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Composition optimization, high-temperature stability and thermal cycling performance of Sc-doped $Gd_2Zr_2O_7$ thermal barrier coatings: theoretical and experimental studies

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Abstract

Sc was doped into $Gd_2Zr_2O_7$ for expanding the potential for thermal barrier coating (TBC) applications. According to first-principles calculation, solid solution mechanism of Sc in $Gd_2Zr_2O_7$ lattice was revealed, i.e., Sc atoms first occupy the lattice interstitial sites followed by substituting for Gd, and the interstitial Sc concentration is less than 11.11 at. %. By considering the mechanical and thermophysical properties comprehensively, the optimum Sc doping content was determined to be 16.67 at. %, and this Sc content was selected to produce TBCs by air plasma spraying with YSZ as a bottom ceramic coating (Gd-Sc/YSZ TBC). After sintering at 1400 °C for 100 h, Gd-Sc coatings retain phase and structural stability indicative of excellent sintering resistance. By thermal cycling tests, Gd-Sc TBCs fail due to the low toughness and the

interface reaction between Gd-Sc and bond coat, while Gd-Sc/YSZ TBCs exhibit much longer thermal cycling lifetime, and the failure mode is YSZ coating cracking.

Keyword: Thermal barrier coatings; First-principles calculation; Solid solution mechanism; High-temperature stability; Thermal cycling.

1. Introduction

Thermal barrier coating (TBC) is a kind of high temperature protective coating used for aero turbine engine blades, prolonging blade working lifetime, improving thrust to weight ratio and thermal efficiency [1-3]. TBCs are generally composed of a ceramic topcoat, thermally grown oxide (TGO), bond coat and superalloy substrate. The ceramic topcoat generally has the properties of low thermal conductivity, high chemical stability and thermal expansion coefficient (TEC) to meet the requirements of reducing the surface temperature of the substrate and the thermal stress between the substrate and bond coat [4-5]. The traditional ceramic topcoat material is Y_2O_3 partially stabilized ZrO_2 (YSZ), which has good thermal and mechanical properties [6-8]. However, a transition from metastable tetragonal phase (t') to monoclinic phase (m) occurs when YSZ is in long-term service above 1200 °C, which is often accompanied by volume expansion, resulting in coating spallation; in addition, YSZ has sintering shrinkage and other problems during long-term service, which greatly reduces the thermal insulation performance of the coating [4, 9-10].

In recent years, rare earth zirconates ($\text{RE}_2\text{Zr}_2\text{O}_7$, RE = rare earth element) have been widely concerned by many scholars. Because of their low thermal conductivity, high TEC and good phase stability, they are a series of good candidates for TBC applications. Among the rare earth zirconates, $\text{Gd}_2\text{Zr}_2\text{O}_7$ has the lowest thermal conductivity and highest TEC, so it is regarded as one of the most promising thermal barrier coating materials [11-12]. In addition, $\text{Gd}_2\text{Zr}_2\text{O}_7$ has low oxygen permeability and structural stability at higher temperature [13]. However, the mechanical properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$ are poor, which limits its application.

$\text{Gd}_2\text{Zr}_2\text{O}_7$ has two crystal structures, namely pyrochlore structure and defect fluorite structure, both of which are face centered cubic space lattice [14-15]. Gd^{3+} and Zr^{4+} lattice sites can be replaced by other ions, and some small ions could also enter the interstitial sites. Therefore, the thermal conductivity of $\text{Gd}_2\text{Zr}_2\text{O}_7$ can be further reduced by selectively doping other ions in a single $\text{Gd}_2\text{Zr}_2\text{O}_7$, which makes it possible to improve its thermophysical properties and mechanical properties. It is reported that the TEC of $\text{RE}_2\text{Zr}_2\text{O}_7$ increases with the decrease of RE^{3+} (rare earth) size [16]. Zhang et al. [11] found that the fracture toughness of $\text{Gd}_2\text{Zr}_2\text{O}_7$ can be increased by doping Yb^{3+} . Lee et al. [17] found that the doping Y^{3+} can significantly improve mechanical properties and insulation performance in $\text{Gd}_2\text{Zr}_2\text{O}_7$. These results show that doping small RE^{3+} in $\text{Gd}_2\text{Zr}_2\text{O}_7$ is beneficial to improve mechanical properties and

thermophysical properties. Among the RE^{3+} , Sc has the smallest atomic radius. Our previous research results show that the addition of Sc^{3+} can increase the fracture toughness and TEC of $Gd_2Zr_2O_7$ [18-20]. However, in previous studies, the doping amount of Sc was not optimized, and the solid solution mechanism of Sc in GZO lattice was not clarified theoretically.

Thermal shock resistance behavior, sintering resistance and phase stability of TBCs at high temperature are of great theoretical significance for the optimization design of aeroengine. Rare earth zirconate coating is resistant to sintering at high temperature, and is not easy to undergo phase transformation, but its fracture toughness and thermal expansion coefficient are relatively low, which will lead to poor thermal shock lifetime. M. Karabas [21] found that the thermal cycle life of $La_2Zr_2O_7$ can be improved by doping rare earth elements. Guo et al. [22] studied the high temperature stability and thermal shock resistance of $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$, and found that $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$ can still maintain good phase stability at 1600 °C, and the thermal cycle life is more than 3700 times. Other studies have shown that the design of double- ceramic-layer (DCL) TBCs structure can also improve the thermal shock lifetime, and YSZ coating can effectively alleviate the thermal stress at high temperature [23-25]. According to the above reports, rare earth zirconate materials have good phase stability at high temperature, and the thermal shock resistance can be improved by doping rare earth elements.

The first-principles calculation method based on density functional theory has developed into an important method to predict the properties of materials in recent years, and has been used by many scholars to study the effect of rare-earth doping on the properties of rare earth zirconate [26-29]. Li et al. [27] found by first-principles calculation that doping Sm^{3+} in $\text{La}_2\text{Zr}_2\text{O}_7$ could improve the mechanical and thermal properties, and $\text{LaSmZr}_2\text{O}_7$ has the optimal mechanical and thermal properties when the Sm content is 50 at. %. Zhao et al. [28] used density functional theory and found that the Young's modulus, Debye temperature and thermal conductivity of $\text{Gd}_2\text{Zr}_2\text{O}_7$ decrease with the Th content. Xiao et al. [29] used first-principles calculation method and found that the Young's modulus of $\text{Gd}_2\text{Zr}_2\text{O}_7$ decreases by 22.2-59.9 GPa with the Ce content, and the thermal conductivity decreases by 21% after completely replacing Ce at Zr site. However, the above doping models are established by replacing the RE-site or Zr-site in the pyrochlore lattice, and the interstitial model is not studied. Additionally, the solid solution mechanism of doped atoms has not been analyzed completely.

Sc has been proved to be a very effective dopant, which can significantly improve the mechanical and thermal properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$, but the solution mechanism and the optimal doping amount are still unclear. For TBC's application, its thermal shock and sintering behavior need to be investigated. Therefore, this study intends to clarify the

solution mechanism of Sc doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ (Sc content is 16.67 at. %) by first-principles method and optimize the doping amount of Sc through the change of mechanical and thermophysical properties, and investigate its thermal shock resistance behavior and sintering behavior under long-term heat treatment conditions.

2. Theoretical calculation methods and experimental procedure

2.1 Theoretical calculation method

The theoretical calculations were carried out by the Vienna Ab initio Simulation Package (VASP) software based on density functional theory (DFT) [30]. The projector augmented wave (PAW) method was used to describe the interaction between electrons and ions, and the generalized gradient approximation (GGA) was used to describe the electron exchange correlation potential [31, 32]. In all calculations, the plane wave cutoff energy was set to 500 eV and the k point is $3\times 3\times 3$. The convergence criterion of structural optimization was that the stress of each atom was less than 0.01 eV/atom. In this work, $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore structure was first established, and then several possible models of Sc doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ solid solution was examined. For the strong interactions caused by the 4f electrons of Gd, we did not adopt the Hubbard U correction method. The 4f electrons are regarded as core states, because 4f electrons do not affect the calculated results of mechanical and thermodynamic properties [33, 34].

In order to elucidate the solid solution mechanism of Sc atom in $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice, the

defect formation energies of different doping models were calculated based on the following equation [35]:

$$E_f = E_{\text{tot}}[\text{defect}] - E_{\text{bulk}}[\text{perfect}] - \sum_i n_i \mu_i \quad (1)$$

where $E_{\text{tot}}[\text{defect}]$ is the energy of the crystal after doping, $E_{\text{bulk}}[\text{perfect}]$ is the energy of an undoped perfect crystal, n_i is the number of doping atoms i , and if this atom is added to the system, $n_i > 0$, if this atom is removed from the system, $n_i < 0$; and μ is the chemical potential of the corresponding atom.

After calculating the mechanical property parameters, the thermophysical properties were obtained, including longitudinal sound velocity v_l , transverse sound velocity v_t , average sound velocity v_m , Debye temperature Θ and minimum thermal conductivity k_{min} . The formulas used are as follows [28, 29]:

$$v_l = \sqrt{\left(B + \frac{4}{3}G\right) / \rho} \quad (2)$$

$$v_t = \sqrt{G / \rho} \quad (3)$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-\frac{1}{3}} \quad (4)$$

$$\Theta = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (5)$$

The minimum thermal conductivity is calculated by Clarke's model and Cahill's model respectively, with the following formulas [28, 29]:

$$K_{\text{min}}^{\text{Clarke}} = 0.87 k_B M_a^{\frac{2}{3}} E^{\frac{1}{2}} \rho^{\frac{1}{6}} \quad (6)$$

$$k_{\text{min}}^{\text{Cahill}} = \frac{k_B}{2.48} \left(\frac{n}{V} \right)^{\frac{2}{3}} (v_l + 2v_t) \quad (7)$$

Where B is bulk modulus, G is shear modulus, E is Young's modulus, ρ is density, n is the number of atoms in the crystal, V_m is the volume of unit cell, h is Planck constant,

N_A is Avogadro constant, k_B is Boltzmann constant, M is Molar mass, and M_a is the average mass per atom.

2.2 Experimental procedure

Sc-doped $Gd_2Zr_2O_7$ (Gd-Sc) powders were prepared by a chemical precipitation and calcination method [36, 37]. Firstly, Gd_2O_3 , Sc_2O_3 and $ZrOCl_2 \cdot 8H_2O$ (99.9 %; Jiang-Tian Chemical, Tianjin) was respectively weighed according to the molar ratio of 5: 1: 12. Gd_2O_3 and Sc_2O_3 were dissolved into excessive concentrated nitric acid (65 %; Jiang-Tian Chemical, Tianjin) to obtain $Gd(NO_3)_3$ and $Sc(NO_3)_3$, and $ZrOCl_2 \cdot 8H_2O$ was dissolved in deionized water. Then the solutions were mixed evenly and slowly dripped into excessive ammonia water with mechanically stirring and ultrasonic oscillated to obtain white precipitation, which was filtered and washed several times with deionized water and anhydrous ethanol until PH 7 was reached. The obtained powders were dried at 120 °C for 10 h and calcined at 900 °C for 5 h for crystallization. Gd-Sc and YSZ powders were agglomerated into microscopic particles by a spray drying method before spraying. The parameters of spray drying were as follows: The inlet and outlet temperatures were 240 °C and 100 °C, respectively. The feed rate is 100 g/min.

Gd-Sc coating and Gd-Sc/YSZ double-ceramic-layer coating (DCL) TBCs were produced by air plasma spraying (APS) (Metro 7 M), the spraying parameters were

shown in Table 1. The bond coat and the substrate were NiCoCrAlY (Shenyang Liming Aero Engine Group Corporation Ltd, 53–91 μm) and Ni-based superalloy (DZ125), respectively. The compositions of them are listed in Table 2. When preparing double layer coating, YSZ coating was first sprayed on the bond coat, followed by the Gd-Sc coating.

Thermal shock tests were conducted by a water quenching method. When the temperature of the furnace was reached 1050 $^{\circ}\text{C}$, Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs were put into the furnace and held for 10 minutes, followed by putting it into deionized water to room temperature. This process was defined as a thermal cycle and the termination condition was that the spallation area of the coating surface exceeds 20%. The sintering behavior of Gd-Sc coatings were investigated at 1400 $^{\circ}\text{C}$ in a furnace (SK-G08163, China) for 20, 50, 100 and 200 h.

Phase compositions of samples were determined by a D8 Advance Bruker diffractometer using Cu $K\alpha$ radiation, the parameters were as follows: the voltage and current was 40 kV and 40 mA, and the scanning range of 2θ was $20^{\circ}\sim 80^{\circ}$ with a rate of 6 $^{\circ}/\text{min}$. The high temperature stability of Gd-Sc powders was examined by STA449C thermal analyzer, with the parameters as follows: the heating rate is 10 $^{\circ}\text{C}/\text{min}$ and the temperature range is from room temperature to 1450 $^{\circ}\text{C}$. The surface morphologies, cross-sectional microstructure and composition analysis were observed

by scanning electron microscope (SEM; Nanosem 430, FEI, USA) equipped with energy dispersive spectroscopy (EDS, IE 350).

3. Results and discussion

3.1 Structural properties of $Gd_2Zr_2O_7$

The optimized $Gd_2Zr_2O_7$ model is shown in Fig. 1. The structure exhibits a typical pyrochlore structure with 16 Gd, 16 Zr and 56 O atoms. In the lattice, Gd occupies 16d (0.5, 0.5, 0.5), Zr occupies 16c (0, 0, 0), and the O has two types of sites, i.e., 48f (x, 0.125, 0.125) and 8b (0.375, 0.375, 0.375). In addition, there is an unoccupied oxygen vacancy of 8a (0.125, 0.125, 0.125) in $Gd_2Zr_2O_7$ lattice.

The two most important parameters for describing the structure of pyrochlore are the lattice constant a_0 and the atomic coordinate parameter x_{O-48f} . The x_{O-48f} is an important parameter for the degree of structural disorder, with a value between 0.3125 and 0.375 [36]. When $x=0.3125$, it is an ideal pyrochlore structure, while when $x=0.375$, the system exhibits a disordered fluorite structure, that is, a larger value of x_{O-48f} means a more disordered lattice structure [39]. After completing structural relaxation, the results of a_0 , x_{O-48f} and density of the $Gd_2Zr_2O_7$ model are obtained as shown in Table 3, which are 10.600 Å, 0.3386 and 6.79 g/cm³, respectively, showing agreement with the published values [40-43]. The above part demonstrates the reliability of our calculation results.

3.2 Solid solution mechanism of Sc-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$

In $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice, the doped Sc has two possible sites, i.e., interstitial site and substitution for Gd. In order to determine the solid solution mechanism of Sc in the lattice, we established models with one Sc atom, two atoms, three atoms and four atoms, which were named $\text{Gd}_{\text{Sc-1-inter}}$ and $\text{Gd}_{\text{Sc-1-sub}}$, $\text{Gd}_{\text{Sc-2-inter}}$ and $\text{Gd}_{\text{Sc-2-inter+sub}}$, $\text{Gd}_{\text{Sc-3-inter}}$ and $\text{Gd}_{\text{Sc-3-2-inter+1-sub}}$, and $\text{Gd}_{\text{Sc-4-2-inter+2-sub}}$, respectively, as listed in [Table 4](#) and shown in [Fig. 2](#). The subscripts of inter and sub stand for a Sc atom occupying an interstitial site and substituting for Gd, respectively. The interstitial sites are 32e (0.25,0.25,0.25), which is the most stable interstitial site in pyrochlore structure [\[35\]](#). The Gd site farthest from the 32e is selected as the substitution site.

Defect formation energy is an important parameter to determine the mechanism of point defect formation. The smaller the value, the easier the doped atom can enter the lattice [\[35, 44-45\]](#). The calculated formation energy values of above models are shown in [Table 4](#). According to the calculation results, the solution mechanisms of Sc atoms in the $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice are analyzed as follows: one Sc atom is easier to enter the interstitial site of the lattice, because the formation energy of $\text{Gd}_{\text{Sc-1-inter}}$ (0.141) is obviously smaller than that of $\text{Gd}_{\text{Sc-1-sub}}$ (1.269), which is also consistent with our previous experimental results [\[17\]](#). It is found that the formation energy of $\text{Gd}_{\text{Sc-2-inter}}$ is slightly lower than that of $\text{Gd}_{\text{Sc-2-inter+sub}}$, which indicates that the lattice may accommodate two interstitial Sc atoms but the second atom has some tendency to

substitute for Gd. However, when three Sc atoms were added, we found that the formation of $\text{Gd}_{\text{Sc-3-inter}}$ significantly increased, which means that the $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice has no ability to accommodate three interstitial Sc atoms; in the case of $\text{Gd}_{\text{Sc-3-2inter+1-sub}}$ model, the formation energy decreases significantly, suggesting that the third atom has to substitute for Gd.

The calculated lattice constant values are also listed in [Table 4](#), and shown in [Fig. 3](#) with variation of the Sc contents. The lattice constant increases to 10.646 Å when the Sc content is below 11.11 at. %, followed by a decrease. The increase is due to the presence of interstitial Sc atoms causing lattice expansion, and the decrease could be attributed to the smaller Sc substitution for Gd. Note that when the Sc content is above 5.88 at. %, the increase rate of lattice constant is reduced. This indicates that the second Sc atom has some possibility to substitute for Gd, offsetting the lattice expansion, which agrees with the formation energy calculation results. As a result, one could conclude that the interstitial Sc concentration in $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice might be less than 11.11%, which is consistent with our previous experimental results [\[18\]](#).

According to the change trend of the defect formation energy and lattice constant, the solid solution mechanism of Sc in $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice might be clear: when the Sc content is 5.88 at. %, the Sc atom enter the interstitial sites (32e) in the lattice; when the Sc content is 5.88 at. %-11.11 at. %, the interstitial Sc atoms reach saturation, after that the

doped Sc begin to substitute for Gd.

3.3 Mechanical and thermophysical properties of Sc-doped $Gd_2Zr_2O_7$

Based on the fully optimized model, we calculated the mechanical properties of Sc doped $Gd_2Zr_2O_7$ with $Gd_{Sc-1-inter}$, $Gd_{Sc-2-inter}$, $Gd_{Sc-3-2-inter+1-sub}$, and $Gd_{Sc-4-2-inter+2-sub}$, including elastic constants, bulk modulus B, shear modulus G and Young's modulus E. For cubic system, there are three independent elastic constants C_{11} , C_{12} and C_{44} . The calculated results are shown in [Table 5](#). For $Gd_2Zr_2O_7$, there are some differences between our calculated results and values in the literature [\[29, 34\]](#). The reason may be that the pseudopotential we used is different from that in the literature. For the ceramic system, we did not consider the spin polarization in the calculation process, while the results in the literature considered it [\[29, 34\]](#). However, for the bulk elastic modulus B, shear elastic modulus G and Young's elastic modulus E, our calculated results are in good agreement with the experimental values, which reveals the reliability of our calculated results.

For the cubic system, the elastic constants C_{11} , C_{12} and C_{44} must meet the following three criteria to be mechanically stable: $C_{11}+2C_{12} > 0$; $C_{44} > 0$; $C_{11}-C_{12} > 0$ [\[46\]](#).

According to the calculation results in [Table 5](#), all models are mechanically stable. The variation trend of elastic constant and elastic modulus with the Sc content is shown in [Fig. 4](#). It can be seen from [Fig. 4a](#) that C_{11} , C_{12} and C_{44} have the lowest value when the

Sc doping amount is 5.88%. Fig. 4b shows the bulk modulus B, shear modulus G and Young's modulus E. When the Sc content is 5.88%, bulk modulus B decreases to the lowest value, and then increases slowly with the increase of Sc content. The shear modulus G decreases gently with the increase of Sc content, which is consistent with the research results of Th-doped $Gd_2Zr_2O_7$, Ti-doped $Gd_2Zr_2O_7$ and La-doped $Gd_2Zr_2O_7$ [28, 29]. Note that doping Sc atom could reduce Young's modulus E by 50-73 GPa. This is because doping smaller Sc atom into $Gd_2Zr_2O_7$ lattice introduce size and coupling force mismatch, which causes fluctuation of strain field and lattice softening, resulting in a significant decrease of Young's modulus [47]. For TBC applications, a low Young's modulus is desirable, which means large strain tolerance of coatings beneficial for thermal shock resistance of TBCs [48].

The calculated results of Pugh's indicator(G/B) and Poisson ratios (σ) of Sc doped $Gd_2Zr_2O_7$ with $Gd_{Sc-1-inter}$, $Gd_{Sc-2-inter}$, $Gd_{Sc-3-2-inter+1-sub}$, and $Gd_{Sc-4-2-inter+2-sub}$ are listed in Table 6. G/B is an important index to describe brittle toughness of materials, with a critical value of 0.5, above which the material exhibits brittleness [49]. In other words, the lower the G/B is, the better toughness the material has. Poisson's ratio σ is also another an important parameter to describe the toughness of materials. For ductile materials, the Poisson's ratio is 0.33, while for strong covalent crystals, the Poisson's ratio is 0.1 [50]. In other words, a higher the Poisson's ratio means better toughness of materials. The calculated G/B and Poisson's ratios of $Gd_2Zr_2O_7$ are 0.545 and 0.269,

which are in good agreement with the literature values [28, 51]. Fig. 5 shows the variation of Pugh's indicator (G/B) and Poisson ratios (σ) with the Sc content. With the increase of the Sc content, G/B decreases first followed by an increase when the doping content reach 16.67%, while σ increases first and then shows a decrease. At a Sc doping level of 16.67%, G/B has the lowest value of 0.408, and σ has the highest value of 0.32, suggesting that the material with this composition has the highest toughness.

The thermophysical properties of different Sc-doped $Gd_2Zr_2O_7$ models are listed in Table 7. The calculated Debye temperature of $Gd_2Zr_2O_7$ is 508.506 K, which is close to the calculated value of 520.7 K by Zhao et al. [28] and the experimental 513.4 K by Shimamura et al. [51]. After doping Sc atoms into $Gd_2Zr_2O_7$, longitudinal sound velocity v_l , transverse sound velocity v_t and average sound velocity v_m all decrease, which leads to the decrease of Debye temperature. The variation of Debye temperature Θ (a) and thermal conductivity (b) with the Sc content is shown in Fig. 6. 5.88 % Sc doping into $Gd_2Zr_2O_7$ lattice reduces the Debye temperature by 72 K, while there is a slight increase in the Debye temperature when the doping content reach 11.11%, and then it decreases again. Debye temperature of a material can reflect its TEC [53]. A low Debye temperature suggests weak interaction between atoms in the lattice, which indicates a high coefficient of thermal expansion [29]. For TBC materials, a high coefficient of thermal expansion benefits to reduce the thermal mismatch between the coating and substrate.

The minimum thermal conductivities were calculated based on Cahill's model and Clarke's model as listed in Table 7, which are present in Fig. 6b as the function of the Sc content. The calculated thermal conductivities of $Gd_2Zr_2O_7$ are 1.23 W/m·K by Clarke's model and 1.35 W/m·K by Cahill's model, which are in agreement with the calculated value of 1.29 W/m·K and 1.35 W/m·K by Zhao et al. [28, 29]. Our calculated results are also within the experimental results range of 1.0-1.6 W/m·K [54-56]. It can be seen from Fig. 6b that the minimum thermal conductivity calculated by Cahill's model is slightly higher than that obtained Clarke's model, which is also in line with the calculation trend of other scholars [28, 29]. Comparing curves in Fig. 6a and 6b, it could be found that the variation trend of thermal conductivity is similar with that of Debye temperature with the increase of Sc content. Compared with $Gd_2Zr_2O_7$, 5.88 % Sc doped $Gd_2Zr_2O_7$ has a significant decrease in the minimum thermal conductivity, but further increasing the Sc doping content enhances the thermal conductivity; when the Sc content is above 11.11%, the minimum thermal conductivity has a declining trend, but the decrease rate becomes slow at higher doping levels. It can be seen from the variation of Debye temperature and thermal conductivity that too much Sc doping has no obvious effect on increasing TEC and decreasing thermal conductivity.

Thermal conductivity is closely related to phonon scattering [22]. When the Sc content is 5.88%, Sc atoms enter the interstitial sites of $Gd_2Zr_2O_7$, which enhances phonon

scattering. However, in order to balance the charge, oxygen vacancies are consumed, which would reduce the phonon scattering, but the thermal conductivity is still greatly reduced, which indicates that interstitial doping atoms play a significant role in enhancing phonon scattering. With the increase of Sc content, Gd is gradually replaced by Sc^{3+} . Due to the smaller Sc^{3+} replaces Gd^{3+} , resulting in Sc^{3+} is loosely bound in an oversized atomic cage and does not easily vibrate with other phonons, acting like a local "rattler", which enhances the scattering of phonons and leads to a decrease in thermal conductivity, but its enhancement effect is not as significant as that brought by interstitial atoms, which leads to a slow decline in thermal conductivity [57].

According to the theoretical calculation, the mechanical and thermophysical properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$ can be designed by Sc doping. When the Sc content is less than 11.11%, all Sc atoms enter the interstitial sites of $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice. Then, the Gd^{3+} sites would be gradually replaced by Sc^{3+} with the increase of Sc content. Young's modulus decreases by 50-64 GPa after doping Sc atom, which benefits the thermal shock resistance and high temperature stability of the coating. However, when the content of Sc exceeds 16.67%, the decreasing trend slows down. The toughness of the material can be improved obviously by doping Sc atoms, but when Sc content exceeds 16.67%, the toughness begins to decrease. Similarly, the downward trend of Debye temperature and thermal conductivity begins to slow down after Sc content exceeds 16.67%. Therefore, when the content of Sc is about 16.67%, all aspects of the performance may

be the most suitable.

3.4 Preparation of Gd-Sc TBCs and their sintering behavior

The XRD patterns of the prepared Gd-Sc powder, Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs (Sc content is 16.67 at. %) are shown in [Fig. 7a](#). All the patterns exhibit similar appearance, which have diffraction peaks ascribed to disordered defect fluorite. This indicates that during plasma spraying processes, Gd-Sc powder keeps phase stability, and our spraying parameters are suitable. [Fig. 7b](#) shows the DSC curve of Gd-Sc powder at a temperature range of 25 °C to 1450 °C. There is an endothermic peak at 388 °C, which may be caused by evaporative heat absorption of crystalline water. No other heat absorption or exothermic peaks can be observed during the whole heating process, which indicates that Gd-Sc can maintain good high temperature stability up to 1450 °C. This is beneficial for Gd-Sc coatings used at elevated temperatures.

Cross-sectional microstructures of Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs are shown in [Fig. 8a](#) and [Fig. 8b](#), respectively. The Gd-Sc coating and YSZ coating show a typical layered structure, and both types of TBCs have integral interface, where there are no obvious defects such as gaps and cracks. In Gd-Sc TBCs, the thickness of the Gd-Sc coating is ~120 μm. In Gd-Sc/YSZ DCL TBCs, the thickness of Gd-Sc coating is ~80 μm and that of YSZ coating is ~150 μm.

The XRD patterns of Gd-Sc/YSZ coatings after heat treatment tests at 1400 °C are shown in Fig. 9. It can be seen that the patterns of the heat-treated coatings are similar to that of the as-fabricated coating except that the peaks become sharp, which indicates the crystallization degree of the coatings increases after heat treatments. No new phases are formed in the coatings during sintering, indicating that Gd-Sc coating has excellent phase stability at 1400 °C.

The surface morphologies of Gd-Sc coatings after heat treatments at 1400 °C are shown in Fig. 10. During the first 100 h heat treatment, the coating surface morphologies have little change indicative of excellent sintering resistance. Prolonging the heat treatment to 200 h, many micro-cracks disappear and some large cracks appear, and in the enlarged image (Fig. 10d), one can find that the grains have some growth. This indicates that the coating experiences some sintering during long-term heat treatment at 1400 °C, but the sintering degree is not severe, and the coating almost keeps its original morphology.

The fracture surface morphology of Gd-Sc coatings after heat treatments at 1400 °C are shown in Fig. 11. It can be seen that the layered structure can be clearly observed in the coatings after 20 h, 50 h and 100 h heat treatments. When the heat treatment time is extended to 200 h, the lamellar structure is not obvious, microcracks and pores are closed, and some vertical cracks begin to appear, which indicates that the coating turns

to sintering. The reason for the vertical cracks may be that sufficient temperature and time provide driving force for the growth of grains during heat treatment. At the beginning of sintering, grains contact with each other, resulting in sintering neck, microcracks and voids gradually heal; with the extension of time to the later stage of sintering, the micro-cracks and voids disappear, which reduces the strain tolerance and thermal insulation of the coating. The thermal stress accumulated during long-term heat treatment couldn't be released through micro-cracks and voids, resulting in stress concentration, which results in cracks during the cooling phase. This will not benefit the thermal shock resistance, corrosion resistance and other properties of the coating, and greatly reduces the service life of the coating.

3.5 Thermal cycling behavior of Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs

The macroscopic morphologies evolution of Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs during thermal cycling tests are shown in [Fig. 12](#). Both types of TBCs spalled from the edge. After 75 and 215 thermal cycles, the spallation area of Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs reaches 20% of the total area, respectively. The superalloy substrates become black, which indicates that substrate oxidation takes place during the thermal cycling test. By comparison, Gd-Sc/YSZ DCL TBCs exhibit much longer lifetime than that of Gd-Sc TBCs, revealing that double-layer design could significantly improve the thermal shock resistance of TBCs.

The XRD patterns of the Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs after thermal cycling tests are shown in Fig. 13. During the tests, Gd-Sc coatings has no phase decomposition, indicating that the coatings have excellent phase stability. AlNi_3 is detected in the Gd-Sc TBCs after 75 thermal cycles, which is the component of the bonding coating [58, 59]. It could be presumed that some regions of Gd-Sc coating have spalled off, leaving the bond coat outside. After 215 thermal cycles, $\text{t}'\text{-ZrO}_2$ and NiO are detected in the Gd-Sc/YSZ DCL TBCs. This indicates that the spallation may occur near the bond coat, causing the TGO being detected.

The spalling edge region and adjacent region of Gd-Sc TBCs and Gd-Sc/YSZ DCL TBCs are marked as A, B, C and D, respectively, as shown in Fig. 12b and d. Fig. 14a shows the cross-sectional morphology of region A. After 75 thermal cycles, the Gd-Sc coating has spalled, and there is a large delamination crack in the coating. The cross-section morphology of region B is shown in Fig. 14b. It can be seen that the coating delamination starts from the region near the bond coat. It has been reported that $\text{Gd}_2\text{Zr}_2\text{O}_7$ can react with TGO during heat treatment, which causes stress growth and crack formation at the interface between $\text{Gd}_2\text{Zr}_2\text{O}_7$ coating and the bond coat [23]. For Gd-Sc coating, it also has large possibility to react with TGO, resulting in delamination crack in the coating region near the bond coat. Additionally, although Gd-Sc has improved toughness compared with $\text{Gd}_2\text{Zr}_2\text{O}_7$, its toughness is still not high enough to resist the thermal stress generated in the thermal cycle process, which inevitably leads

to the formation of cracks in the Gd-Sc coating.

[Fig. 15a](#) shows the cross-sectional microstructure of region C. After 215 thermal cycles, the interface between Gd-Sc and YSZ coatings is well bonded, without any defect, and both coating maintains good structural integrity. However, a larger delamination crack forms in the YSZ coating, above which the coatings are spalled. The cross-sectional morphology of region D is shown in [Fig. 15b](#). Although the coatings here are not spalled, some delamination cracks can be found in the YSZ coating, which could cause coating spallation like [Fig. 15a](#) by further thermal shock. At the interface between the YSZ coating and the bond coat, some dark contrast products are observed, which are denoted as E. EDS analysis results show that the product is mainly composed of Ni, Al, O and a small amount of Cr. Combined with the XRD results, we can determine that the products in this region are mainly NiO, as well as some Cr and Al oxides, which is the component of TGO.

Based on the results of SEM and EDS, the failure mechanisms of Gd-Sc/YSZ DCL TBCs could be analyzed as follows. Since the bottom and side of substrate are not covered with the coating, and the thickness of the bond coat is thin, which results in serious oxidation of the alloy substrates and bond coat during thermal cycling. The thickness of the TGO increased with a larger volume expansion, thereby producing a large stress concentration near the oxidation product, resulting in the initiation and

propagation of cracks, which lead to the YSZ coating cracking. Note that Gd-Sc coating still maintains good structural integrity and the interface with YSZ coating is intact. This is because the doping of Sc improves the toughness and TEC, and reduces the Young's modulus, which ensures the tolerance in the process of thermal cycle, and has a good thermal match with YSZ. YSZ coating plays a good buffer role during thermal cycling, and prevents the reaction of Gd-Sc with the bond coat to form GdAlO_3 phase. Therefore, Gd-Sc/YSZ DCL TBCs have better thermal shock resistance.

Thermal cycling life is an important index to evaluate the practical performance of TBCs. Long thermal cycle life is more suitable for TBCs candidate. There are many factors that affect the thermal cycle life, such as cooling rate, temperature, high temperature dwell time and so on. Under similar experimental conditions, the thermal cycling life of $\text{La}_2\text{Zr}_2\text{O}_7/\text{YSZ}$ -TBCs is 160 times, GdPO_4/YSZ -TBC is 70 times and $(\text{La}_{0.8}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7/\text{YSZ}$ -TBC is 32 times [60-62]. The thermal cycling life of these new thermal barrier coatings is less than that of Gd-Sc/YSZ DCL TBCs. In particular, compared with $\text{Gd}_2\text{Zr}_2\text{O}_7$, the thermal cycling life is increased by 55% [63]. Therefore, Gd-Sc/YSZ TBCs have excellent thermal shock resistance and good application prospects in the newly developed thermal barrier coating materials.

4. Conclusions

In this work, the first-principles method is used to study the solid solution mechanism

of Sc atom in $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice. The variation of mechanical and thermophysical properties of Sc-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ (Gd-Sc) with the Sc content is also investigated. Based on theoretical calculation results, the Sc doping content was optimized. Then, Gd-Sc TBCs and Gd-Sc/YSZ TBCs were produced by air plasma spraying, and the phase composition, microstructure, sintering behavior and thermal cycling performance of the coatings were investigated. Following conclusions can be drawn:

- (1) When the content of Sc is 5.88%, Sc atoms occupies the interstitial sites in the $\text{Gd}_2\text{Zr}_2\text{O}_7$ lattice because the formation energy of interstitial doping is significantly lower than that of substitution doping. The variation trend of the lattice constant shows that the Sc interstitial concentration might be less than 11.11%. After that, Gd would be gradually replaced by Sc with the increase of the doping content.
- (2) Compared with $\text{Gd}_2\text{Zr}_2\text{O}_7$, Gd-Sc has lower Young's modulus and Pugh's indicator(G/B) and a higher Poisson ratio (σ) suggesting better thermal shock resistance and higher toughness. At the Sc doping level of 16.67%, Gd-Sc exhibited the lowest G/B and the highest σ indicative of the highest toughness. With the increase of the Sc content, the Debye temperature and thermal conductivity have similar variation trends, which have a significant decrease when doping 5.88 % Sc, and then increase slightly followed by a decrease with further doping. When the Sc content exceeds 16.67%, the decreasing trend of Debye temperature and thermal conductivity reduce. Therefore, the Sc doping content in $\text{Gd}_2\text{Zr}_2\text{O}_7$ is optimized to be 16.67%.

(3) Gd-Sc coatings maintain excellent phase and structural stability after heat treatment at 1400 °C for 100 h. The thermal shock resistance of Gd-Sc/YSZ DCL TBCs is better than that of Gd-Sc TBCs. Due to the improvement in the toughness and thermal expansion coefficient and the decrease in Young's modulus, Gd-Sc coatings have good structural integrity and excellent matching with YSZ coating during thermal cycling. In addition, YSZ coating plays a good buffer role during thermal cycling and prevents the reaction of Gd-Sc with the bond coat. Gd-Sc coatings reveal excellent thermal shock resistance and sintering resistance, which has a promising application prospect.

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Figure Captions

Fig. 1. Crystal structure of $Gd_2Zr_2O_7$

Fig. 2. Solid solution mode of Sc in $Gd_2Zr_2O_7$ lattice with different doping contents

Fig. 3. The variations of lattice constants with the Sc content

Fig. 4. The variations of (a) Elastic constants C_{11} , C_{12} , C_{44} and (b) Bulk modulus B, Shear modulus G and Young's modulus E with the Sc content

Fig. 5. The variations of Pugh's indicator(G/B) and Poisson ratios (σ) with the Sc content

Fig. 6. The variation of Debye temperature Θ (a) and thermal conductivity (b) with the Sc content

Fig. 7. XRD patterns of Gd-Sc powders and coatings (a), and DSC curve of Gd-Sc powders (b)

Fig. 8. Cross-section microstructures of the Gd-Sc TBC (a) and the Gd-Sc/YSZ DCL TBC (b)

Fig. 9. XRD patterns of Gd-Sc coatings after different heat treatment time

Fig. 10. Surface morphologies of Gd-Sc coatings after heat treatment at 1400 °C for (a) 20 h, (b) 50 h, (c) 100 h and (d) 200 h

Fig. 11. Fracture surface morphologies of Gd-Sc coatings after heat treatment at 1400 °C for (a) 20 h, (b) 50 h, (c) 100 h and (d) 200 h

Fig. 12. Macroscopic morphologies evolution of Gd-Sc TBCs (a and b) and Gd-Sc/YSZ DCL TBCs (c and d) during thermal cycling tests

Fig. 13. XRD patterns of Gd-Sc TBCs (a) and Gd-Sc/YSZ DCL TBCs (b) after thermal

cycling tests

Fig. 14. Cross-sectional microstructures of regions A (a) and B (b) of Gd-Sc TBCs after 75 thermal cycles

Fig. 15. Cross-sectional microstructures of regions C (a) and D (b) of Gd-Sc/YSZ DCL TBCs after 215 thermal cycles

Table 1

The plasma spray parameters of Gd-Sc/YSZ coatings

Parameter	Gd-Sc	YSZ
Current (A)	760	800
Power (KW)	32	30
Plasma gas, Ar/H ₂ (SCFH)	80/4	80/4
Carrier gas, Ar (SCFH)	8	8
Spray distance (mm)	100	100

Table 2

Composition (wt. %) of NiCoCrAlY and Ni-based superalloy (DZ125)

	Ni	Co	Cr	Al	Y	W	Others
NiCoCrAlY	42.5	22.6	23.4	10	1.5	-	-
DZ125	59.6	10.5	9.1	5.2	-	7	9.2

Table 3

The structural parameters of Gd₂Zr₂O₇

	a_0	x_{O-48f}	$\rho(\text{g/cm}^3)$
Gd ₂ Zr ₂ O ₇	10.600	0.3386	6.79
Cal. [37]	10.682	0.338	6.629
Cal. [27]	10.452	0.342	
Cal. [38]	10.66	0.339	
Exp. [39]	10.54	0.344	6.8 [40]

Table 4

Lattice constants and formation energy calculations of Sc-doped $Gd_2Zr_2O_7$

	Sc content	a_0	E_f
Gd_{Sc-sub}	6.25%	10.581	1.269
$Gd_{Sc-inter}$	5.88%	10.646	0.141
$Gd_{Sc-2-inter}$	11.11%	10.663	0.659
$Gd_{Sc-2-inter+sub}$	11.76%	10.632	0.745
$Gd_{Sc-3-inter}$	15.79%	10.758	3.347
$Gd_{Sc-3-2inter+1-sub}$	16.67%	10.647	0.953
$Gd_{Sc-4-2-inter+2-sub}$	22.22%	10.623	1.621

Table 5

Elastic constant and elastic modulus of Sc-doped $Gd_2Zr_2O_7$

	C_{11}	C_{12}	C_{44}	B	G	E
$Gd_2Zr_2O_7$	296.521	101.943	86.824	166.803	90.869	230.712
Cal. [27]	324.7	125.3	94	191.8	96.2	247.3
Cal. [32]	277	110	52	165	63	214
Exp. [49]	-	-	-	174	93	236
Exp. [50]	-	-	-	153	80	205
$Gd_{Sc-inter}$	263.328	69.894	48.769	123.007	66.713	169.497
$Gd_{Sc-2-inter}$	285.407	81.656	55.201	147.880	69.716	180.745
$Gd_{Sc-3-2inter+1-sub}$	281.431	99.205	58.998	154.205	62.964	166.263
$Gd_{Sc-4-2-inter+2-sub}$	273.801	86.689	53.527	140.88	60.089	157.827

Table 6

Pugh's indicator(G/B) and Poisson ratios (σ) of Sc-doped $Gd_2Zr_2O_7$

	G/B	σ
$Gd_2Zr_2O_7$	0.545	0.269
Cal. [26]	0.500	0.285
Exp. [49]	0.530	0.273
$Gd_{Sc-inter}$	0.542	0.270
$Gd_{Sc-2-inter}$	0.471	0.296
$Gd_{Sc-3-2inter+1-sub}$	0.408	0.32
$Gd_{Sc-4-2-inter+2-sub}$	0.427	0.313

Table 7

Thermophysical properties of Sc-doped $Gd_2Zr_2O_7$

	V_l	V_t	V_m	Θ	k_{Clarke}	k_{Cahill}
GZO	6512.44	3658.179	4070.692	508.506	1.23	1.35
Cal. [26]			4108.0	520.7	1.29	1.42
Exp.				513.4[49]	1.0-1.6	[52-54]
$Gd_{Sc-inter}$	5595.406	3139.157	3493.509	436.277	1.06	1.16
$Gd_{Sc-2-inter}$	5955.415	3204.201	3577.345	447.505	1.17	1.21
$Gd_{Sc-3-2inter+1-sub}$	5968.192	3068.724	3436.649	430.97	1.06	1.20
$Gd_{Sc-4-2-inter+2-sub}$	5809.301	3029.188	3389.289	425.403	1.05	1.17

Figures

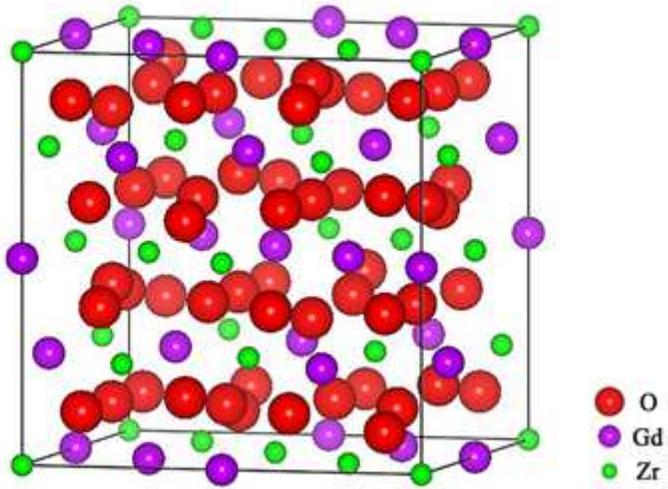


Figure 1

Crystal structure of $Gd_2Zr_2O_7$

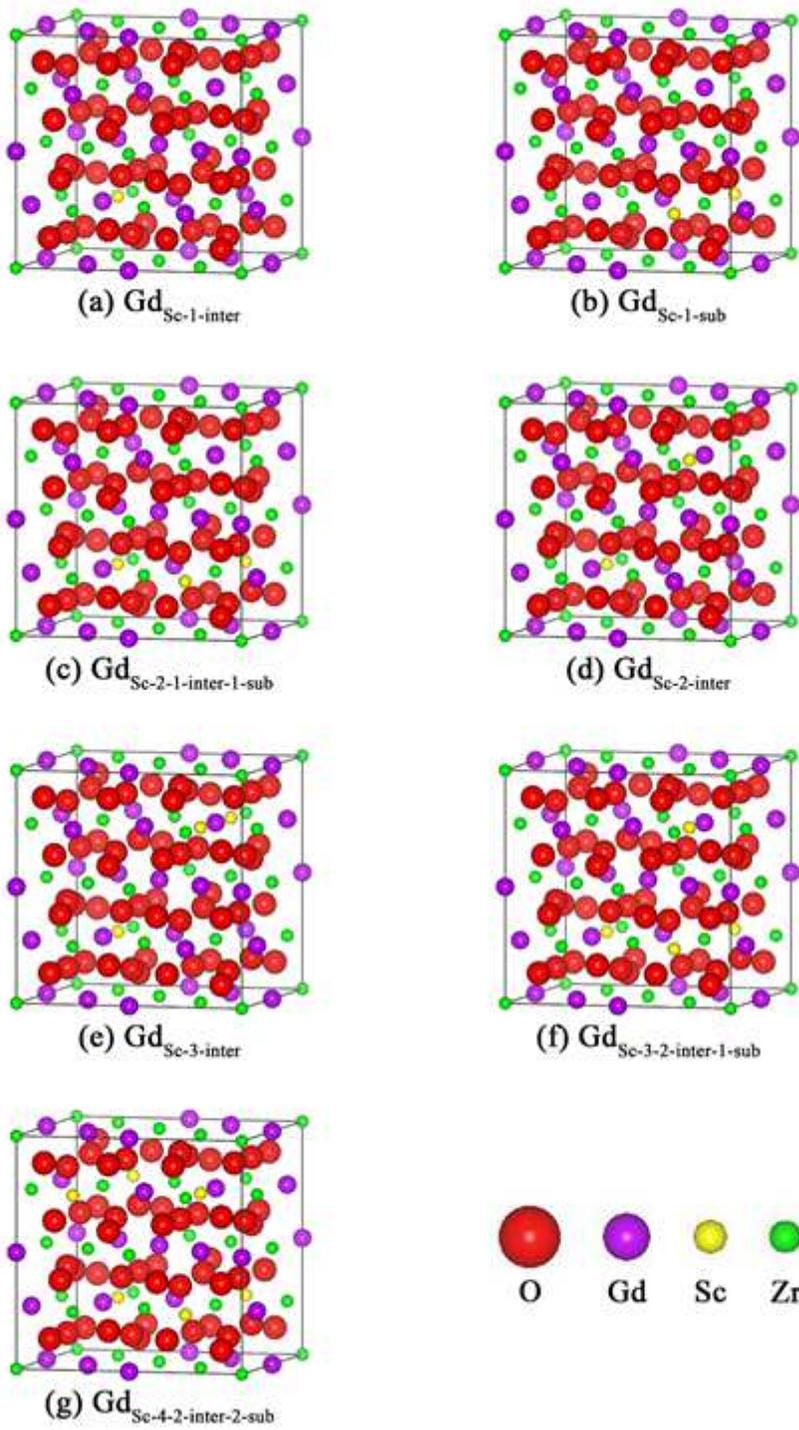


Figure 2

Solid solution mode of Sc in $Gd_2Zr_2O_7$ lattice with different doping contents

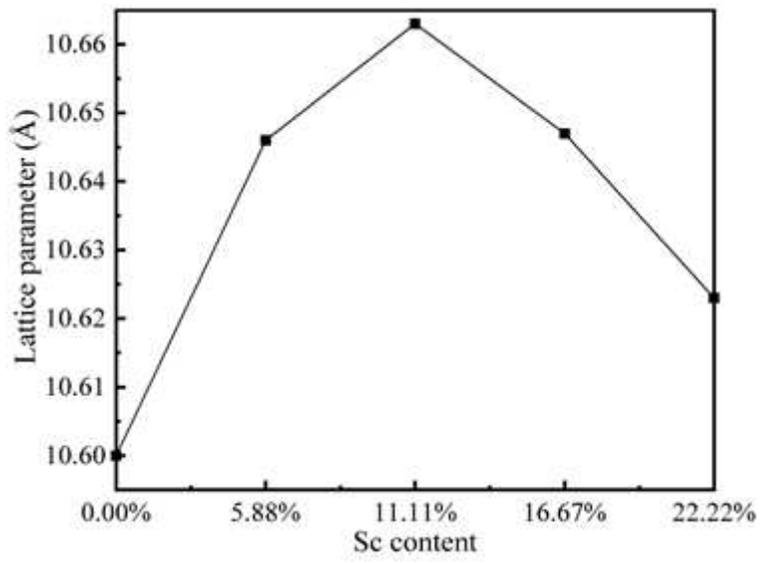


Figure 3

The variations of lattice constants with the Sc content

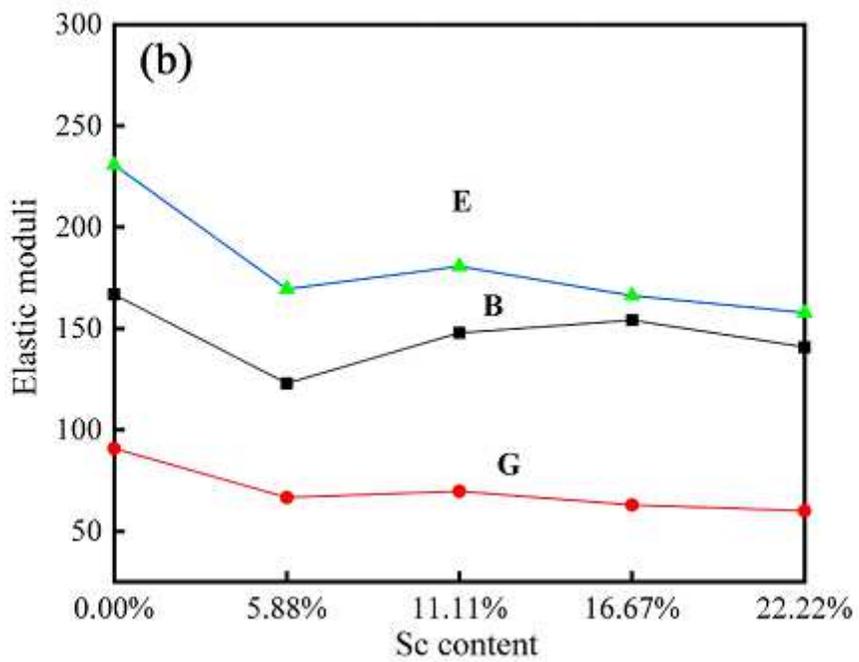
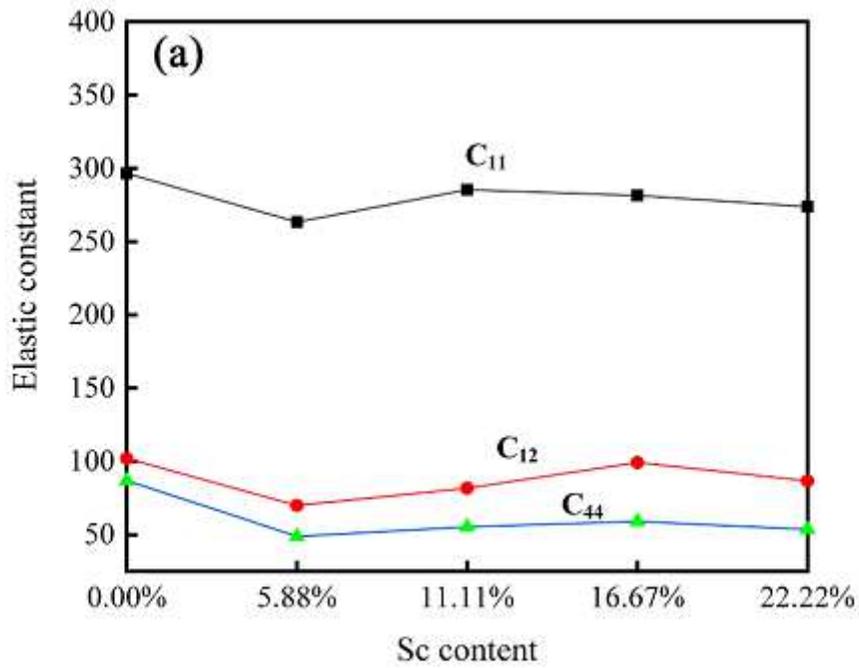


Figure 4

The variations of (a) Elastic constants C_{11} , C_{12} , C_{44} and (b) Bulk modulus B, Shear modulus G and Young's modulus E with the Sc content

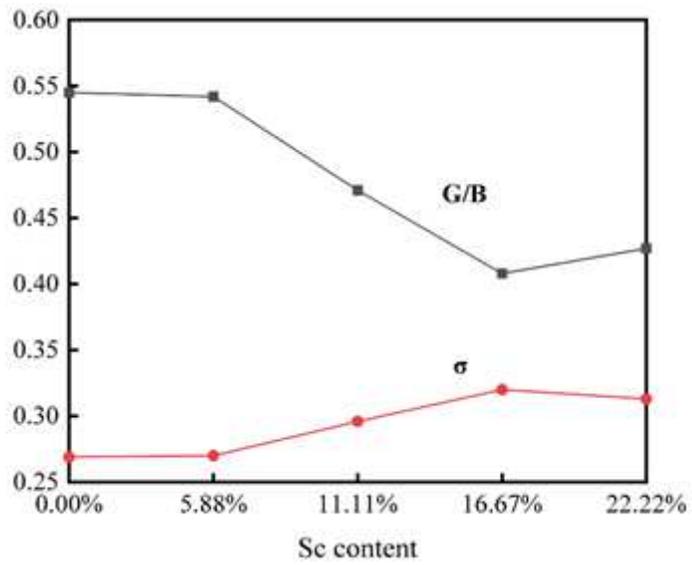


Figure 5

The variations of Pugh's indicator(G/B) and Poisson ratios (σ) with the Sc content

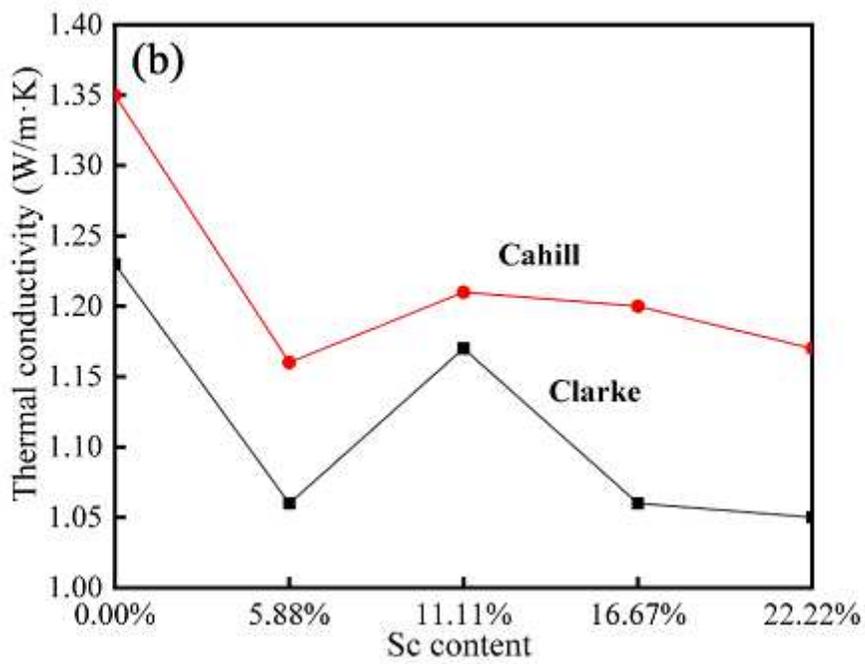
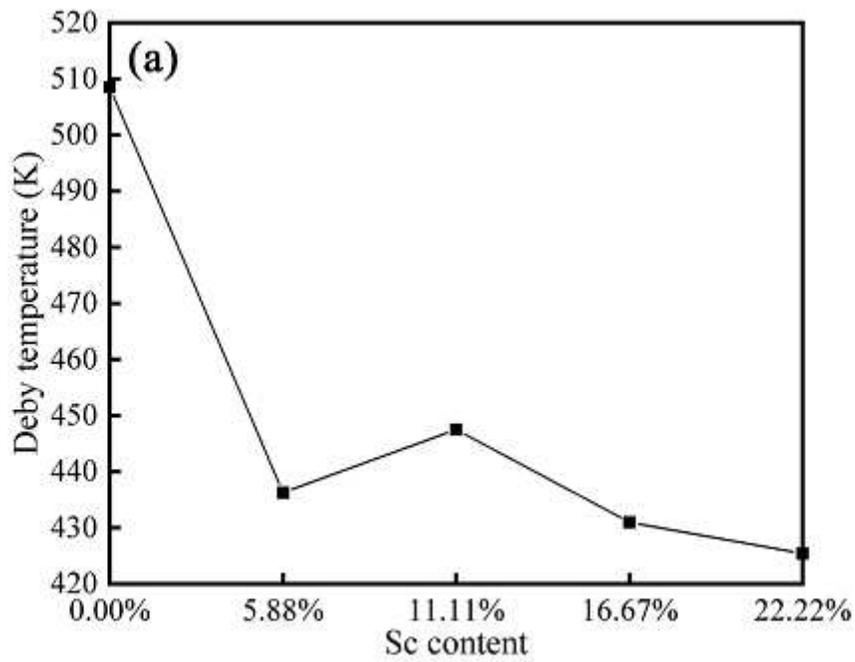


Figure 6

The variation of Debye temperature Θ (a) and thermal conductivity (b) with the Sc content

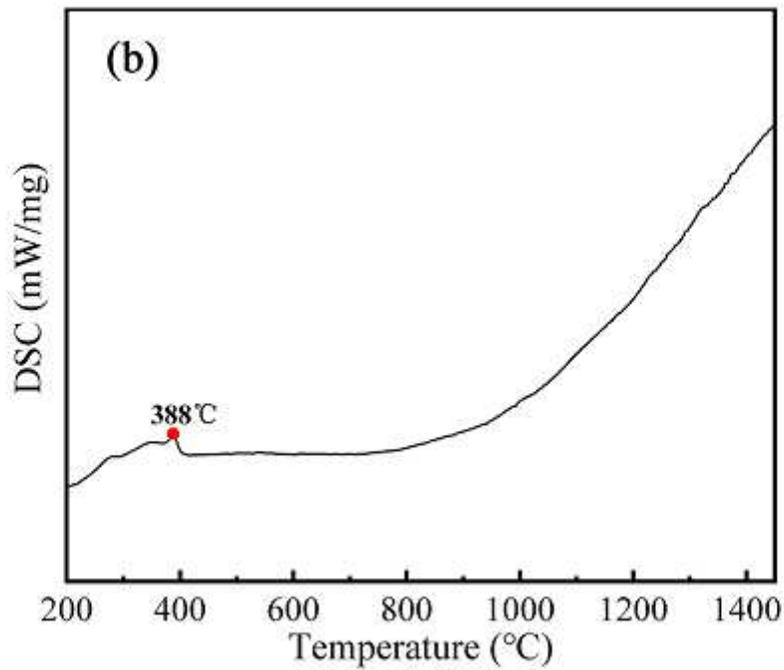
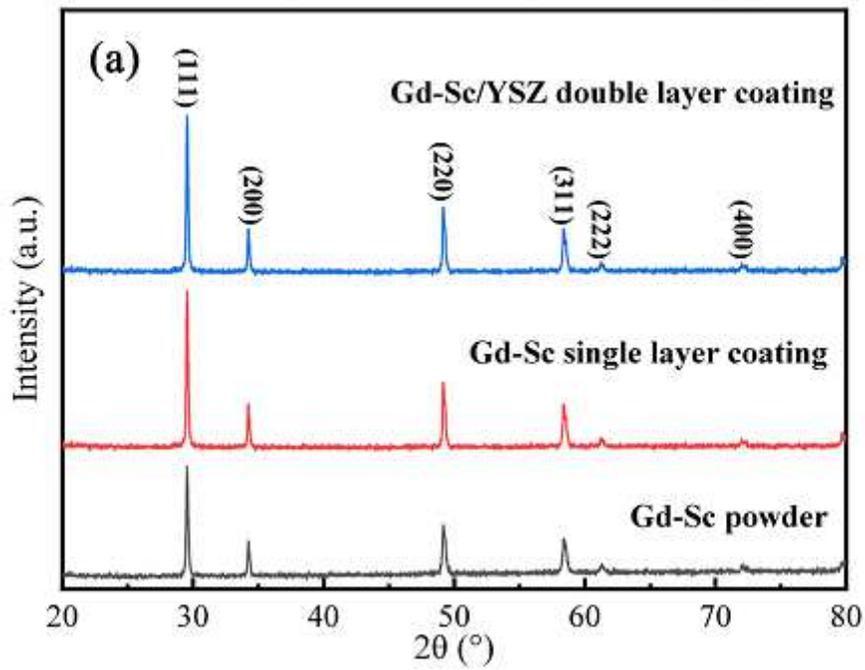


Figure 7

XRD patterns of Gd-Sc powders and coatings (a), and DSC curve of Gd-Sc powders (b)

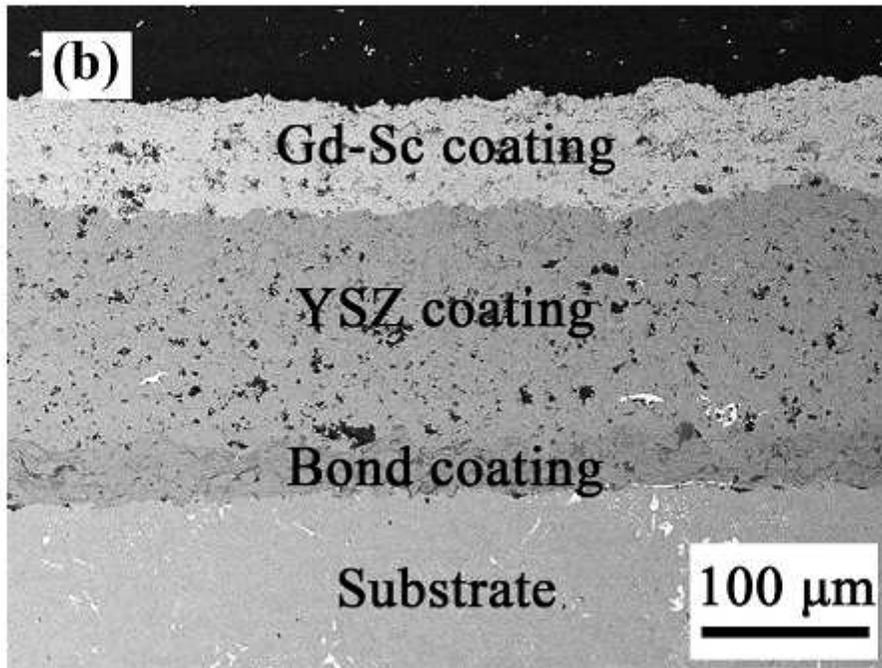
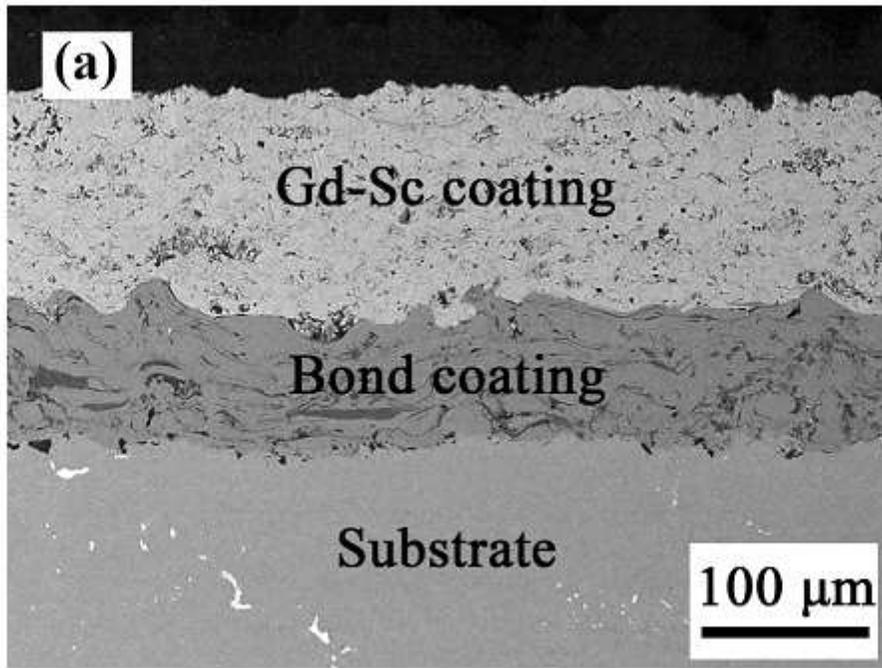


Figure 8

Cross-section microstructures of the Gd-Sc TBC (a) and the Gd-Sc/YSZ DCL TBC (b)

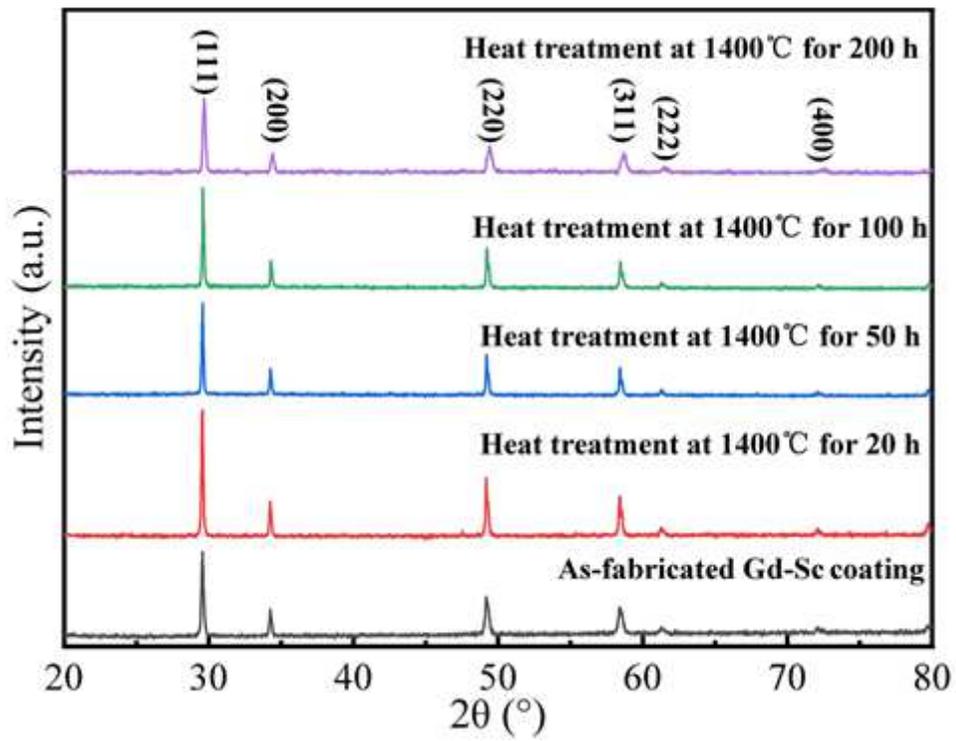


Figure 9

XRD patterns of Gd-Sc coatings after different heat treatment time

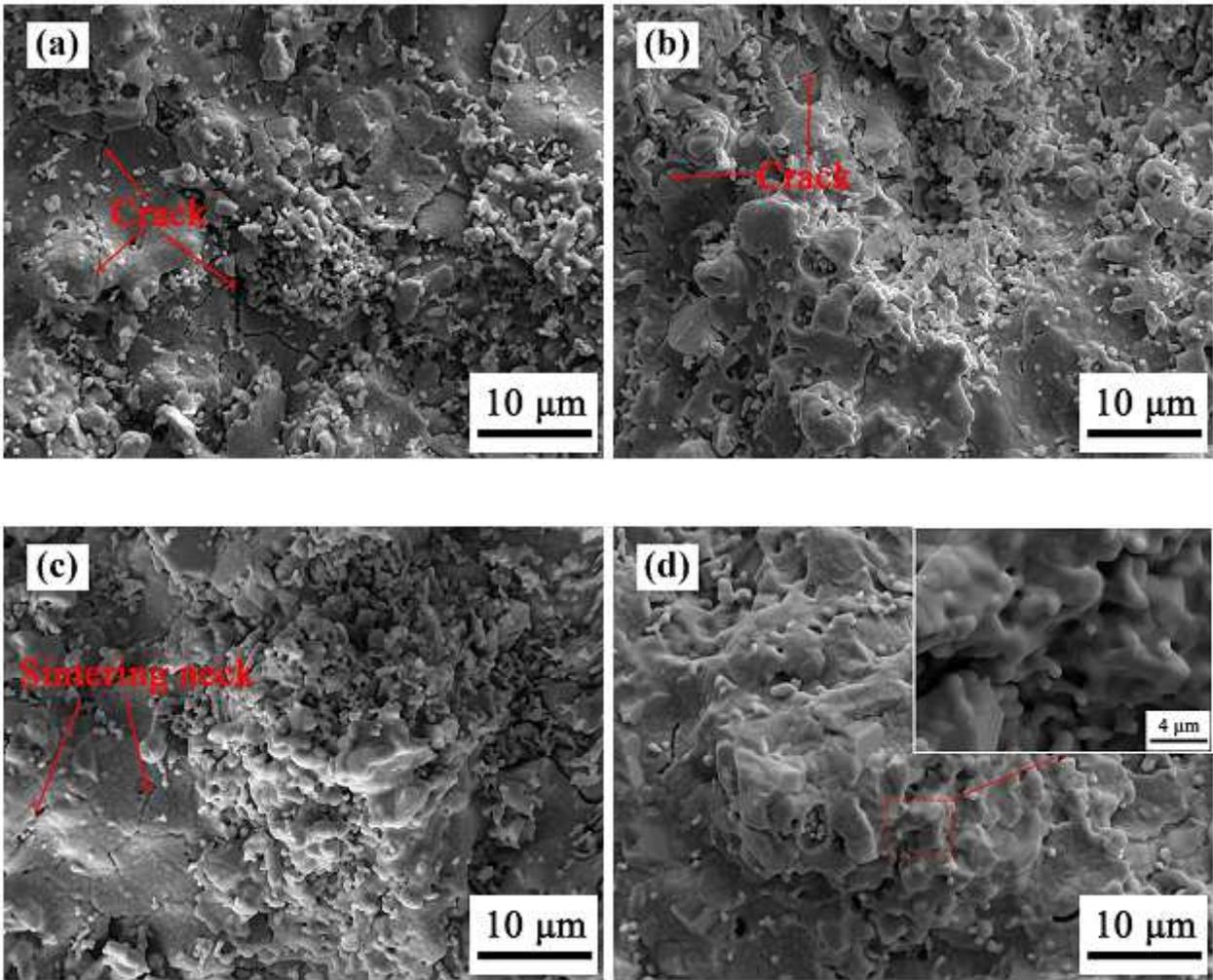


Figure 10

Surface morphologies of Gd-Sc coatings after heat treatment at 1400 °C for (a) 20 h, (b) 50 h, (c) 100 h and (d) 200 h

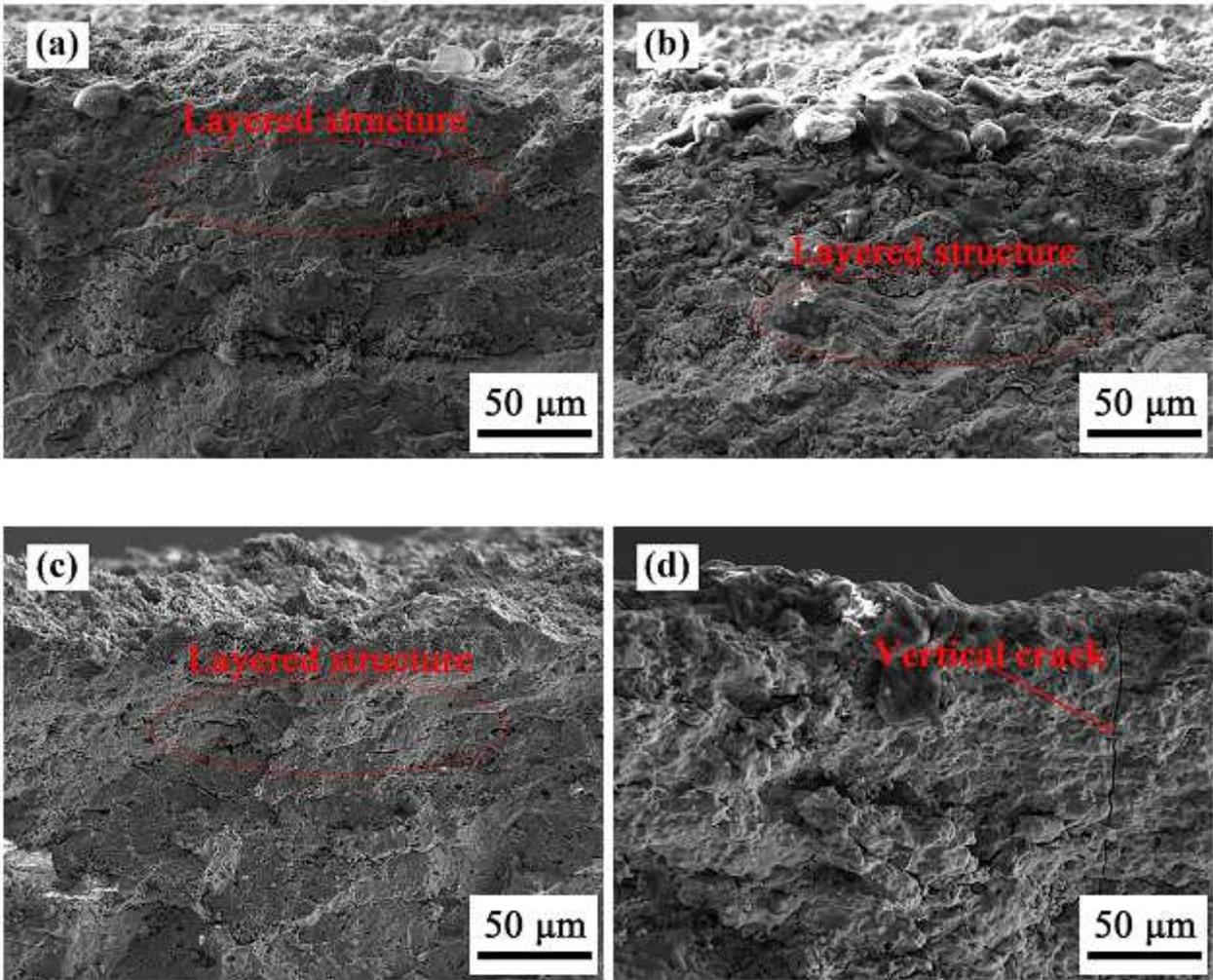


Figure 11

Fracture surface morphologies of Gd-Sc coatings after heat treatment at 1400 °C for (a) 20 h, (b) 50 h, (c) 100 h and (d) 200 h

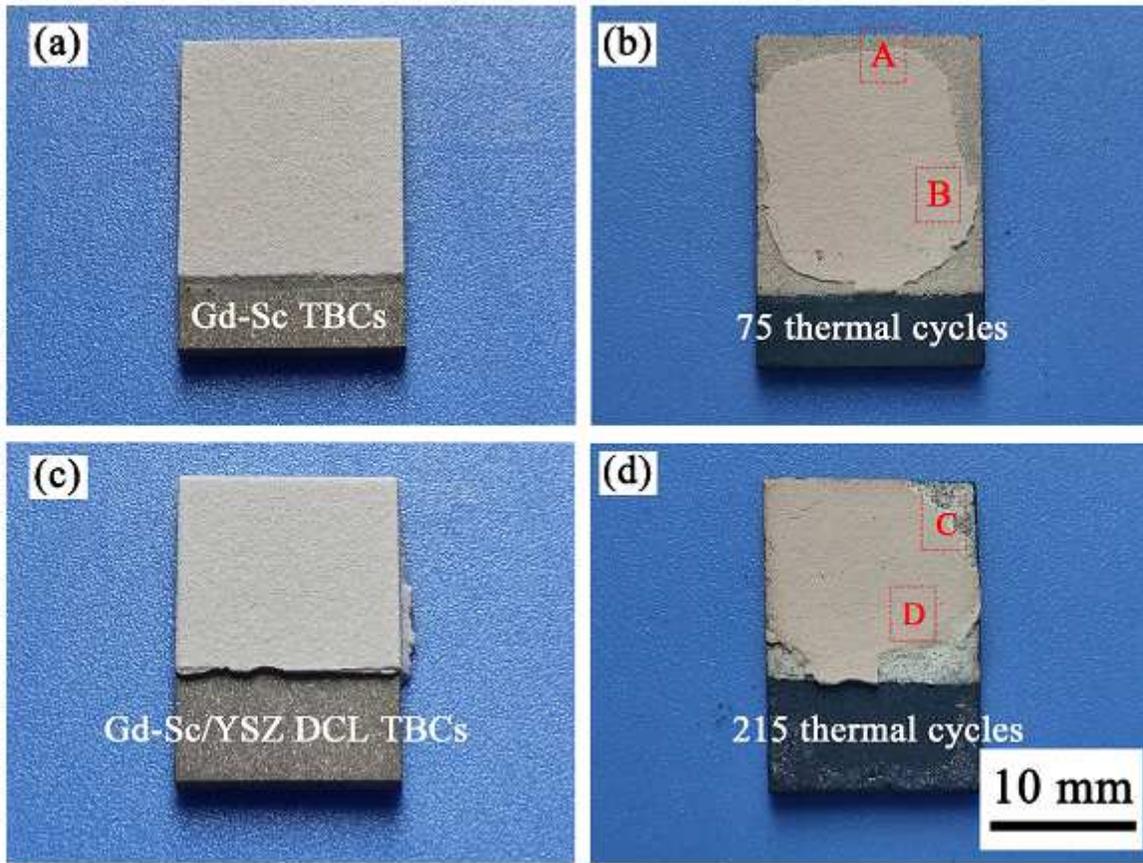


Figure 12

Macroscopic morphologies evolution of Gd-Sc TBCs (a and b) and Gd-Sc/YSZ DCL TBCs (c and d) during thermal cycling tests

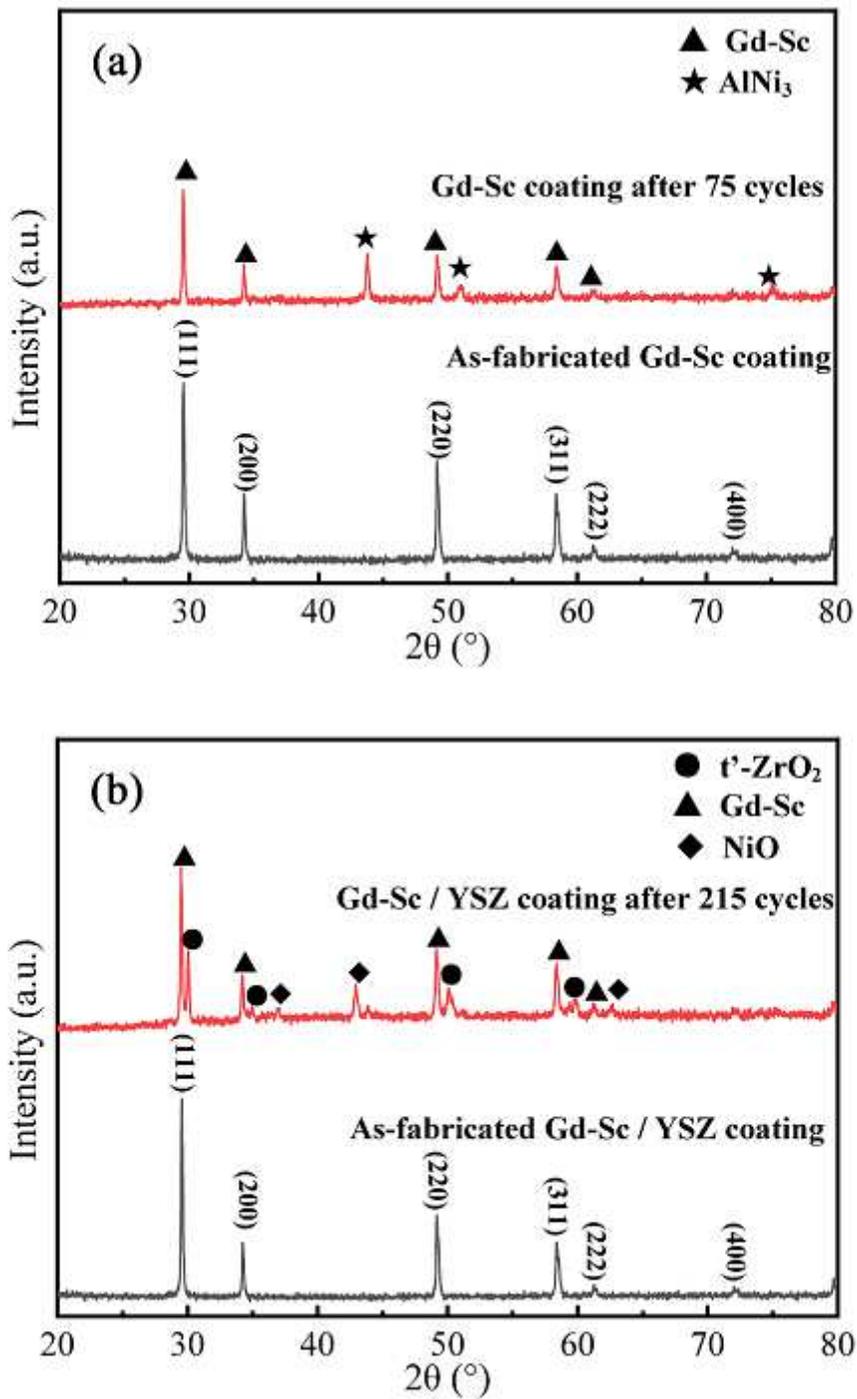


Figure 13

XRD patterns of Gd-Sc TBCs (a) and Gd-Sc/YSZ DCL TBCs (b) after thermal cycling tests

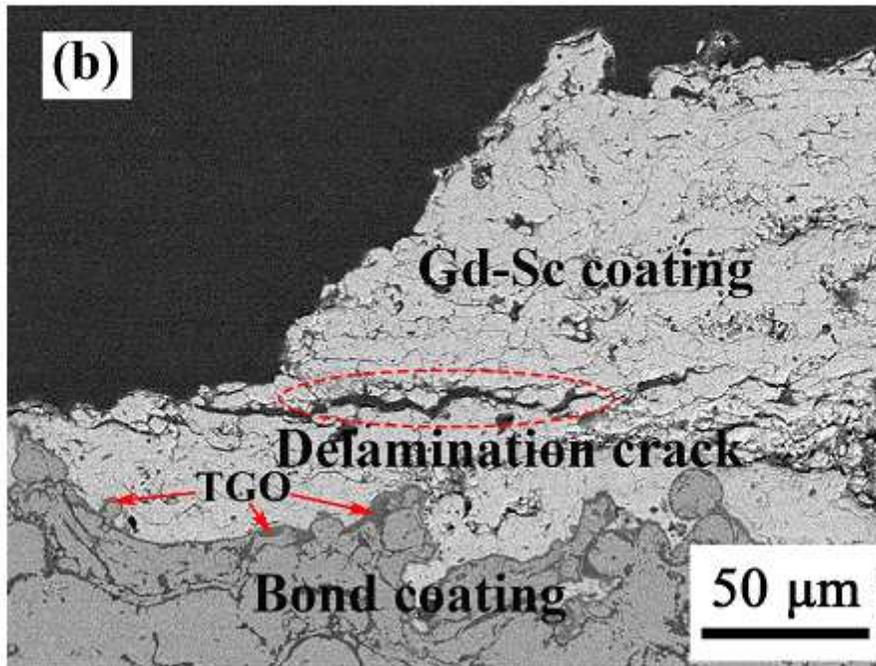
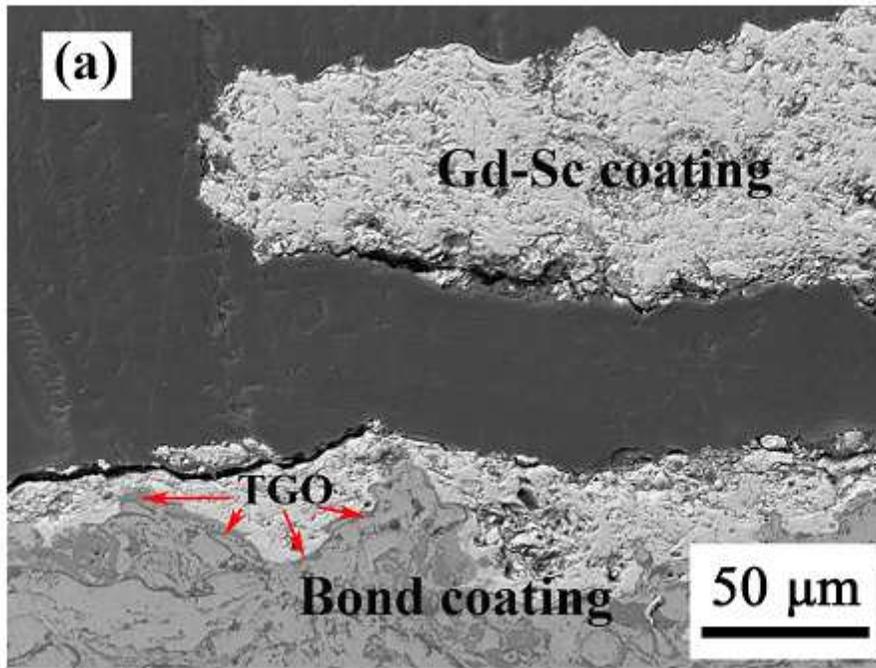


Figure 14

Cross-sectional microstructures of regions A (a) and B (b) of Gd-Sc TBCs after 75 thermal cycles

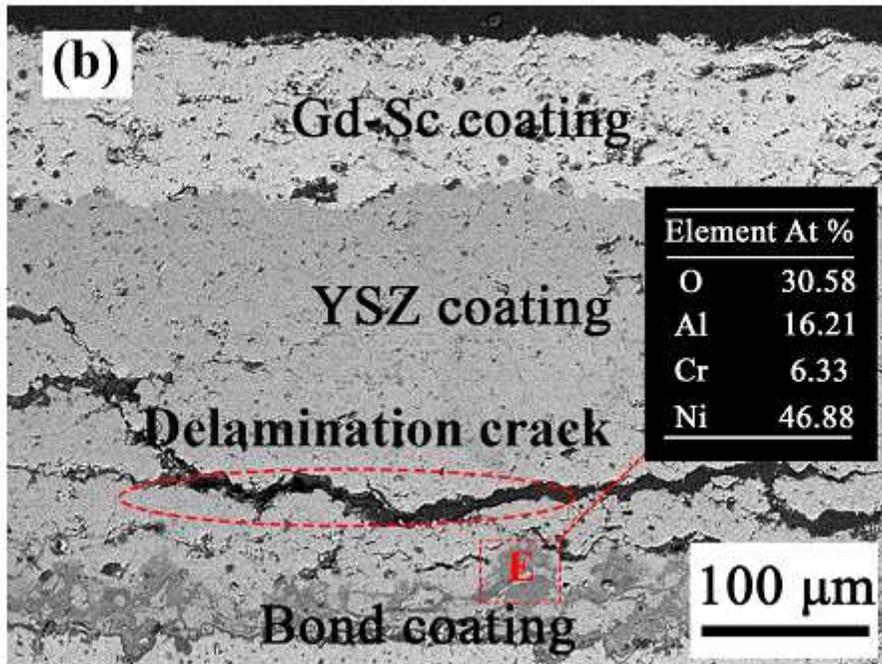
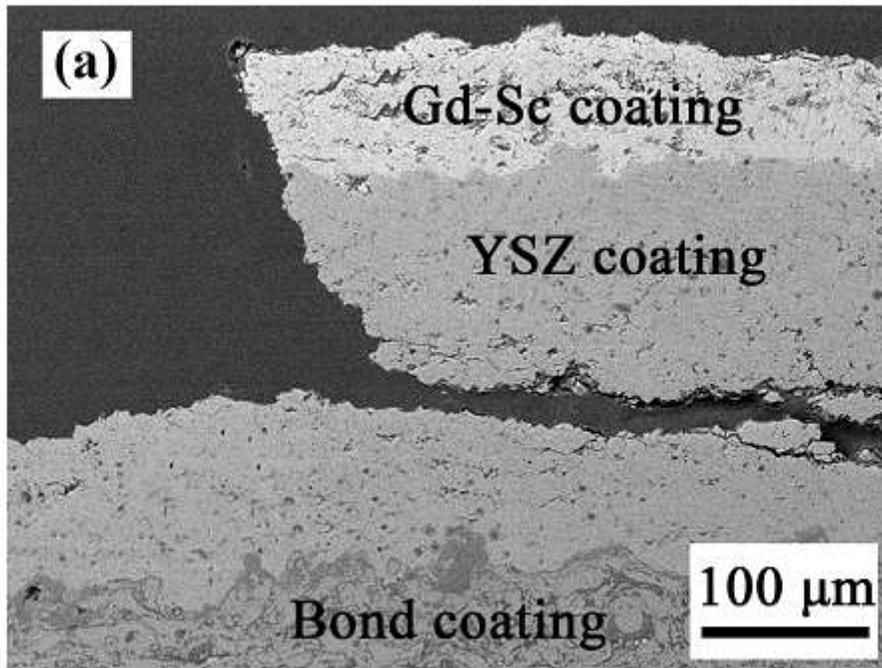


Figure 15

Cross-sectional microstructures of regions C (a) and D (b) of Gd-Sc/YSZ DCL TBCs after 215 thermal cycles