ABSTRACT

Pyrochlore $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.05, 0.1, 0.15, 0.2) ceramic materials were synthesized using a high-temperature solid-state reaction method. The thermal expansion coefficient, thermal conductivity, and calcium-magnesium-aluminosilicate (CMAS) corrosion to $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ were investigated in this work. The results show that with the increase of Nb_2O_5, $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic materials present a cubic pyrochlore structure with clear grain boundaries. The thermal expansion coefficient of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic materials reduces from 11.4576×10^{-6} K^{-1} to 10.3547×10^{-6} K^{-1} (larger than 10×10^{-6} K^{-1}), while its thermal conductivity gradually increases with the increase of Nb^{5+} ions. Additionally, it can be found that the introduction of Nb_2O_5 into $Gd_2Zr_2O_7$ could inhibit the flow of CMAS melting to the ceramic matrix and alleviate the degree of corrosion of ceramic materials. Considering their comprehensive thermophysical properties, $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ compounds may be promising thermal barrier coatings materials.

Key words: $Gd_2Zr_2O_7$; Nb_2O_5 doping; Thermophysical properties; CMAS corrosion

1. Introduction

Thermal barrier coatings (TBCs) have been utilized to resist the oxidation, corrosion, and wear of the substrate caused by the harsh operating environments in the hot sections of gas turbines. Further, these materials improve the engine efficiency by their better thermal insulation

capacity [1,2]. At present, the thermal barrier coating ceramic layer material, which has been widely used in the aerospace field, is 6-~8wt.% by weight Y$_2$O$_3$ (6-~8wt.% is the mass fraction) partially stabilized ZrO$_2$ (YSZ) [3,4]. However, the 6-~8% YSZ has the limitations that it would be no longer effective if its service temperature is higher than 1,200°C°C due to the volume expansion caused by YSZ martensitic transformation. Therefore, it is necessary to seek for a new kind of new thermal barrier coating ceramic materials with better stability and low thermal conductivity.

During the pastrecent decades, rare earth zirconates (Re$_2$Zr$_2$O$_7$) with pyrochlore structure have been applied as the prevalent ceramic top materials due to their good high-~temperature phase stability and thermophysical properties [5-8]. Among these compounds, gadolinium zirconate (Gd$_2$Zr$_2$O$_7$) has attracted much attention for its optimum comprehensive performance. It is reported that Gd$_2$Zr$_2$O$_7$ TBCs has have a better high-~temperature performance and thermal insulation properties compared to YSZ TBCs. Studies have shown that the doping of Gd$_2$Zr$_2$O$_7$ at the A and B sites can enhance the thermophysical properties such as sintering properties, thermal conductivity, and coefficient of thermal expansion. For example, the aliovalent substitution of Sm^{3+} for Zr^{4+} sites provides a new way to modify the thermo-physical properties of Gd$_2$Zr$_2$O$_7$ [9]. Pan wei Wei [10] selected Ti^{4+} as the substituted element of for the Zr- site in Gd$_2$Zr$_2$O$_7$, and the result revealed that the thermophysical properties of Gd$_2$Zr$_2$O$_7$ had been improved and could be used as one of a potential candidate for high-temperature thermal insulation materials. F. A. Zhao [11,12] found that the thermal

conductivity of $Gd_2Zr_2O_7$ had been improved to some extent as Th integration into the Zr- site, and the decrease in thermal conductivity, is related to the content of the Th substituent. Their research group also investigated a series of Zr-site substituted $Gd_2Zr_2O_7$ pyrochlores by first-principles calculations (Ti^{4+}, Hf^{4+}, Ce^{4+}), and found that the displacement of Ce^{4+} for the Zr^{4+} site lowers its thermal conductivity.

Additionally, it is believed that a liquid substance. , Calcium Magnesium Alumino Silicate calcium-magnesium-aluminosilicate (CMAS), will inhale through the intake port when the internal turbine was is working above 1,200°C. The CMAS, including CaO, MgO, Al_2O_3, SiO_2, and a small amount of oxides of Ni and Fe, will cause severe corrosion to the thermal barrier coatings and damage the working life and the reliability of the engine [13]. Studies have shown that the traditional 6- 8% YSZ material cannot resist the erosion of CMAS, because Y_2O_3 and ZrO_2 will dissolve into and react with CMAS [14-16]. It has been found that $A_2B_2O_7$ materials are much more resistant to CMAS corrosion than YSZ [17]. Krause et al. [15] used CMAS to erode three rare earth zirconates ($Y_2Zr_2O_7$, $Gd_2Zr_2O_7$, and $Yb_2Zr_2O_7$) three rare earth zirconates and found the that further corrosion from CMAS could be effectively inhibited owing to the reaction of anorthite and apatite with three rare earth zirconates.

As the above mentioned previously, doping substitutional cations into $Gd_2Zr_2O_7$ can modify its thermalphysical thermophysical properties significantly. The introduction of substitutional cations will be of great significance for further experimental and theoretical research on high- temperature applications. Therefore, in

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this paper, we investigate the structure and thermophysical properties of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$, which will lay a foundation for exploring the development of thermal barrier coating candidate materials.

2. Experimental Procedure
2.1 Preparation

The $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x = 0$, 0.05, 0.1, 0.15, 0.2) samples were synthesized using a solid-state reaction sintering method. Oxide powders Gd_2O_3, ZrO_2, and Nb_2O_5 were selected as the reagents. The stoichiometric ratio weighted oxide raw materials were ball-milled in ethanol using a planetary ball mill for 24 h. The green body was prepared by dry pressing and compacted with 200 MPa pressure, and then pressureless sintered at 1,600 °C for 6 h in air. Then these samples applied to the corrosion resistance test of CMAS (CaO-MgO-Al$_2$O$_3$-SiO$_2$ powders) were prepared by covering the CMAS powder on the surface of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x = 0$, 0.1, 0.2) ceramic materials.

2.2. Characterization

The crystal phase constituents of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramics were characterized by X-ray diffraction (XRD) (Rigaku Miniflex 600), and the micromorphology of samples was observed by scanning electron microscopy (SEM) (sigma 500 AMCS). The density was measured adopting the Archimedes principle. The theoretical densities of specimens were figured out on the basis of the cell parameter from the XRD results and the molecular mass of each unit cell.

2.3. Thermophysical properties measurement

The thermal expansion coefficients (TECs) of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic with

the size approximately 25 mm × 3 mm × 4 mm were measured by high-temperature dilatometry (Netzsch DIL 402C) at temperatures from 25 °C to 1,300 °C at a heating rate of 5 °C/min in air. The thermal diffusivity, K, of the synthesized ceramics with the size 12.5 mm × 2 mm was conducted employing a laser-flash device (Netzsch LFA 427) at temperatures from 25 °C to 1,000 °C under a vacuum environment. Prior to the thermal diffusivity measurements, the sintered sample surfaces were sprayed with a layer of graphite for the absorption of the laser beam, because the laser beam will penetrate through the sample at high temperatures. The thermal diffusivity value of each sample was tested three times at each test temperature then averaged. The heat capacity of the ceramic, C_P, was obtained from the values of each oxide based on the Neumann–Kopp rule [18] with the reference specific heat values [19,20] of Gd_2O_3, ZrO_2, and Nb_2O_5 with 5% deviation. The thermal conductivity, (λ) of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic was then determined using the following formula:

$$\lambda = C_p \times \kappa \times \rho \tag{1}$$

Due to the non-compactness of sintered ceramics, the measured value of thermal conductivity was further normalized for the actual data (λ_0) by the following equation [21]:

$$\frac{\lambda}{\lambda_0} = 1 - \frac{4}{3}\varphi \tag{2}$$

$$\varphi = 1 - \frac{\rho}{\rho_t} \tag{3}$$

Where φ, ρ_t, and ρ ~~is~~ are the fractional porosity, theoretical density, and ~~the~~ bulk density ~~in the formula mentioned above~~, respectively.

2.4 CMAS measurement

CMAS corrosion is also a significant factor in TBCs. The degree of CMAS corrosion of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.1, 0.2) ceramic is characterized by SEM. Before the SEM test, the CMAS bulk prepared by the experiment is slightly larger than the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.1, 0.2) ceramic bulk for convenience. The ~~product of produced~~ corrosion layer is characterized by ~~analysing~~ analyzing the phase composition of the powder, mixing the CMAS powder with $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ powder in a ratio of 1:1 and heating at 1,250°C for 5 h.

3. Results and ~~discussion~~ Discussion

3.1 XRD analysis

Fig. 1 indicates the XRD images of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.05, 0.1, 0.15, 0.20) ceramics sintered at 1,600~~°C~~°C for 6 h. It can be found that $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0.05, 0.1, 0.15, 0.20) exhibits a single pyrochlore structure ~~as~~ the same as the pure $Gd_2Zr_2O_7$, which is identified by the diffraction peaks at 27° (311), 37° (331) and 45° (511) [22]. It can be observed that the intensity of these peaks varies as the Nb_2O_5 content changes. The relative intensity of these peaks is related to the degree of ordering, and the modification of the scattering factors of the oxides doping percentage in the solid solution [23]. Therefore, it is believed that Nb^{5+} completely dissolves in $Gd_2Zr_2O_7$ and forms a solid solution of pyrochlore structure, which shows that the Nb^{5+} had been

incorporated in the Zr-~~Site~~ site of $Gd_2Zr_2O_7$ ceramic material. ~~As is known~~ Given that the ionic radius of Nb^{5+} (0.064nm) is less than that of Zr^{4+}(0.072 nm), the incorporation of Nb^{5+} into $Gd_2Zr_2O_7$ lowers the lattice parameter. The lattice parameter and ionic radius of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramics are shown in Table 1.

3.2 Microstructure

Figs. 2(a) – (e) present the microstructures of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.05, 0.1, 0.15, 0.2) ceramics for each value of x, respectively. It can be seen that the grain shape is regular and no other precipitates appear. Simultaneously, combining the microstructure and the ~~dates~~ data of their bulk densities, the samples all have a dense cell structure and clear grain boundaries. The ~~datum~~ data of bulk densities are listed in Table 2. Additionally, according to the microstructure of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ samples and the ~~dates~~ data of their bulk densities, it can be found that the grain size of the ceramic material has the smallest size when doping amount x is 0.1.

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3.3 Coefficient of thermal expansion

The thermal expansion coefficient is also significant to TBCs materials. It is known that the thermal expansion coefficients of ceramic materials is are usually much less than that of the metallic substrate much more. The greater difference between the thermal expansion coefficient of the ceramic materials and metallic substrate, the more easily the coating fails and falls off. Therefore, in order to minimize the thermal mismatch caused by the residual stresses between the TBCs materials and the bonding layer at high temperature, it is a better solution to elevate the TEC of ceramic materials [24,25].

The thermal expansion coefficients of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramics thermal expansion are drawn in Fig. 3. As shown in Fig. 3, with the increase of Nb^{5+}, the coefficient of thermal expansion gradually decreases. The TEC of solid materials is related to the average distance between geains grains in the crystal lattice. And the lattice vibration increases as the temperature increases, leading to an increase of TEC. Based on the thermal expansion theory of solids, the coefficient of thermal expansion is related to the crystal structure and lattice energy of the material [26]. And the TEC is proportional to the average distance between grains in the crystal lattice, which is determined to by the ionic bond strength of the crystal constituent elements. The intensity of the ionic bond is given by the following equation [27]:

$$I_{A-B} = 1 - e^{\frac{-(X_A - X_B)^2}{4}} \qquad (4)$$

where I_{A-B} is the intensity of the ionic bond between A and B sites cations, X_A is the

average electronegativity of cations at A-site, and X_B is the average electronegativity of cations at B-site. According to the Eq. (4), the thermal expansion coefficient ~~has a raise~~ rises ~~as~~ with the decrease of electronegativity of the A and B cations. It is known that the electronegativity of Nb^{5+} ions (1.60) is larger than that of the substituted Zr^{4+}(1.33) ions~~;~~ thus, substituting Zr^{4+} ions with Nb^{5+} ions will increase the average electronegativity of ions at the Zr site, which increases the electronegativity difference of A and B sites' cations. Therefore, with the increase of doping amount of Nb^{5+}, the thermal expansion coefficient of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramics decreases.

3.4 Thermal diffusivities coefficient

The thermal diffusivity curves of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ (x = 0, 0.05, 0.1, 0.15, 0.2) ceramics ~~were~~ are shown in Fig. 4. As shown in Fig. 4, with the increase of temperature, the thermal diffusivity coefficient of all the ceramic~~s~~ material~~s~~ with different compositions decrease by and large. This phenomenon is consistent with the thermal diffusion characteristics of ceramic materials from room temperature to high temperature, indicating that the phonon conduction behavior is dominant [28,29]. However, the thermal diffusivity coefficient of all ceramics has an intersection point when the temperature approaches ~~to~~ 400°C. Then, all the coordinate values of curves increase ~~as~~ with the increase of doping amount of Nb_2O_5 at the same temperature above 400°C.

3.5 Thermal conductivity

Fig. 5 expresses that the thermal conductivity of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic materials decreases as the temperature increases from room temperature to 600°C firstly, then increases slightly when the temperature rises from 600°C to 1,000°C. The thermal conductivity values of all the ceramics are in the range of 1.4463–1.5878 W/(m·K) at 200°C and 1.2743–1.3416 W/(m·K) at 1,000°C. Especially, the thermal conductivity values are at the range of 1.1942–1.2883 W/(m·K) at 600°C, which is lower than that of YSZ. As shown in Fig. 5, the values of thermal conductivity decrease with the increasing doping amount of Nb_2O_5 before 400°C. When the temperature exceeds 400°C, the thermal conductivity gradually increases along with the increase of dopant content. This phenomenon may be attributed to the intrinsic properties of Nb_2O_5 and the nature of the material microstructure.

It is known that thermal conductivity of different doping components depends on the type and concentration of point defects in the material. Additionally, Fig. 5 shows that the values of thermal conductivity gradually increase along with the increase of Nb_2O_5 content above 400°C, which may be related to the solid solution mechanism. The substitution process did not occur after the incorporation of Nb_2O_5, which formed the interstitial Nb^{5+} ions in the $Gd_2Zr_2O_7$ crystal lattice [30]. The formation of interstitial Nb^{5+} ions reduces the oxygen vacancy concentration for balancing the imbalance of electricity valence. Therefore, the decreased concentration of oxygen vacancy and the strong phonon scattering center lead to the increase of thermal

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conductivity.

3.6 CMAS Measurement

3.6.1 Macroscopic appearance

The macroscopic morphology of Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) ceramic materials before and after CMAS corrosion at 1,250°C is shown in Fig. 6. Fig. 6-(a) shows that the CMAS bulk prepared by the experiment is slightly larger than the Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) ceramic bulk. Fig. 6-(b) shows the morphology of Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) etched by CMAS at 1,250°C; it is covered by a glass-like CMAS body after being sintered at 1,250°C.

3.6.2 Microscopic appearance

The cross-section microstructure of Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) ceramic material after CMAS corrosion at 1,250°C for 1 h is shown in Fig. 7.

It can be seen that a new corrosion layer has formed between the CMAS layer and the ceramic layer, and a large number of fine balls are clearly arranged in the corrosion layer. Additionally, the thicknesses of the corrosion layers of the three Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) ceramic materials corroded by CMAS are approximately 10 μm, 15 μm, and 15 μm, respectively. It can be seen that the addition of Nb$_2$O$_5$ has an effect on the corrosion behavior of CMAS, that is, the corrosion layer will become wider along with the addition of Nb$_2$O$_5$.

It is known from Fig. 8 that CMAS has a greater degree of corrosion on Gd$_2$(Zr$_{1-x}$Nb$_x$)$_2$O$_{7+x}$ (x = 0, 0.1, 0.2) ceramic materials after being treated for 3 h at

1,250°C. The thickness of the corrosion layer between the CMAS layer and the ceramic layer is apparently wider than the materials ~~after~~ being treated for 1 h at 1,250°C. And ~~its~~ the thickness~~es~~ approach~~es~~ approximately 20 μm, 25 μm, and 20 μm, respectively. A large number of fine spheres are still closely arranged in the corrosion layer, and the size of the spherical particles has a decrease in the direction from the CMAS layer to the ceramic matrix. As the ~~above~~ mentioned previously, the doping amount of Nb_2O_5 also has a certain influence on the corrosion behavior of CMAS.

From Fig. 9, it can be seen that the corrosion degree of ceramic materials after 5 h CMAS corrosion increased compared to the material ~~which~~ that was heated at 1,250~~°C~~°C for 3 h, and the thickness~~es~~ of the corrosion layer~~s~~ ~~was~~ were approximately 25 μm, 30 μm, and 25 μm, respectively.

The addition of Nb_2O_5 does affect the corrosion behavior of CMAS after being treated at 1,250°C for different periods of time. The thickness of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic corrosion layer increases firstly and then decreases.

The ~~Grain~~ grain size of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic materials decreases because of the introduction of Nb^{5+}, which increases the specific surface area of the ceramic materials. The increase in specific surface area promotes the reaction between CMAS and the ceramic matrix~~;~~ therefore, when $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic materials ~~were~~ are corroded by CMAS, the newly formed corrosion layer after the introduction of Nb^{5+} will be wider than the corrosion layer compared to the pure $Gd_2Zr_2O_7$. To some extent, when the corrosion product (sphere) approaches a certain thickness, it will act as a

barrier to counteract the corrosion of CMAS to the ceramic matrix.

3.6.3 Corrosion product phase analysis

In order to ~~analyse~~ analyze the corrosion product of the $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x =$ 0, 0.1, 0.2) ceramic material after corrosion by CMAS at a high temperature of 1,250°C, the CMAS powder was mixed with $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ powder in a ratio of 1:1 and heated at 1,250°C for 5 h to study the phase composition of the corrosion product. Fig. 10 shows ~~that~~ the XRD pattern of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x =$ 0, 0.1, 0.2) before and after being mixed with CMAS powder. It can be seen from Fig. 10 that after mixing, the product ~~appears~~ contains cubic phase c-ZrO_2, apatite phase $Ca_2Gd_8(SiO_4)_6O_2$, as well as $Gd_{9.33}(SiO_4)_6O_2$.

As ~~the above~~ mentioned previously, it can be concluded that a barrier including c-ZrO_2, apatite phase $Ca_2Gd_8(SiO_4)_6O_2$, $Ca_2Nb_2O_7$, and $Gd_{9.33}(SiO_4)_6O_2$ has been formed due to the reaction between $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x =$ 0, 0.1, 0.2) coating and CMAS, which inhibits the flow of CMAS melt to the ceramic matrix and alleviates the corrosion degree of ceramic materials.

4. Conclusions

In this work, the thermal properties and CMAS corrosion of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x = 0$, 0.05, 0.1, 0.15, 0.2) ceramic materials synthesized by high-temperature solid-state reaction sintering method were investigated. The results show that $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ($x = 0$, 0.05, 0.1, 0.15, 0.2) ceramic materials present a single pyrochlore structure, and it has have dense cell structures and clear grain boundaries. XRD results suggest that incorporation of Nb^{5+} into $Gd_2Zr_2O_7$ promotes long-range ordering of the pyrochlore structure because of the increase of the cation radius ratio $R(A)/R(B)$. Its thermal expansion coefficient has a decline due to the electronegativity difference between A- and B-sites. The thermal conductivity gradually increases along with the increase of Nb_2O_5 content because of the formation of interstitial Nb^{5+} ions. In addition, the corrosion of $Gd_2(Zr_{1-x}Nb_x)_2O_{7+x}$ ceramic material by CMAS indicates that the incorporation of Nb^{5+} into $Gd_2Zr_2O_7$ could inhibit the flow of CMAS melt to the ceramic matrix and alleviate the degree of corrosion of ceramic materials to some extent.