptional high-temperature thermoelectric (TE) performance, but their practical deployment is hindered by insufficient oxidation resistance. Here, a surface aluminization technology is introduced to improve oxidation resistance by forming in-situ intermetallic compounds on the material surface. During this process, a dense coating with a thickness of 20-60 μm is formed through a solid/gas reaction between Al and the main constituents of HHs, exhibiting a lamellar structure composed of $\text{Al}_{13}\text{Fe}_4$, $\text{Al}_3(\text{Nb,Hf})$ and AlSb in sequence. The coating and substrate exhibit a robust metallurgical bond. Benefiting from the intrinsic oxidation resistance of aluminides, the coating serves as an effective diffusion barrier against oxygen penetration. Diffusion kinetics analysis reveals that the coating/substrate interface maintains an ultra-low diffusion rate in air, extending the predicted service life to over 10 years. The coated elements demonstrate negligible degradation in TE properties during prolonged aging at 973 K. The surface aluminization method effectively improves the feasibility and thermal stability of NbFeSb-based HHs in air, thus advancing their practical applications.

Keywords: thermoelectric, half-Heusler, thermal stability, oxidation resistance, surface aluminization



1. Introduction

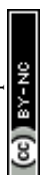
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Waste heat recovery has become a key issue of improving energy efficiency in the face of the growing energy crisis in contemporary society.¹⁻³ The environmentally friendly TE power generators, which can directly convert heat into electricity, have great potential especially in low-grade waste heat recovery.⁴⁻⁹

As the determinant of theoretical conversion efficiency of TE devices, the dimensionless figure of merit (zT) of TE materials became the research focus in the past decades, and many novel TE materials have been discovered.¹⁰⁻²⁰ Among them, HH compounds are considered as the ideal candidates for high-temperature power generators due to their excellent TE and mechanical properties.^{14, 15, 21-26} With deep understanding of thermal and electrical transport mechanisms, the TE performance of HHs has been greatly improved. Recently, the zT of p-type NbFeSb and n-type ZrNiSn based HHs reached 1.60 and 1.12,^{14, 15} respectively. The energy conversion efficiency of single and segmented HH devices have crossed 11.1% and 13.3%, respectively.²⁷

In practical services, the thermal stability of TE materials and devices is more critical than their zT and efficiency.²⁸⁻³⁰ Most TE materials,³¹⁻³⁸ including Mg₂Si, CoSb₃, HH, etc., exhibit poor oxidation resistance especially at high temperatures and air environment. The formation of electrically insulating oxide results in the change of chemical composition, thereby causing deterioration of zT .³⁹ Take CoSb₃-based skutterudite as an example, the formation of Sb₂O₃ significantly degrades electrical conductivity, which causes a 29.2% deterioration in zT .³² The easily oxidized p-type (Zr,Hf,Ti)Co(Sb,Sn) exhibits a 49.5% decrease of output power in TE generator after working in air for 115 hours at a temperature gradient of 823 K/294 K.³⁵ Similarly, the output power of n-type (Zr,Hf)Ni(Sb,Sn) TE device drops to 61% of the initial value after operation at 778 K/300 K for 15 days in air.³⁴

To make the applications of HHs feasible in air, the oxidation resistance should be considered as an essential evaluation criterion. The strong composition-property coupling inherent in TE materials presents a critical challenge in developing oxidation-resistant materials. Some efforts have been made for developing protective coatings for TE materials. For example, 8 mol% yttria-stabilized zirconia (YSZ), yttria (Y₂O₃) and



alumina (Al_2O_3) coatings are designed for Mg_2Si .⁴⁰ Nevertheless, conventional plasma spraying techniques struggle to prevent process-induced thermal damage of TE materials. Aerogel coatings have been tried to protect CoSb_3 based skutterudites. However, the interconnected micro and mesopores in aerogels provide oxygen migration channels, which cause progressive degradation during long-term operation.³⁹ The designed CrSi coating for $(\text{Zr,Ti})\text{Ni}(\text{Sn,Sb})$ and $(\text{Zr,Ti})\text{Co}(\text{Sn,Sb})$ prepared by magnetron sputtering can prevent the diffusion of oxygen, but the limits of coating thickness ($< 2 \mu\text{m}$) severely affect its service life.⁴¹ By controlled oxidation treatments, in-situ dense oxide layers can be formed on the surface of n-type $(\text{Zr,Hf})\text{Ni}(\text{SnSb})$ and p-type $(\text{Zr,Hf})\text{Co}(\text{Sb,Sn})$.^{34, 36} However, the formation of such dense oxide coatings is governed by chemical composition, thereby restricting the applicability of this strategy to specific material systems.

As high-temperature TE materials, $\text{Nb}_{0.86}\text{Hf}_{0.14}\text{FeSb}$ -based half-Heusler (NHFS) alloys inevitably undergo oxidative degradation during service in oxygen-containing environments. Conventional spray or deposition coatings often suffer from interfacial compatibility issues. The pack cementation method, as an in-situ diffusion coating technique, utilizes intrinsic elements from NHFS to form a lamellar aluminide coating on the surface. Benefiting from interlayer inter-diffusion and matched coefficients of thermal expansion, a robust metallurgical bond forms at the coating/substrate interface. This aluminide coating effectively blocks inward oxygen diffusion, preventing oxidation-induced cracking. Although interfacial diffusion occurs at elevated temperatures, the thickening rate of the diffusion layer is significantly suppressed due to attenuation of the aluminum concentration gradient. Furthermore, coated NHFS elements exhibit negligible degradation in TE performance after aging at 973 K, demonstrating exceptional service stability of surface-aluminized NHFS in air.

2. Materials and methods

2.1. Synthesis of NHFS

$\text{Nb}_{0.86}\text{Hf}_{0.14}\text{FeSb}$ was synthesized by induction melting in vacuum. High purity raw materials of Nb (99.9%, Alfa Aesar), Hf (99.9%, Alfa Aesar), Fe (99.99%, Alfa



Aesar), Sb (99.95%, Alfa Aesar) were weighed in stoichiometric mass and melt by induction melting method. The obtained ingots were then crushed and ball milled into fine powders, followed by consolidation using hot-pressure sintering under 60 MPa pressure at 1243 K and holding for 15 min. The details of the synthesis process are shown in our previous works.⁴² The sintered wafer was cut into small pieces for coating experiments and aging tests in air.

2.2. Pack cementation aluminizing

The NHFS samples were aluminized by the pack cementation method. The composition of the coating powder mixture was 30 wt% Al, 4 wt% AlCl₃, 66 wt% Al₂O₃. The powders were mixed well by high energy ball milling. The NHFS samples covered by coating powders were placed in an alumina crucible, then placed in a quartz tube and encapsulated under vacuum. The encapsulated quartz tube was placed in a muffle furnace and held at 973-1073 K.

2.3. Aging test

The uncoated NHFS and coated NHFS samples were placed in open quartz crucibles and placed in a muffle furnace in air, and aging at 873 K, 923 K and 973 K. The mass of samples before and after aging were weighed by electronic balance (QUINTIX35-1CN) with accuracy of 10⁻⁵ g.

2.4. Characterization

X-ray diffraction analysis (XRD, Bruker, Cu K α) and Micro-region XRD (micro-XRD, Rigaku Rint2000, Cu K α) were performed to determine the phase composition. Scanning electron microscopy (SEM, ZEISS Supra 55) coupled with energy-dispersive spectroscopy (EDS, OXFORD Aztec X- Max80) was used to investigate the microstructure and morphology. The thickness of diffusion layer was measured from the SEM image. The Seebeck coefficient (S) and electrical conductivity (σ) were simultaneously measured from room temperature to 1000 K by the ordinary four-probe



DC method using ZEM-3 (Ulvac-Riko) in a sealed chamber with a small amount of helium gas.

3. Result and discussion

3.1. Characterization of the aluminide coating

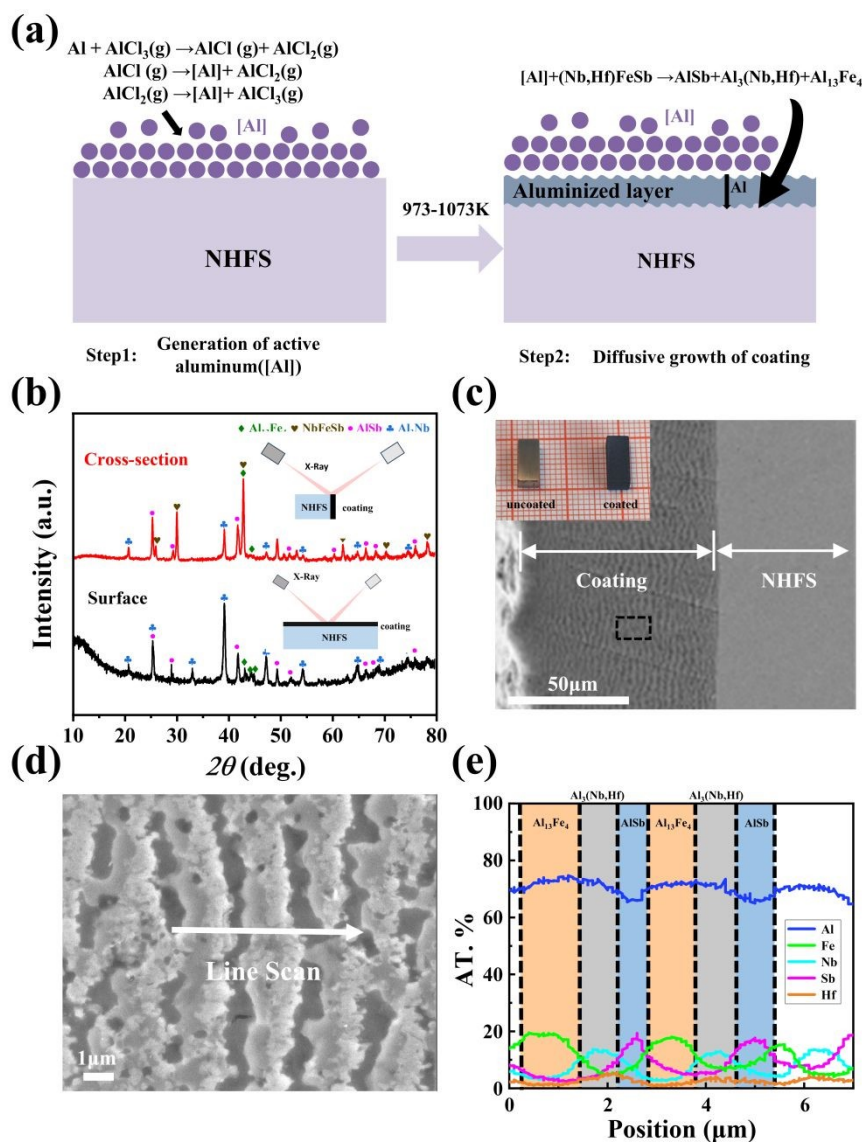


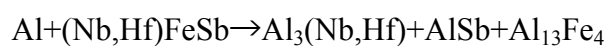
Fig. 1 (a) Schematic diagram of the coating formation mechanism; (b) Cross-sectional micro-XRD and surface XRD patterns of the aluminide layer; (c-d) Cross-sectional SEM image of the coated NHFS: (c) overall view and (d) the amplified view of selected black dashed rectangle area in (c); (e) The corresponding elemental line-scan profiling along the white arrow in (d).

An aluminide coating was fabricated on NHFS via pack cementation, in which the NHFS samples were embedded in mixture powders of Al, AlCl_3 and Al_2O_3 and heated at 973-1073 K. AlCl_3 was introduced as an activator to promote aluminizing kinetics.

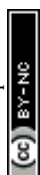


The schematic diagram of the coating formation mechanism is shown in Fig. 1(a). The preparation process consists of two steps: the generation of active aluminum and the diffusion growth of the coating layer. At high temperatures, AlCl_3 decomposes to generate gaseous AlCl_2 and AlCl ,^{43, 44} which subsequently release active Al atoms ($[\text{Al}]$). $[\text{Al}]$ adsorbs to the surface of the substrate and dissolves into NHFS to form a solid solution. When Al reaches a certain concentration, the aluminized layer starts to form. When the processing temperature is below 973 K, the NHFS surface cannot form a continuous aluminide coating due to insufficient reaction kinetics. Conversely, at temperatures exceeding 1073 K, the quartz tube reacts with AlCl_3 , introducing silicon impurities into the aluminide layer. Therefore, the optimum processing temperatures for coating fabrication is 973-1073 K.

The surface secondary electron image of coated NHFS is presented in Fig. A1. The rough surface is a characteristic metallurgical phenomenon inherent to pack cementation processes, which originates from non-uniform $[\text{Al}]$ concentration gradients. The cross-sectional micro-XRD and surface XRD patterns of the aluminide layer are shown in Fig.1(b) to determine the phase composition. The diffraction peaks of three aluminide phases in coating are observed in surface XRD, namely, $\text{Al}_3(\text{Nb,Hf})$, AlSb , $\text{Al}_{13}\text{Fe}_4$. The absence of NHFS peak indicates that the coating is thick enough beyond the detection depth of surficial XRD. The phase composition of the coating is also supported by the cross-sectional micro-XRD. Due to the relatively large detection range of the micro-XRD, the host phase NHFS is detected in the micro-XRD. This demonstrates compositional homogeneity throughout the coating. The overall reaction at the coating interface is:



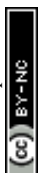
The cross-sectional secondary electron image of the coated NHFS is shown in Fig.1(c). The coating exhibits no cracks or pores and maintains strong interfacial bonding with the substrate. The secondary electron image and elemental line profiling of the amplified view of selected area in Fig.1(c) are shown in Fig.1 (d) and (e). Combined with elemental mapping results (Fig. A2), Al uniformly distributed



throughout the coating, while Nb, Fe, Sb distributed as a hierarchical structure. The Al content is maintained at approximately 72%. The observed decline of Al content is attributable to the lower Al concentration in AlSb than that in both $\text{Al}_3(\text{Nb,Hf})$ and $\text{Al}_{13}\text{Fe}_4$. The observed layered architecture demonstrates sequential formation of three aluminide phases within localized regions. The reaction enthalpy (ΔH) values of the compounds directly correlate with their formation tendency, where lower ΔH indicates higher thermodynamic stability. As shown in Fig. A3, the progressively decreasing ΔH values of Al_3Nb , AlSb and $\text{Al}_{13}\text{Fe}_4$ (-0.66, -0.51, and -0.43 eV/Al) align with their distribution in the layered structure. These findings align with the formation mechanism of alternate layered oxides.³⁶ Thus, the distinct reaction enthalpies drive sequential precipitation of these phases in constrained diffusion zones.

Due to the inter-diffusion of Al, a robust metallurgical bond at the coating/substrate interface, possesses a coefficient of thermal expansion (CTE) closely aligned with NHFS ($\text{Al}_3\text{Nb} \sim 9.6 \times 10^{-6} \text{ K}^{-1}$, $\text{Al}_{13}\text{Fe}_4 \sim 11.9 \times 10^{-6} \text{ K}^{-1}$, NHFS $\sim 10 \times 10^{-6} \text{ K}^{-1}$),^{45, 46} effectively mitigating CTE mismatch between the coating and substrate. In addition, each aluminide layer maintains a thickness of merely 1-2 μm , effectively suppressing thermal stress within the coating. The interlayer diffusion significantly enhances the bonding strength, thereby preventing any observable cracking at elevated temperatures. In addition, the thickness of the coating can be precisely controlled to meet specific application requirements. The thickness shows a parabolic growth with holding time (see Fig. A4), indicating that the coating process is dominated by the diffusion process of Al.⁴⁴ When the thickness is too thin, the substrate may become exposed, leading to insufficient protective performance. Conversely, an excessively thick coating can result in cracking at the edges and corners (see Fig. A5). Considering of the protective effect, the optimal thickness the coating is range in 20–60 μm .

3.2. Antioxidant properties and kinetic analysis



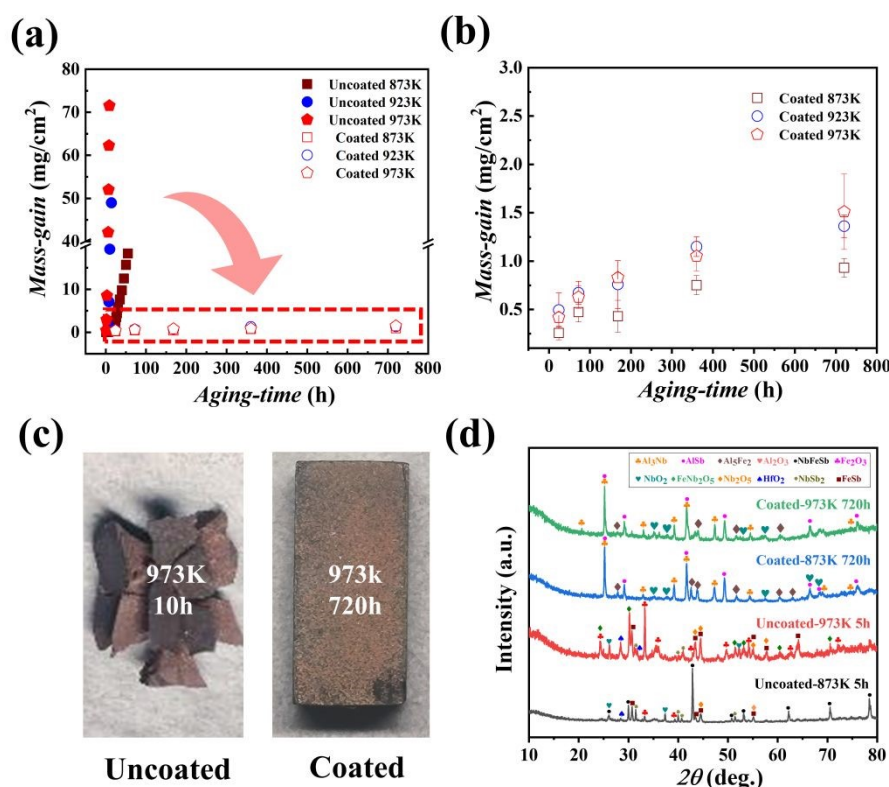
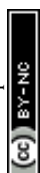


Fig. 2 (a) Mass-gain vs. aging time for uncoated and coated NHFS at different aging temperatures; (b) Detailed data of the coated samples in (a); (c) The appearance of uncoated and coated NHFS after aging at 973 K for 10 h and 720 h, respectively. (d) The XRD patterns of uncoated and coated NHFS after aging at different temperatures.

To ascertain the oxidation resistance of the coating, long-term oxidation aging tests were conducted in air at 873 K, 923 K and 973 K. The mass gain of uncoated and coated NHFS over time are presented in Fig. 2(a) and (b). For uncoated NHFS, the mass gain shows a sudden transition to exponential growth kinetics after an initial stabilization phase. The average oxidation rates are 0.46, 3.28 and 7.28 mg/cm²/hour at 873 K, 923 K, and 973 K, respectively. Compared to uncoated samples, the mass gain rates of the coated NHFS drop by ~99%. The parabolic rate constants (K_p) for coated NHFS are 3.82×10^{-7} , 3.94×10^{-7} and 5.68×10^{-7} mg²cm⁻⁴s⁻¹ at 873 K, 923 K and 973 K, respectively (Fig. A6). The introduction of the coating transforms the weight gain curve from linear to parabolic, indicating a shift from reaction-controlled to a diffusion-controlled process.

Fig. 2(c) shows the appearance of uncoated and coated NHFS after aging at 973 K. The uncoated sample exhibits severe cracking oxidation after 10 h, resulting in



complete material failure. The cracks firstly appeared at the corners, which are the stress concentration zones. Under prolonged aging exposure, the progressive inward propagation of cracks ultimately induces the complete failure of NHFS. The catastrophic oxidation renders NHFS completely unsuitable for any application in oxygen-containing atmospheres. With coating applied, the sample exhibits no visible degradation after aging at 973 K for 720 h. This remarkable improvement originates from the formation of thermal stable Al_2O_3 , as confirmed by XRD analysis and EDS results (Fig.2(d) and Fig.A7).

The XRD patterns of the uncoated and coated NHFS after aging at 873 K and 973 K are shown in Fig. 2(d). For coated NHFS, four phases of Al_2O_3 , Al_3Nb , AlSb and Al_5Fe_2 are observed. Compared to the sample before aging, $\text{Al}_{13}\text{Fe}_4$ transferred into Al_5Fe_2 , and Al_3Nb and AlSb phases remain within the coating matrix. Table. A1 shows the calculated enthalpies of formation of the possible reaction for the oxidation process of aluminide coating. All three aluminum compounds can generate Al_2O_3 and corresponding oxides upon reaction with O_2 . This endows the coating with both oxidation resistance and self-healing capability. Fig. 2(d) also presents the XRD patterns of the uncoated NHFS after aging for 5 hours at 873 K and 973 K. The diffraction peaks of eight phases are observed, namely NbFeSb , Fe_2O_3 , Nb_2O_5 , NbO_2 , HfO_2 , FeNb_2O_6 , FeSb and NbSb_2 . The CTEs for the main oxidation products were shown in Table. A2. Due to the large difference in CTE between NHFS ($9.0 \times 10^{-6} \text{ K}^{-1}$) and Fe_2O_3 ($\sim 12.0 \times 10^{-6} \text{ K}^{-1}$), Nb_2O_5 ($\sim 5.9 \times 10^{-6} \text{ K}^{-1}$), HfO_2 ($\sim 5.8 \times 10^{-6} \text{ K}^{-1}$),⁴⁷⁻⁴⁹ and the relatively high Pilling-Bedworth ratio of $\text{Nb}/\text{Nb}_2\text{O}_5$ (2.67) and $\text{Fe}/\text{Fe}_2\text{O}_3$ (2.09),⁵⁰ substantial intrinsic compressive stresses are generated within the oxides and then evolved into cracks.



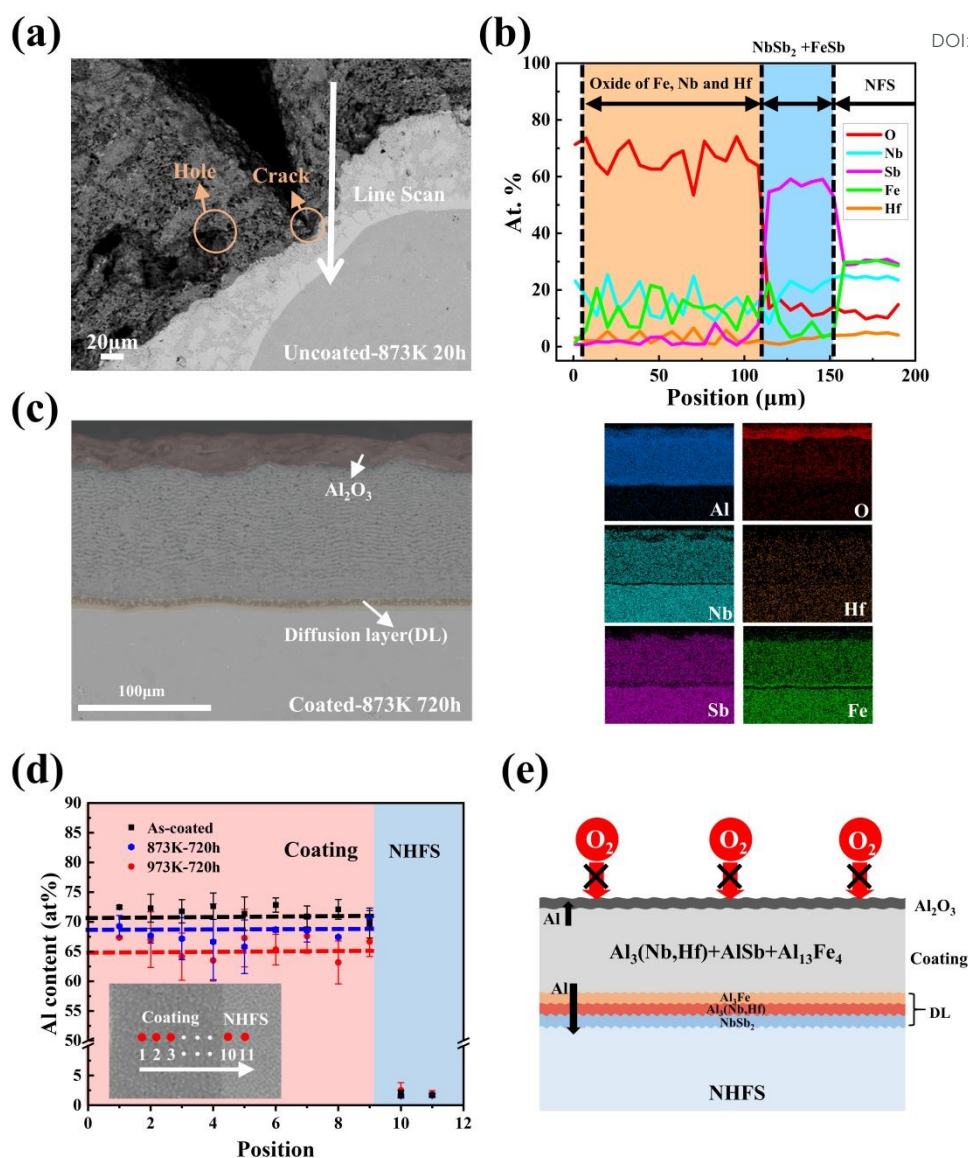
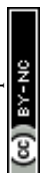


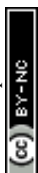
Fig. 3 (a) The cross-sectional BSE image of the uncoated NHFS after aging at 873 K for 20 h; (b) The elemental line-scan profiles along the white arrow marked in (a); (c) The cross-sectional BSE image of the coated NHFS after aging at 873 K for 720 h in air and corresponding elemental mapping results; (d) Al content distribution in the coating layer for coated NHFS; (e) Schematic diagram of oxidation protection mechanism by the aluminized coating layer on the surface of NHFS sample.

The cross-sectional BSE image of the uncoated NHFS after aging at 873K for 20 h and the corresponding elemental line-scan profiles along the white arrows are shown in Fig. 3(a) and (b). From the BSE image observation, a two-layer structure is formed on the surface of material. The elemental line-scan results indicate that the outer layer is composed of Fe, Nb and Hf oxides. The oxide layer exhibits a porous structure with visible cracks. The inner layer is composed of FeSb and NbSb₂ mixtures. Unfortunately,



these oxide layer structures fail to inhibit further oxidation. The total thickness of these two oxidation layers has been over 200 μm , which caused by the accelerated the oxidation rate in the porous structures.

Fig. 3(c) shows a representative backscattered electron (BSE) image and corresponding elemental mapping result of the coated NHFS after aging at 873 K for 720 h in air, revealing characteristic structure evolution. Compared to uncoated NHFS, the coated NHFS maintains structural integrity throughout the aging process. The Al_2O_3 surface layer serves as an effective barrier against inward diffusion of O_2 . Notably, a significant diffusion occurs at the interface. Al gradually diffuses into NHFS, forming a ~ 15 μm diffusion layer (DL). This further strengthens the bonding between the aluminide coating and NHFS. Al content distribution in the coating layer for coated NHFS before and after long-term aging at 873 K and 973 K from coating to substrate are shown in Fig. 3(d). After aging at 873 K and 973 K for 720 h, the Al content decreases by 3.83% and 6.02% compared to the coated NHFS before aging, respectively. This is primarily attributed to diffusion into the substrate and the self-healing of the protect layer.



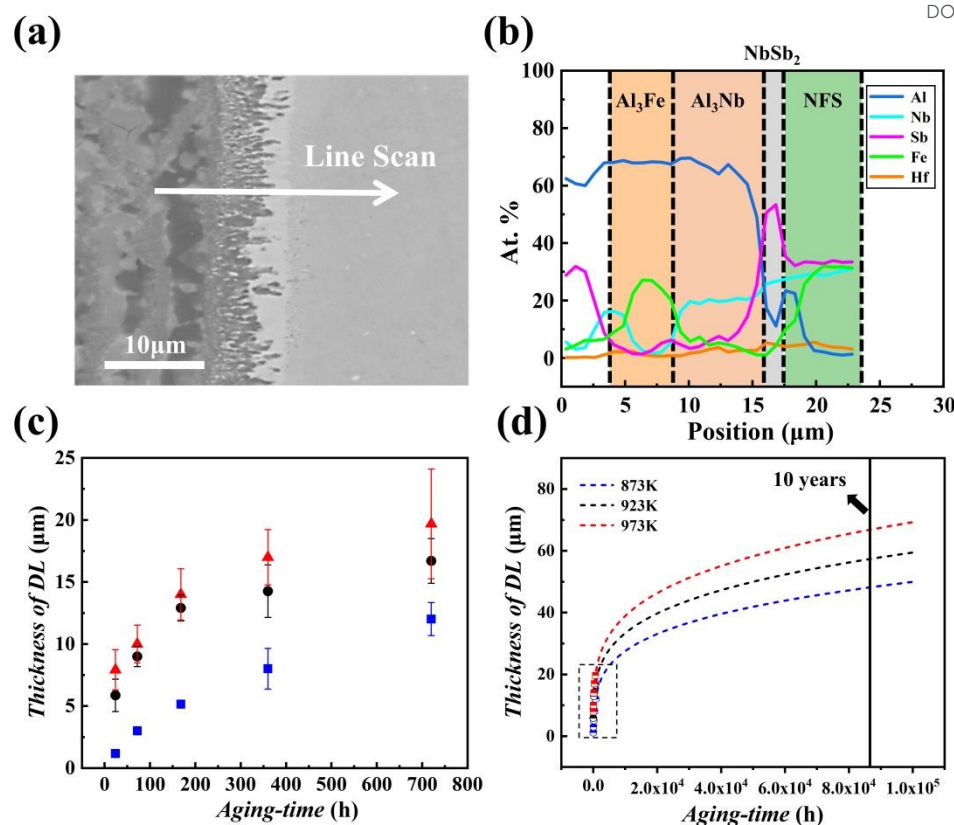


Fig. 4 (a) The BSE images of the diffusion layer of the coated NHFS sample after aging at 973 K for 720 h; (b) The elemental line-scan profiles along the white arrows marked in (a). (c) The thickness of DL vs aging time; (d) Predicted variation of DL thickness vs aging time at different temperatures.

The BSE image of the diffusion layer and the corresponding elemental line-scan profiles along the white arrows are shown in Fig. 4(a) and (b). It indicates that the diffusion layer consists of Al₃Fe, Al₃Nb and NbSb₂. The thickness of the diffusion layer increases progressively with both elevated aging temperature and prolonged exposure time. This may adversely affect the performance of NHFS.

The cross-sectional morphology of the coated NHFS exhibits negligible microstructural degradation following prolonged aging at temperatures below 973 K. The reaction-diffusion kinetics model is introduced to describe the kinetics of diffusion layer (see Note. A1).⁵¹ The thickness of DL at different aging temperatures are determined from the cross-sectional SEM images (see Fig. A9) and shown in Fig. 4(c). The thickness of the diffusion layer follows a parabolic relationship with time. This is attributed to the depletion of additional aluminum sources and the decline in aluminum



concentration gradient, which significantly suppresses the growth rate of the diffusion layer.

The parameters, including the chemical reaction constant k_0 , diffusion constant k_1 , activation energy of chemical reaction E_0 , and activation energy of diffusion E_1 are calculated by the time-dependent thickness of diffusion layer from 873 K to 973 K and shown in Table A3. The obtained E_0 and E_1 are 230.00 kJ/mol and 91.09 kJ/mol, respectively, suggesting that the formation of DL is a process controlled by diffusion. Based on the kinetic data, the relationship between the predicted thickness of DL and time is shown in Fig. 4(d). After aging at 873 K, 923 K, and 973 K for 10 years, the predicted DL thicknesses are only 48.32 μm , 57.53 μm and 67.02 μm , respectively. These are within the acceptable range for the practical TE devices.

3.3. Electrical performance analysis

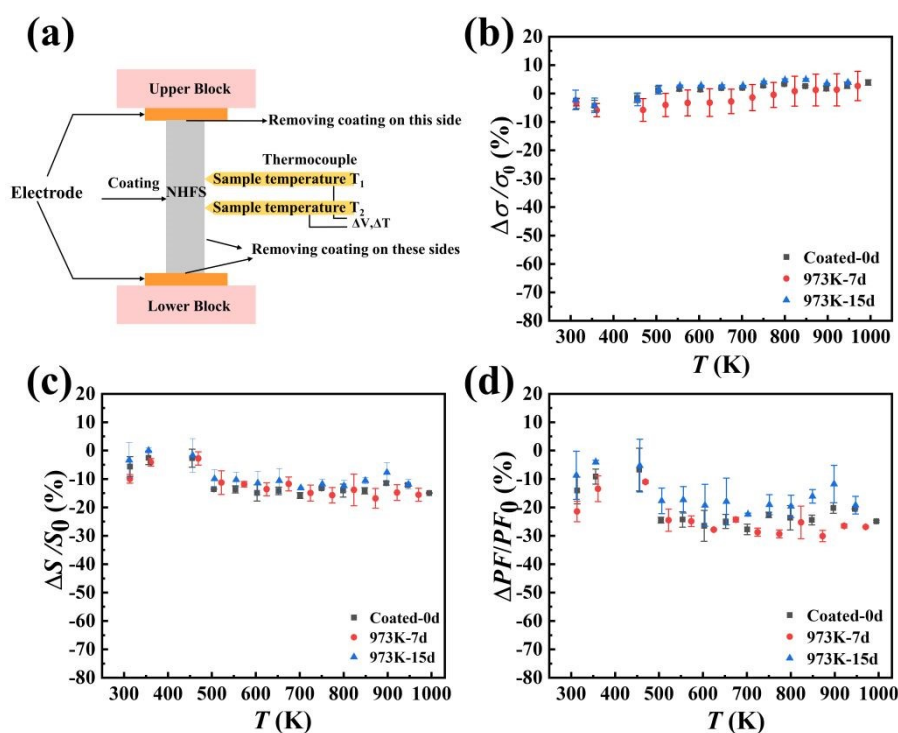


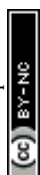
Fig. 5 (a) Schematic diagram of the electrical performance test. (b-d) The relative change in electric properties for coated NHFS and coated NHFS after aging at 973 K for 7 d and 15 d, where σ_0 , S_0 and PF_0 represent the electrical conductivity, Seebeck coefficient and power factor of as-prepared coated NHFS.



The electrical properties of samples with coating were characterized to evaluate the change of thermoelectric device performance. Before the measurement, the coatings on the upper, lower, and one side surfaces were removed to achieve good contacts with electrode and thermal couples (see Fig. 5(a)). The relative change in electric properties for coated NHFS and coated NHFS after aging at 973 K for 7 d and 15 d in air are summarized in Fig. 5(b-d), where σ_0 , S_0 and PF_0 represent the electrical conductivity, Seebeck coefficient and power factor ($PF = S^2\sigma$) of as-prepared NHFS. The σ of Al_3Nb is higher than that of NHFS, but the σ of AlSb is much lower (see in Fig. A10). Based on the theory of thermoelectric composite material (see Note A2), the average σ of AlSb and Al_3Nb are comparable to that of NHFS substrate, resulting in an unchanged σ of the coated sample. Meanwhile, the S of AlSb and Al_3Nb are both lower than that of NHFS, which leading to the S degradation of the coated sample. After complete removal of the coating, the electrical properties return to those of the as-prepared state (see in Fig. A12). Compared to the coated NHFS before aging, the electrical performance exhibited no deterioration after aging in air at 973 K. This indicates that under the protective coating, the material's internal structure remained completely intact, allowing it to maintain optimal electrical performance.

4. Conclusion

To improve the oxidation resistance of NHFS, we prepared a dense layered coating by surface aluminizing using a pack cementation method, in which the NHFS samples are embedded in the mixture powders of Al, AlCl_3 and Al_2O_3 and then heated at 973~1073 K. During this process, dense coating with thickness of 20-60 μm is formed by the solid/gas reactions between Al and the main constituents of NHFS, which are lamellar-structured and composed of $\text{Al}_{13}\text{Fe}_4$, $\text{Al}_3(\text{Nb},\text{Hf})$ and AlSb . Such a lamellar-structured coating acts as an effective barrier for blocking oxygen diffusion and protect the HH substrate from oxidizing. The mass-gain rate of coated NHFS decreases by 99% compared to uncoated sample at 873-973 K for 30 days. Moreover, the in-situ coating maintains structural integrity throughout prolonged aging tests, with neither observable crack propagation nor interfacial delamination. The coated NHFS exhibits no



deterioration in TE properties after aging in air at 973 K, demonstrating excellent feasibility of NHFS-based TE devices operating in air.

Author contributions

Qihao Shen: Writing – original draft, Data curation, Methodology, Investigation, Resources. Jinyu Gu: Data curation. Lei Wang: Investigation. Qingfeng Song: Data curation, Investigation, Resources, Funding acquisition. Chao Wang: Assistant for element fabrication. Xugui Xia: Assistant for element fabrication. Jincheng Liao: Assistant for characterization. Lidong Chen: Validation, Writing - Review & Editing. Shengqiang Bai: Methodology, Writing - Review & Editing, Supervision, Validation, Funding acquisition.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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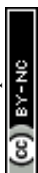
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Data Availability Statement

The authors declare that the data of this manuscript will be made available on request.

