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Improved oxidation resistance of thermoelectric skutterudites coated with composite glass

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Abstract

Composite glass coating was fabricated on thermoelectric (TE) skutterudite (SKD) materials by using the dispersion system of modified nano-silica aerogel and micro glass powder. The organosilane was used as the binder in the slurry-blade process and isolated pores in micrometer size are formed due to the decomposition of polymerization product derived from organosilane and nano-silica aerogel particles at high temperature. These pores can effectively decrease the thermal conductivity of coating layer. The composite glass coating shows good stability at 823 K in air. However, significant microstructural changes in the coating were observed after aging at 923 K, at which the isolated micro-sized pores grew to sub-millimeter pores while the continuous composite glass coating was still maintained. The glass coated skutterudite materials show good oxidation resistance, i. e. no oxides are observed even after heating at 923 K in ambient air. The present glass-coating approach is expected to be applied in fabricating skutterudite-based thermoelectric devices.

Keywords: Composite glass; Coating; Skutterudite; Oxidation resistance

1. Introduction

The direct energy conversion between heat and electricity based on Seebeck and Peltier effects using thermoelectric (TE) materials is attractive for many applications. The performance of TE materials is defined as $ZT = S^2\sigma T/\kappa$, where T, S, σ, and κ are the absolute temperature, Seebeck coefficient, electrical conductivity, and total thermal conductivity, respectively. The efficiency of a thermoelectric generator can be described as follows:

$$\eta = \frac{[(T_h - T_c)/T_h][(1+ZT)^{1/2}-1]}{[(1+ZT)^{1/2} - T_c/T_h]}$$

where T_h and T_c are the temperatures of the hot and cold junctions of thermoelectric leg, respectively. Filled skutterudites (SKDs) have been proposed as promising thermoelectric materials for high temperature power generation applications such as the conversion of waste heat energy into electricity [1–7]. Recently, great progresses have been achieved in the improvement of TE properties of skutterudites, and a maximum $ZT_{\max}$ up to 1.7 or ~1.8 has been obtained for triple-filled skutterudites [8,9]. However, the antimony sublimation and poor oxidation resistance of SKDs at elevated temperatures severely limit the wide range of applications. When operating in air at the service temperature, oxidation and volatilization lead to a rapid degradation of TE properties which obviously shortens the device lifetime [10–20]. Therefore it is of vital importance to protect SKDs from oxidation and Sb sublimation at high temperature.

Creating a protective coating on TE materials is considered as an effective and applicable approach for device

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engineering, and several coating materials have been reported [21–26]. So far, the most promising coating materials reported include metallic films [21], ceramics [22], enamel layers [23], aerogel [24] and composite coatings [25]. To solve simultaneously the antimony sublimation and oxidation of skutterudites at high temperature, previously, we proposed a multi-layer structure consisting of dense inner metallic film and outer thicker oxide layer [26]. However, the fabrication of overlaid coating for SKDs remains a considerable challenge. The current leakage through the inner metallic film is not ignorable when considering the device efficiency. Besides, if ceramic or enamel is used, mismatches between the thermal expansion coefficients of the coating layer and SKDs are difficult to avoid. With respect to the aerogel coating, although it has been reported to have an ultra-low thermal conductivity and good adhesion with SKD matrix, the aerogels are almost entirely composed of empty space with low strength and brittleness, and therefore they are liable to crack or break. Furthermore, the interconnected micropores or mesopores in the aerogels may provide the migration pathway to Sb vapor and oxygen and therefore may cause gradual degradation during long term operation.

With the development of TE power generation technology, a protective coating to prevent SKDs from both Sb sublimation and oxidation is absolutely needed. Moreover, developing a coating with lower thermal conductivity is of practical significance, since the energy loss caused by heat leakage through the coating layer cannot be ignored when a coating is applied. The present study is attempting to propose a simple approach to realize the protective coating on skutterudite materials by using a glass-based composite coating. The thermal expansion coefficient of borosilicate glass was adjusted by chemical composition. Silica-based aerogel particles were added as an enforcement phase. Organic silane was used as a crosslinking binder in the paste blading process. High temperature oxidation tests showed that the glass-coated SKDs possess good resistance to both oxidation and Sb sublimation.

2. Experimental

Dense bulk SKD specimens used as the matrix were fabricated through melting, quenching, annealing and spark plasma sintering (SPS) at 853–873 K. Before painting, the specimens were polished by using metallographic abrasive paper and ultrasonically cleaned with ethanol and water, subsequently. The commercial borosilicate glass used in the present experiment as the coating material contains major components as follows: Na_2O, 18.9 wt%; K_2O, 1.7 wt%; MnO, 1.3%; CaO, 8.0 wt%; BaO, 4.3 wt%; B_2O_3, 17.4 wt%; SiO_2, 39.8 wt%; and Al_2O_3, 4.4 wt%. The B_2O_3 content of glass was determined by chemical analysis, and the other chemical composition analyses were carried out on a PANalytical Axios Advanced sequential X-ray fluorescence (XRF) spectrometer.

The composite glass coating processing is schematically shown in Fig. 1. In a typical process, the γ-Aminopropyltriethoxysilane (APS) and silica aerogel nano-particles and deionized water were mixed evenly in a mass ratio of 36.7:1:74.8, forming an aminopropylsiloxane polymer containing dispersion in which the silica aerogel nano-particles were modified by aminopropylsiloxane molecule. As the hydrolysis and condensation proceed, aminopropylsiloxane grows and becomes highly branched, causing the solution to become more viscous and forming a hybrid sol. The composite coating paste was obtained by mixing the glass powder and the hybrid sol mentioned above evenly. The coating thickness was controlled artificially by the blade times. After being dried in the oven at 353 K, the as-coated samples were then heated to 1023 K for 10 min in a flowing H_2–Ar mixture gas to make the glass particles convert into a continuous layer.

The as-coated SKD specimens were heated to 823 K and 923 K in air in an electrical furnace for a certain period to investigate the isothermal oxidation behavior. The morphology and composition analyses of the composite glass coated SKD samples before and after oxidation test were performed by a JXA-8100 electron probe micro-analyzer (EPMA) equipped with energy dispersive spectroscopy (EDS). The high temperature dimensional change, deformation and wetting behavior of the borosilicate glass bulk were measured through a Thermo-Optical-Measurement system (TOM-AC, Fraunhofer Institute for Silicate Research ISC) up to 1073 K in Ar atmosphere.

3. Results and discussion

The slurry-blade coating process is attractive, since it is simple, inexpensive, and offers good processibility and compositional flexibility. In a typical SEM result, it can clearly be seen that there are some visible cracks distributed in the as-fabricated coating before high temperature treatment. That is due to multi-interface stress, as well as the capillary force of volatility from the coating during the solidification process. As can be seen from Fig. 2(a), a hair-like crack was observed in a typical cross sectional SEM image. However, the coating is still bonded to the SKD substrate due to the robust combination derived from effectiveness of active Si–OH groups which make the organosilane modified silica aerogel rather cross-linked. The gross coatings are composed of hybrid silica matrix and glass powder filling dispersed in the matrix; the hybrid silica appears to envelop the glass frit like a shell. The composite glass coating becomes a continuous layer with isolated pores after heat treatment in flowing H_2–Ar gas at 1023 K (Fig. 2 (b)). A crack-free and continuous coating surface can be observed, which implies that the glass coated SKDs are expected to possess good oxidation resistance. Good adhesion and continuous structure are generated by the stickiness and binding effect of composite glass formed at high temperature heat-treatment (1023 K). Generally, the occurrence of voids in the glass coating is

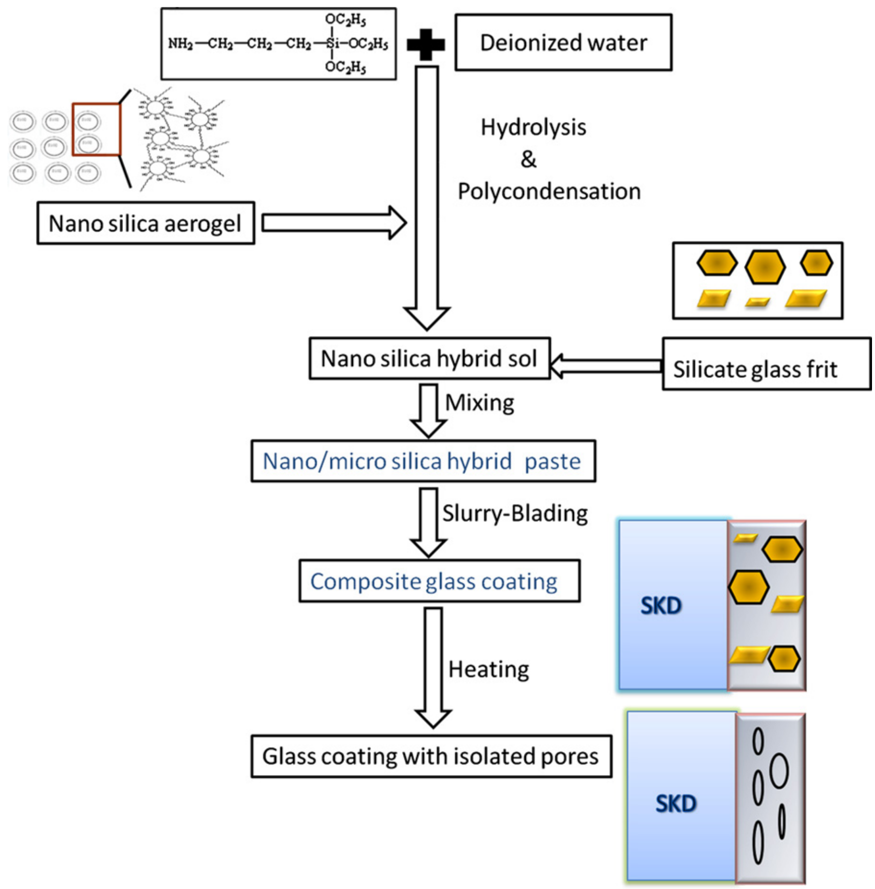

Fig. 1. Schematic representation of the fabrication procedure for the composite glass coating with isolated pores.

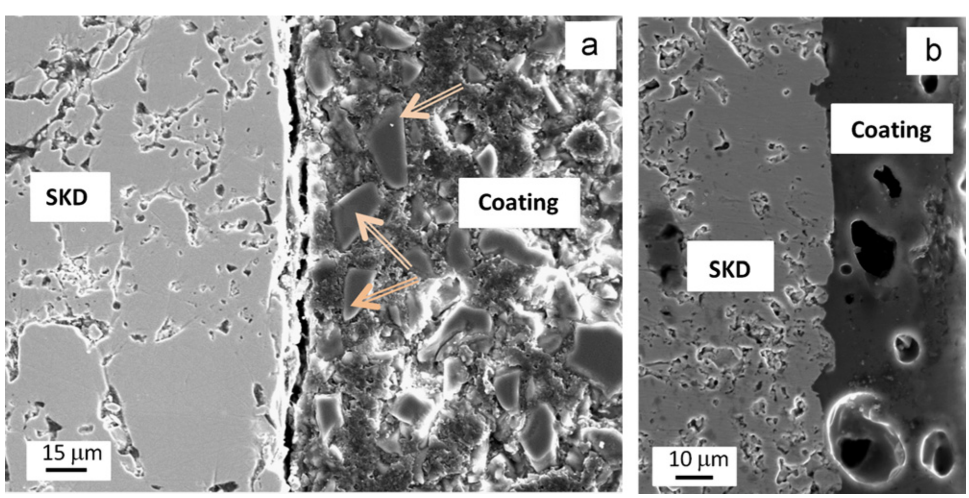

Fig. 2. SEM images of cross section of the as-prepared specimen (a) and glass coated sample treated at 1023 K (b). Arrows in (a) indicate the glass particle dispersed in the as-dried composite glass coating.

particularly troublesome [27]. However, here we present a distinguished isolated porous structure which can reduce the lateral thermal loss, while preventing the SKD materials from oxidation. The pores are closed, and not perforative from the coating surface to the underlying SKD substrate, and thus are distinct from those in the inorganic coatings fabricated by thermal spraying technique. Even though the coating contains pores, the integrity of the coating materials is maintained by virtue of the continuous glass network structure. Furthermore, the SKD matrix remains intact. No obvious cracks are found in the cross-sectional images of the coated SKD component, which implies that the coefficients of thermal expansion for the coating and matrix are matchable.

SKD-based TE devices are anticipated to operate under a temperature gradient of more than 400 K with a hot side temperature of about 750–850 K. Therefore, the SKD materials are required to withstand long term heating as high as or higher than 800 K. In the present experiments, the oxidation behavior of $Yb_{0.3}Co_4Sb_{12}$ SKD specimens has been examined at 823 K and 923 K for different periods. Fig. 3 shows cross sectional morphologies and EDS line scan maps of bare $Yb_{0.3}Co_4Sb_{12}$ after oxidation at 823 K for 72 h and at 923 K for 24 h in air. The oxide scale on the SKD surface is observed. The thickness of oxide layer reaches ~60 μm and ~100 μm for the samples oxidized at 823 K for 72 h and 923 K for 24 h, respectively. Meanwhile some micro-cracks are observed around the SKD/oxide layer boundary at the corner. Some oxidation products for the uncoated SKDs even extend into the inside of SKDs along the grain boundaries, where the solubility and diffusivity of oxygen might be higher than inside the grains. Antimony oxide is inclined to sublimate from the oxide layer, which makes the oxide scale not dense enough for preventing SKD matrix from oxidation. Fig. 4 presents a cross sectional image and corresponding elements distribution line-scanning map of glass-coated $Yb_{0.3}Co_4Sb_{12}$ after oxidation at 823 K for 72 h in air. In the case of the coated SKD sample, the matrix is not oxidized, and no diffusion layer is detected between the SKD and glass layer after isothermally aging at 823 K. These results suggest that the SKD specimens are well adhered to the coating without the formation of oxide scale, while the bare SKDs were oxidized severely. It is known that the oxygen diffusion rate in silicate glass is extremely low at 823 K and antimony is not active enough to diffuse outward into the composite silicate glass layer at this temperature. Notably, the porous structure with isolated closed pores can also hinder the crack propagation by absorbing the propagation energy. As shown in Fig. 5, even after oxidation at 923 K, the coated specimens still remain intact without the attack of oxygen. When temperature is increased to 923 K, a minor amount of antimony is detected in the coating layer because the driving force of Sb migration is enhanced. Furthermore, the size and shape of pores become bigger and more round which is partially due to the aggregation of small pores and/or the evaporation of Sb into the coating layer. At such a high temperature, the glass softens and gradually becomes viscoelastic with increasing temperature. As is obviously seen from the TOM AC results (Fig. 6(a–c)), we can obtain a straightforward evidence. The antimony gas formed by the decomposition of SKD at high temperature may lead to the formation of a large number of bubbles. The antimony agglomerated particles arrange on the bubble/glass surface after cooling (Fig. 6(d), inset). As shown in Fig. 6(e), the bubble is initiated at the interface between SKD and composite glass coating.

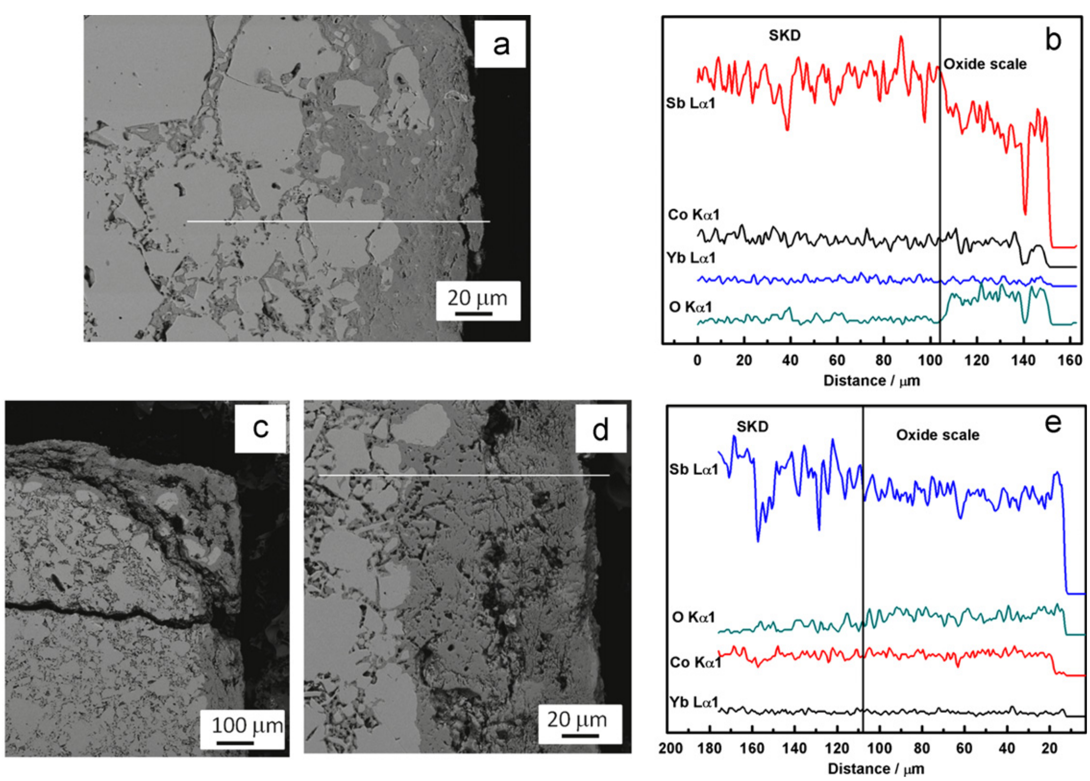

Fig. 3. Cross sectional image (a) and elements distribution EDS line scan maps (b) of the bare $Yb_{0.3}Co_4Sb_{12}$ sample after being isothermally aged at 823 K in air for 72 h. Cross sectional images (c, d) and elements distribution EDS line scan maps (e) of the bare SKD sample after being isothermally aged at 923 K in air for 24 h.

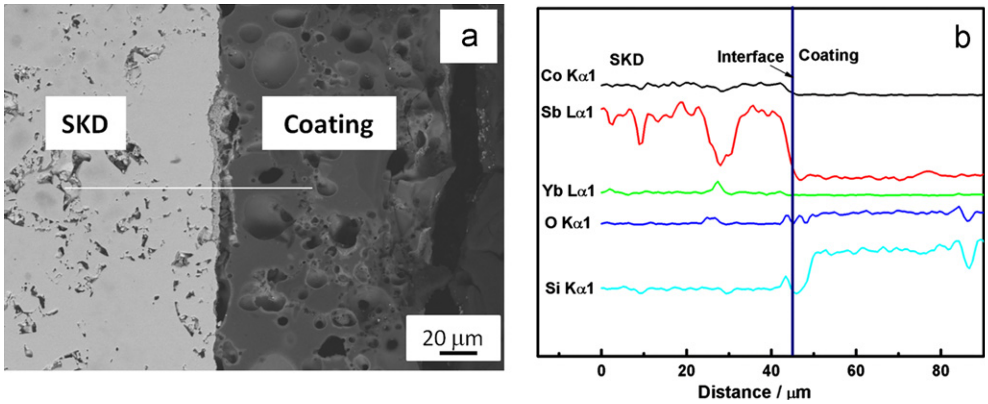

Fig. 4. Cross sectional image (a) and elements distribution EDS line scan maps (b) of the glass coated $Yb_{0.3}Co_4Sb_{12}$ sample after being isothermally aged at 823 K in air for 72 h.

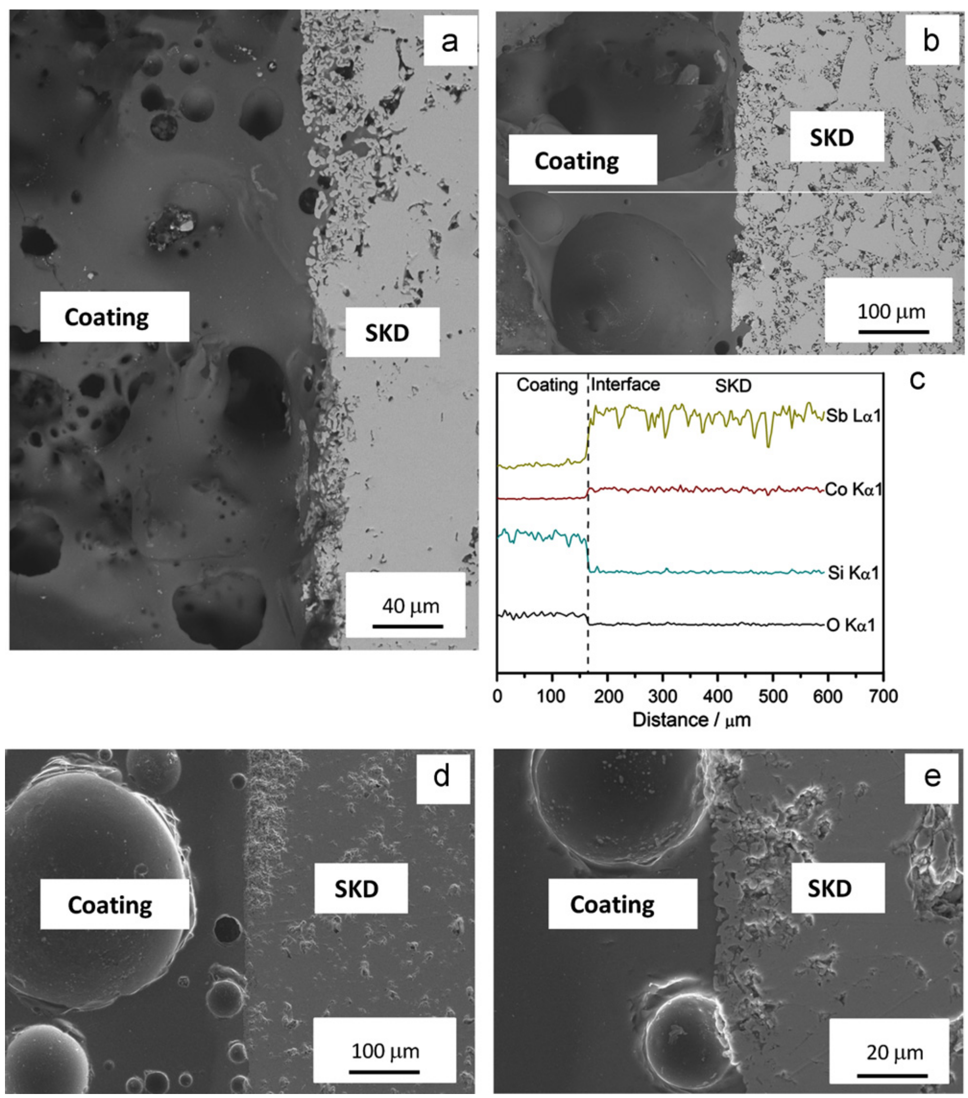

Fig. 5. Cross sectional images (a, b, d, e) and elements distribution EDS line scan maps (c) of the glass coated $Yb_{0.3}Co_4Sb_{12}$ sample after oxidation at 923 K in air for different periods: (a) 24 h, (b, c) 48 h, and (d, e) 72 h.

Remarkably, Na or other glass-component elements in the composite glass have not been detected by EPMA inside the SKD matrix after the high temperature oxidation test. The structure of a glass is conveniently described by the rules of Zachariasen [28]. Silicon and boron are the network forming cations and serve as basic

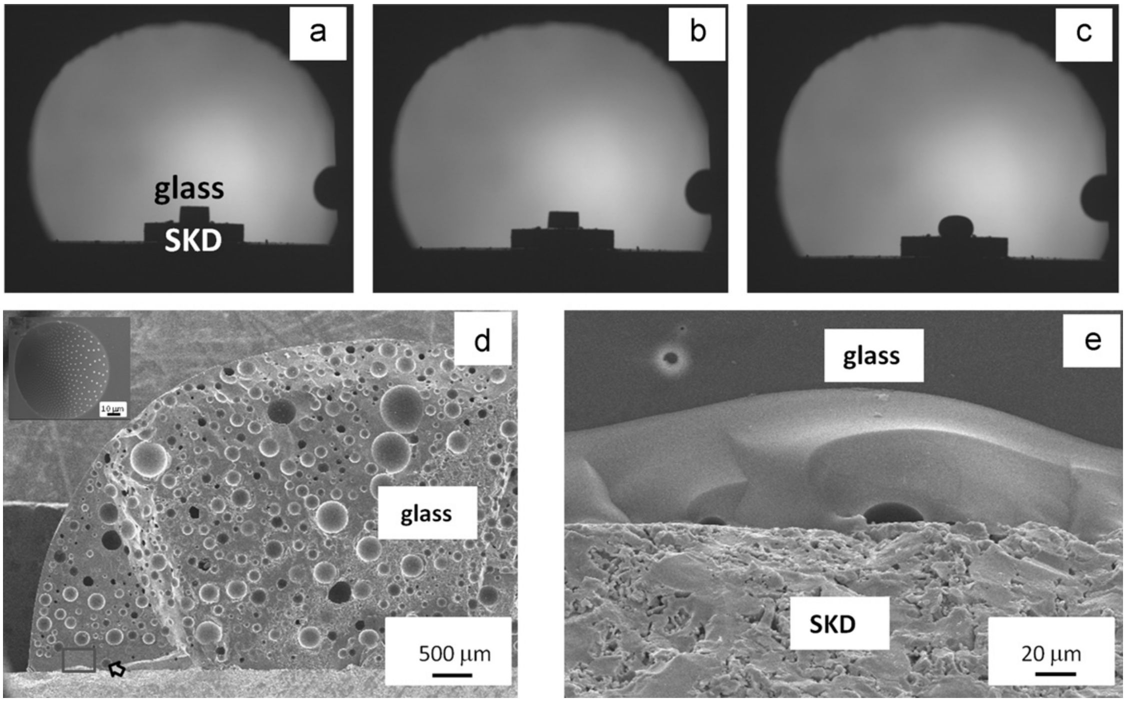

Fig. 6. TOM AC result at 291 K (a); 824 K (b); 924 K (c); and cross sectional SEM images (d, e) after TOM AC test. The inset of (d) shows the higher magnification backscattering electronic microstructure image of the pore labeled with an arrow in (d). The white points, shown in the inset of (d), are antimony particles. Scale bar = 10 μm. (e) is the higher magnification image of the area labeled with blue rectangle in (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

building blocks of the glass network. If modifier cations are introduced into the network, some Si–O–Si bridges are broken. Then oxygen atoms occupy free ends of separated tetrahedral and form non-bridging oxygen (NBO) units. The NBO units are the anionic counterparts of sodium and calcium cations. The modifier cations are mainly incorporated at the severance sites of the silica network. This structure provides a stronger linkage of the network to the divalent alkaline-earth ions than to the monovalent alkali ions. Thereof, the Na ions are considerably more mobile than the Ca^{2+} ions [29]. Additionally, alkaline earth ions may block the diffusion paths of the Na^{+} ions [30]. The composite glass with the addition of hybrid nano-silica has a higher content of SiO_2 in the glassy matrix, which also might reduce the diffusion rates of cations such as sodium and calcium. Nevertheless, the composite glass coating still adheres well to the SKD matrix and seems to be crack-free. Also, the interface between the coating and substrate is continuous. As a result, the coating can effectively prevent the SKD from oxidation.

The typical results shown above reveal that by using the hydrolysis and condensation of organosilane and modification of silica aerogel particles, a useful coating can be fabricated on the SKD surface. Here a robust coating with protective function on TE skutterudites based on composite glass has come into view by a facile and versatile procedure. Note that in our case thickness and functions of the coating can be tuned by adding different fillings, not just limited to borosilicate glass. The method mentioned above heralds the manufacture of robust surface coatings from cheap base materials.

4. Conclusions

We have developed a novel and simple method to protect TE materials using the composites of glass frit and cross-linked organosilane modified silica particles. This technique does not need any specific chemical reaction equipment and can be easily and readily manipulated in a rapid manner. The composite coating, derived from the blending of micro glass powder and modified nano-silica dispersion, can prevent antimonide SKDs from oxidation at high temperatures in air. There is no diffusion observed between coating and SKDs after 823 K aging; nevertheless, minor antimony is detected in the composite coating after 923 K testing. In addition, the isolated porous structure of the composite coating can decrease not only the total mass, but also the lateral thermal loss. The new approach promises a method that can be scaled up to industrial processes, making mass production feasible. We envision that this method can become useful for the convenient and economical manufacture of protective coating for a wide range of materials. Especially, as filled SKDs are required to be used at high temperatures in the oxygen containing atmosphere, oxidation resistance of SKDs had to be enhanced. The results of this work show that the coating can be utilized for the protection of SKD used in the TE device under ambient atmosphere. The effectiveness of the composite glass on the protection for substrate was demonstrated on a range of materials, such as stainless steel and copper alloys.

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