1. Introduction

Thermal barrier coatings (TBCs) are advanced materials usually applied to the surface of metallic components operating at elevated temperatures, such as on superalloy components in a gas turbine engine to protect them against environmental invasions like high-temperature oxidation and hot corrosion. They can also act as a thermal barrier to prevent temperature rise in the components, enhancing the working efficiency of the engine and reducing the fuel consumption [1,2].

Most common TBCs consist of an oxidation-resistant metallic bond coat (usually with MCrAlY composition where M could be Co, Ni or a combination of both) and a thermally stable ceramic top coat (typically zirconia-ZrO₂ based) which is and usually deposited on the surface using thermal spray technique [2,3].

Pure zirconia has three polymorphs including the monoclinic phase at temperatures up to about 1175°C, tetragonal phase in the temperature range of 1175-2370°C, and cubic phase in the temperature range of 2370-2760°C [2]. This means that upon cooling zirconia undergoes cubic to tetragonal and tetragonal to monoclinic phase transformations, among which the latter has a large volume change (ΔV ~ 4%) which results in degradation of TBCs [1,4].

There are two approaches to stabilize the high-temperature tetragonal zirconia phase at room temperature. One approach is to incorporate dopant ions such as Y³⁺ into zirconia lattice, which have a cationic radius bigger than Zr⁴⁺. The other solution is the reduction of the particle size of zirconia to a critical value (~30 nm), as some researchers reported that the stability of the tetragonal phase at temperatures below 1175°C shows a dependency on the particle size [5–9].

Yttria stabilized Zirconia (YSZ) compound has two allotropes including tetragonal with 4 mol. % Y₂O₃ (low-yttria) and cubic with 8 mol. % Y₂O₃ (high-yttria). The tetragonal phase has low intrinsic thermal conductivity and high fracture toughness, making it a favorable choice for TBCs [2,10,11].

In thermal spray techniques (for example atmospheric plasma spray or APS), upon rapid cooling of the tetragonal YSZ from high temperature to room temperature, a non-diffusional phase transformation occurs, forming a “non-transformable” metastable tetragonal zirconia known as “t-prime” phase [11–13]. The t-prime phase is similar to tetragonal zirconia but with a smaller lattice ratio (c/a) and a higher metal oxide dopants content [12].

In common gas turbines, YSZ coating is preferred to consist of t-prime phase not only for having low intrinsic thermal conductivity and high fracture toughness, also because it does not transform directly to the monoclinic phase during cooling to room temperature [11,14,15].
However, in advanced gas turbines when the operating temperature is above 1200°C, the t-prime phase decomposes into the low-yttria tetragonal and high-yttria cubic phases. The low-yttria tetragonal phase subsequently transforms into a monoclinic phase upon cooling, while the cubic phase retains its fluorite structure to room temperature because of the higher content of doping ions [16].

In recent years, zirconia combined with a primary stabilizer (about 6 Mol.%) and at least two additional cationic oxide dopants (about 4 Mol.% of two oxides), known as “defect cluster TBCs” [1,5,17,18] have attracted considerable attention due to their higher phase stability and higher service temperatures compared to YSZ [5,17].

Generally, the proposed compound is “ZrO₂-primary stabilizer oxides – RE1 (group A) – RE2 (group B)”. The group A dopant is selected such that the ionic radius of the group A dopant cation is larger than the ionic radius of the primary stabilizer cation in the solid solution. The group B dopant is selected such that the ionic radius of the group B dopant cation is smaller than the ionic radius of the primary stabilizer cation in the solid solution. The lanthanides or rare earth elements (atomic numbers 57 through 71) typically are selected for RE1 and RE2 groups [1,19].

Qi-Lian Li et al. [17] reported that 5.5 Mol.%Sc₂O₃ -2 Mol.%Gd₂O₃ -2 Mol.%Yb₂O₃-ZrO₂ exhibits excellent stability to retain t-prime zirconia phase even after exposure to high temperature (1400°C) for 500 h, which was associated with no tetragonal to monoclinic phase transition upon cooling.

Recently Bahamirian et al. [5,16] have studied YGdYbZr: 5.86 Mol.%Yb₂O₃-1.99 Mol.%Gd₂O₃ -1.98 Mol.%Yb₂O₃-ZrO₂ compound synthesized by co-precipitation method, for which the phase stability was investigated after a heat treatment at 1300°C for 50 h. Their study showed that the given compound exhibited an excellent phase stability due to full retention of t-prime zirconia phase and restriction of tetragonal to monoclinic phase transition upon cooling. Bahamirian et al. [5] and Qi-Lian Li et al. [17] suggested the co-precipitation method as a technologically simple, cost-effective, and capable of producing homogenously dispersed nanopowders with complex composition.

Further, it has been reported that t-prime phase partitioning is diffusion controlled, therefore, large cationic diffusion energy is required for decomposition of the t-prime phase based on kinetic considerations [10]. As it is known, the larger cation is the more diffusion energy is needed, resulting in a better t-prime phase stability in YSZ doped with larger cations.

The ionic radii of La³⁺ (1.160 Å) is the largest in RE elements [20]. In this study, a nanopowder with a new compound (5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂) was synthesized using chemical co-precipitation method, for which important features such as crystallographic structure and phase stability after being heat treated at 1300°C for 50 h were investigated.

2. Experimental procedures

2.1. Synthesis and characterization of zirconia-lanthania-ytterbia-yttria

Co-precipitation technique was used to synthesize zirconia-lanthania-ytterbia- yttria (YLaYbZr: 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂) nanopowder. In this process, the starting materials consisted of zirconium oxychloride (ZrOCl₂.8H₂O), lanthana (La₂O₃), ytterbia (Yb₂O₃) and yttria (Y₂O₃) powders with the specifications given in Table 1.

Zirconium oxychloride was dissolved in distilled water, while La₂O₃, Y₂O₃ and Yb₂O₃ powders were dissolved in hydrochloric acid to release La³⁺, Y³⁺ and Yb³⁺ ions.

After separating the desired ions, a mixture of solutions was prepared, to which ammonium hydroxide (NH₄OH) was added gradually in order to initiate a rapid reaction (at pH > 11). The precipitated product was rinsed in distilled water and thereafter was dried at 70°C for 24 h to obtain the precursor powder. This was followed by the calcination process performed at 1000°C for 2 h, which has also been reported by other researchers for the synthesis of similar defect cluster TBCs [5,17].

The morphology of the products was studied using a field emission scanning electron microscopy (FESEM: MIRA3 TESCAN-XMU) and the phase analysis was performed using X-ray diffraction (XRD) technique. This was done using a Philips X’pert unit equipped with a Cu-Kα λ = 1.540598 Å, 40 kV and 40 mA with the diffraction angle (2θ) of 10-80°, step size of 0.02 and dwell time of 0.5 s. Furthermore, Cohen’s method [21] and Rietveld refinement technique (Material Analysis Using Diffraction software – MAUD) were applied to perform the quantitative analysis on the obtained XRD results.

2.2. Phase stability of zirconia-lanthania-ytterbia-yttria

To study the phase stability of synthesized zirconia-lanthania-ytterbia- yttria nanopowder, the product was heated to 1300°C at a rate of 10°C per minute and kept for 10, 20 and 50 h, then was kept within the furnace to cool down to the room temperature.

| Material               | Chemical formula | Purity | Company |
|------------------------|------------------|--------|---------|
| Zirconium oxychloride  | ZrOCl₂.8H₂O      | 99.9%  | Merck   |
| Lanthanum oxide        | La₂O₃            | 99.9%  | Aldrich |
| Yttrium oxide          | Y₂O₃             | 99.9%  | Aldrich |
| Ytterbium oxide        | Yb₂O₃            | 99.9%  | Aldrich |
3. Results and discussion

Figure 1 shows FESEM micrographs and the corresponding EDS analysis of the synthesized YLaYbZr nanopowder after being dried at 70ºC for 24 h (Figure 1(a,c)) and after the calcination process (Figure 1(b,d)) performed at 1000ºC for 2 h. In Figure 1(a) shows that YLaYbZr nanopowder consists of agglomerates with irregular shapes and large blocks of chips. Whereas Figure 1(b), the grains in YLaYbZr nanopowder are inhomogeneous with the grain size within 30–60 nm, corresponding to the as-synthesized condition.

Comparing EDS analyses of YLaYbZr nanopowders before (Figure 1(c)) and after (Figure 1(d)) calcination confirms the presence of La, Y, Yb and Zr elements while indicating that chlorine was removed during the calcination process.

It seems that the synthesis process occurs in three different steps. First La\(^{3+}\), Yb\(^{3+}\) and Y\(^{3+}\) were released into the HCl acid solution. In the next step, Zr\(^{4+}\) ions were also released and the pH of the solution was stabilized with the aid of NH\(_4\)OH (regarding zeta potential for zirconia solution), so that a white gel was produced. Finally, upon removal of NH\(_4\)Cl and evaporation of water, crystalline form of zirconia was developed with the doping ions of La\(^{3+}\), Yb\(^{3+}\) and Y\(^{3+}\).

Figure 2 shows the phase analysis of YLaYbZr nanopowder after calcination at 1000ºC for 2 h. It is seen that YLaYbZr nanopowder mainly consists of a tetragonal zirconia phase which indicates a successful synthesis of YLaYbZr compound. However, monoclinic zirconia was no more detected after calcination at 1000ºC for 2 h. Also, it is seen that there is no trace of Yb\(_2\)O\(_3\), La\(_2\)O\(_3\) and Y\(_2\)O\(_3\) peaks in the related XRD pattern which confirms the complete dissolving of these oxides in zirconia structure. It is well-known that substituting La\(^{3+}\), Yb\(^{3+}\) and Y\(^{3+}\) for Zr\(^{4+}\) stabilize zirconia structure.

Tetragonality parameter (\(\sqrt{c/a}\)) is an important factor for ZrO\(_2\) tetragonal phase investigation [5,17]. In compounds such as M\(_2\)O\(_3\)-ZrO\(_2\), where M is Yttrium or a rare earth element, the tetragonality depends on the cooling rate of calcination process and also dopant concentration but independent of dopant type [22–24]. The tetragonality of t-prime and t-ZrO\(_2\) phases is different. If tetragonality is less than 1.01, it is t-prime ZrO\(_2\) phase, while if exceeds 1.01, then it is t-ZrO\(_2\) phase [5,22].

Utilizing Cohen’s method for calculating crystalline lattice parameters of YLaYbZr nanopowder after calcination, lattice parameters for tetragonal crystalline were calculated as \(a = b = 3.643\ \text{Å}\) and \(c = 5.175\ \text{Å}\). This results in a tetragonality value (\(\sqrt{c/a}\)) [22] lower.
than 1.01 for YLaYbZr nanopowder, where the formed phase is t-prime. The precise cell parameters of the t-prime phase of YLaYbZr nanopowder indicated the best zirconia phase for TBC applications.

In addition to the role of La$_2$O$_3$, Yb$_2$O$_3$ and Y$_2$O$_3$ as zirconia stabilizers, the presence of tetragonal phase at temperatures lower than 1175°C can be explained by the nano-scale size of powders and the thermodynamic calculations based on Equation (1) [6,25]:

$$G = \frac{4}{3}\pi r^3 G_v + 4\pi r^2 \gamma$$

(1)

In this equation, $G$ represents the free energy of spherical particles, $r$ is the particle radius, and $\gamma$ denotes the surface energy of the particles. To calculate the free energy difference of tetragonal and monoclinic phases, Equation (2) can be proposed [6,25]:

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 (\gamma_t - \gamma_m). Y_{tetragonal}$$

$$= 0.77 Jm^{-2}, Y_{monoclinic} = 1.13 Jm^{-2}$$

(2)

Calculating the critical radius ($r^*$) by taking the derivative of Equation (2) results in Equation (3), as follows [6,25]:

$$r^* = -2 \frac{(\gamma_t - \gamma_m)}{\Delta H(1 - \frac{1}{r^*})}$$

(3)

where $\Delta H = 2.82 \times 10^8 Jm^{-3}$ (all being determined from calorimetry studies) is the heat of transformation per unit volume of an infinite crystal, and $T_p = 1175°C$ shows the transformation temperature of an infinite crystal [6,25].

Other researchers reported that in the nanocrystalline ZrO$_2$ (<100 nm), the tetragonal phase can be stabilized at room temperature below a critical size of ~30 nm [7,25]. They reported that below such a critical size, generation of excess oxygen ion vacancies within the nanocrystalline ZrO$_2$ is primarily responsible for the room temperature tetragonal phase stabilization [25].

The critical radius $r^*$ of YLaYbZr nanopowder is calculated as 25 nm. Therefore, the reason for the emergence of tetragonal phase at temperatures below the 1175°C and formation of the tetragonal phase in YLaYbZr nanopowders can be explained with regard to the fact that, the critical radius of tetragonal phase is lower than that of the monoclinic phase.

On the other hand, based on Kroger–Vink equation (Equation (4)) [26], it can be stated that the presence of stabilizing oxide elements in zirconia structure will create oxygen vacancies.

$$M_2O_3 + 2M'_2 + 3O_2' + V_o$$

(4)

When a low valency dopant cation, such as Y$^{3+}$, is introduced into the ZrO$_2$ lattice, oxygen vacancies are created for the charge balance. Therefore, by increase of stabilizing elements, the percentage of oxygen vacancies will increase as well.

Moreover, when the zirconia compound is heated in the normal atmosphere, oxygen atoms would be added to these vacancies [17]. Consequently, enhancement of zirconia stabilizers concentrations may increase the oxygen vacancies, resulting in the formation of the tetragonal phase.

The results of XRD analysis of YLaYbZr nanopowder after heat treatment at 1300°C for 10, 20 and 50 h are presented in Figure 3. Also, the results of this study were compared to the work reported by Bahamirian et al. [16], suggesting that the use of Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$ can improve the phase stability properties of YSZ.

According to ZrO$_2$-Y$_2$O$_3$ phase diagram [27], t-prime phase decomposes into cubic and tetragonal phases at temperatures above 1200°C. The monoclinic phase is formed by the decomposition of t-prime phase, so its content can be used to characterize the t-prime phase stability. From Figure 3 and by applying the Rietveld refinement, no monoclinic ZrO$_2$ phase was found to exist in YGdYbZr compound after 50 h of heat treatment at 1300°C, while the content of monoclinic ZrO$_2$ phase in of YLaYbZr compound was calculated as 13 wt.% in similar conditions.
Although ionic radii of La$^{3+}$ is larger than Gd$^{3+}$, and we expected that the phase stability of YLaYbZr compound would be better than YGdYbZr compound, a reverse variation for the tendency of t-prime phase stability was observed in our experiment.

Other researchers [28] reported that apart from diffusion kinetics, the driving force for t-prime phase partitioning also affects the t-prime phase stability.

According to [29,30], large size mismatch between RE$^{3+}$ and Zr$^{4+}$ ions in ZrO$_2$-based ceramics could provide great driving force for the formation of the “t’” phase. The “t’” phase is similar to t-prime phase with the difference that it has a smaller lattice parameter ratio of $c/a$ and also, upon cooling, “t’” can easily be transformed to t and monoclinic phases. Subsequently, the decomposition of “t’” phase to t phase is diffusion controlled.

Although in YLaYbZr compound the average RE$^{3+}$ ionic radius is larger than that of Zr$^{4+}$ in comparison to YGdYbZr compound, but the size mismatch between the RE$^{3+}$ ions and Zr$^{4+}$ ions in the YGdYbZr compound decreases compared to that in YLaYbZr compound. As a result, the driving force for the formation of the “t’” phase decreases in YGdYbZr compound.

The crystal lattice parameters, the values for tetragonality and critical radius, $r^*$, of YLaYbZr nanopowder after heat treatment at 1300°C for 0, 10, 20 and 50 h are, listed in Table 2, indicating that YLaYbZr nanopowder consisting of t-prime phase has the best zirconia compound for advanced TBC applications.

Based on the equilibrium diagram phase of ZrO$_2$-Y$_2$O$_3$, cubic and tetragonal phase can be formed at 1000°C [2,27]. Cubic structure of zirconia could be distinguished from the tetragonal structure by the presence of the characteristic splitting of the tetragonal phase, such as (004) (400) at 2$\theta$ regions of 72–76°, whereas the cubic phase exhibited only single peaks at all these diffraction angles [31]. Therefore, X-ray diffraction results were carefully studied to ensure the formation of the tetragonal phase.
structure and the absence of the cubic structure in the YLaYbZr nanopowder. Figure 4 provides peaks for (400) (004) planes for tetragonal zirconia in YLaYbZr nanopowder before and after heat treatment at 1300°C for 0, 10, 20 and 50 h.

Full width at Half Maximum (FWHM) is reduced by the grain growth, so its value can be used to characterize the t-prime phase stability. Studying FWHM variations with the heat treatment time at 1300°C (Figure 5) revealed that the reduction of peak width with an increase of heat treatment time can reflect the increased particle growth rate for YLaYbZr nanopowder. From Figure 5, FWHM-time treatment curve can be divided into two stages: (i) short heat treatment times (10 h) in which the decrease in FWHM was sharp; (ii) long heat treat times (10–50 h) where FWHM reached a nearly uniform trend.

Activation energy is an essential parameter used to explain the grain growth behavior of YLaYbZr nanopowder, as shown in Equation (5):

$$D = D_0 \times e^{-\frac{Q}{RT}}$$

where “$D_0$” and “$D$” are the initial and final crystallite sizes, respectively, “$R$” is the gas constant (J.K$^{-1}$.Mol$^{-1}$), and “$T$” is the calcination temperature (K).

At the beginning of the heat treatment process, it seems that the activation energy for the grain growth of YLaYbZr nanopowder is lower than the final stages.

Table 2. Crystal lattice parameters, tetragonality and “$r^*$” of YLaYbZr nanopowder after heat treatment at 1300°C for 0, 10, 20 and 50 h.

| Composition | YLaYbZr |
|-------------|---------|
| Time treatment (h) | 0 | 10 | 20 | 50 |
| Temperature treatment (°C) | 1300 |
| Phase composition | 100 wt.% T | 88 wt.% T, 12 wt.% M | 86 wt.% T, 14 wt.% M | 85 wt.% T, 15 wt.% M |
| Unit cell dimensions | $a = b$ (Å) | 3.643 | 3.648 | 3.643 | 3.645 |
| | $c$ (Å) | 5.175 | 5.177 | 5.174 | 5.179 |
| $r^*$ (nm) | 2.5 | 2.5 | 2.5 | 2.5 |
| Tetragonality | 1.0044 | 1.0034 | 1.0042 | 1.0046 |

T: Tetragonal ZrO$_2$

M: Monoclinic ZrO$_2$

Figure 4. Results of XRD analysis: (a) (27–33°) and (b) (72–76°) for YLaYbZr and YGdYbZr [16] nanopowders after heat treatment at 1300°C for 0, 10, 20 and 50 h.
A similar observation has been reported [32] for ZrO$_2$, where the activation energy for the growth in the nanocrystalline grains is observed to be $\sim 20$ kJ/mol, while that for microcrystalline grains is observed to be $\sim 275$ kJ/mol.

On the other hand, Shukla et al. [33] believe that reduction in the activation energy value in nanocrystalline YSZ is due to the possible presence of a large amount of oxygen vacancies within nanocrystalline YSZ. They have reported that nanocrystalline ceramic particles show an increase in the concentration of oxygen vacancies with a decrease in the nanoparticle size. Therefore, it seems that due to the combined effect of doping of La$^{3+}$, Yb$^{3+}$ and Y$^{3+}$ cations and the small size of YLaYbZr nanoparticle, large concentration of oxygen vacancies may exist within the nanocrystalline YLaYbZr particles, which can drastically reduce the activation energy for the grain growth.

A very large concentration of oxygen vacancies can enhance the tetragonal phase stability of nanocrystalline YLaYbZr relative to that of the microcrystalline counterpart.

As a result, nanocrystalline YLaYbZr having large concentration of oxygen vacancies seems to be the best candidate material as a highly stable ceramic phase for TBCs in applications such as current and advanced gas turbines.

After heat treating the nano-sized YLaYbZr powder at 1300°C for 50 h, the average YLaYbZr particle size was observed to increase to $\sim 300$-500 nm, as shown in Figure 6. It is also seen that the grain boundaries in YLaYbZr nanopowders are without the presence of any other phases.

The comparison of Figures 1(b) and 6 suggests the growth of particles due to heat treatment at high temperatures. It seems that after the heat treatment at high temperatures, grain rotation among neighboring grains occurs, producing a coherent grain–grain interface, associated with the disappearance of grain boundaries, and consequently with the grain coalescence. This
4. Conclusions
The present study was conducted to improve the performance of thermal barrier coatings in terms of phase stability in order to increase the working temperature of new and advanced gas turbines. For this purpose, 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂ nanopowder was successfully synthesized through the co-precipitation method and calcinated at 1000°C for 2 h. The phase stability of the product was investigated within the operating temperature range for new generation turbines. Obtained results can be summarized as follows:

- FESEM images of 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂ powder confirmed the formation of nanoparticles.
- Non-transformable tetragonal phase of zirconia was achieved by co-precipitation method for 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂ nanopowder.
- Rietveld refinement of the XRD data from 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂ nanopowder sample after heat treating at 1300°C for 50 h suggests stabilization of zirconia in the t-prime phase with around 15% monoclinic impurity.
- Small crystallite size plays an important role in the stabilization of zirconia into the tetragonal phase.
- Based on the observed results in this work, 5.86 Mol.%Y₂O₃-1.99 Mol.%La₂O₃-1.98 Mol.%Yb₂O₃-ZrO₂ nanopowder is suggested as a candidate for potential TBC applications at ultra-high temperatures. However, this conclusion needs additional studies on the phase stability at longer exposure times and the size of La³⁺ ion in relation to other lanthanides elements.

Research Highlights

- ZrO₂ 9.5Y₂O₃ 5.6Yb₂O₃ 5.2La₂O₃ nanopowder was synthesized by chemical co-precipitation method consists of single non-transformable tetragonal ZrO₂.
- The phase stability behavior of ZrO₂ 9.5Y₂O₃ 5.6Yb₂O₃ 5.2La₂O₃ compound was investigated at 1300°C for 50 h.
- ZrO₂ 9.5Y₂O₃ 5.6Yb₂O₃ 5.2La₂O₃ compound showed a highly stable t-prime phase ZrO₂ at ultra-high temperature.

Disclosure statement
No potential conflict of interest was reported by the authors.

References

[1] Vaßen R, Jarligo MO, Steinkie T, et al. Overview on advanced thermal barrier coatings. Surf Coat Technol. 2010;205:938–942.
[2] Cao X, Vassen R, Stoever D. “Ceramic materials for thermal barrier coatings. J Eur Ceram Soc. 2004;24:1–10.
[3] Clarke DR, Phillpot SR. Thermal barrier coating materials. Mater Today. 2005;8:22–29.
[4] Kelly JR, Denny I. “Stabilized zirconia as a structural ceramic: an overview. Dent Mater. 2008;24:289–298.
[5] Bahamirian M, Hadavi S, Rahimipour M, et al. “Synthesis and characterization of Yttria-stabilized Zirconia nanoparticles doped with Ytterbium and Gadolinium: zrO₂ 9.5 Y₂O₃ 5.6 Yb₂O₃ 5.2 Gd₂O₃. Metall Mater Trans A. 2018;49:2523–2532.
[6] Chraska T, King AH, Berndt CC. On the size-dependent phase transformation in nanoparticulate zirconia. Mater Sci Eng A. 2000;286:169–178.
[7] Garvie R, Goss M. Intrinsic size dependence of the phase transformation temperature in zirconia microcrystals. J Mater Sci. 1986;21:1253–1257.
[8] Garvie R. Stabilization of the tetragonal structure in zirconia microcrystals. J Phys Chem. 1978;82:218–224.
[9] Garvie RC. The occurrence of metastable tetragonal zirconia as a crystallite size effect. J Phys Chem. 1965;69:1238–1243.
[10] Guo L, Li M, Ye F. Phase stability and thermal conductivity of RE₂O₃ (RE= La, Nd, Gd, Yb) and Yb₂O₃ co-doped Y₂O₃ stabilized ZrO₂ ceramics. Ceram Int. 2016;42:7360–7365.
[11] Liang B, Ding C, Liao H, et al. Phase composition and stability of nanostructured 4.7 wt.% yttria-stabilized zirconia coatings deposited by atmospheric plasma spraying. Surf Coat Technol. 2006;200:4549–4556.
[12] Hajizadeh-Oghaz M, Razavi RS, Loghman-Estark MR. Synthesis and characterization of non-transformable tetragonal YSZ nanopowder by means of Pechini method for thermal barrier coatings (TBCs) applications. J Sol Gel Sci Techn. 2014;70:6–13.
[13] Loghman-Estark MR, Razavi RS, Edris H. Synthesis and thermal stability of nontransformable tetragonal (ZrO₂) 0.96 (REO₁₋₀.₀₄ (RE= Sc⁴⁺, V³⁺) nanocrystals In Defect and Diffusion Forum. Trans Tech Publications, Ltd., Switzerland. 2013. p. 60–64.
[14] Lima RS, Marple BR. Thermal spray coatings engineered from nanostructured ceramic agglomerated powders for structural, thermal barrier and biomedical applications: a review. J Therm Spray Technol. 2007;16:40–63.
[15] Li J, Liao H, Wang X, et al. Plasma spraying of nanostructured partially yttria stabilized zirconia powders. Thin Solid Films. 2004;460:101–115.
[16] Bahamirian M, Hadavi S, Farvizi M, et al. Phase stability of ZrO₂ 9.5 Y₂O₃ 5.6 Yb₂O₃ 5.2 Gd₂O₃ compound at 1100°C and 1300°C for advanced TBC applications. Ceram Int. 2019;45:7344–7350.
[17] Li Q-L, Cui X-Z, Li S-Q, et al. Synthesis and phase stability of Scandia, Gadolinia, and Ytterbia co-doped Zirconia for thermal barrier coating application. J Therm Spray Technol. 2015;24:136–143.
[18] Zhu D, Chen YL, Miller RA. Defect clustering and nano-phase structure characterization of multicomponent rare earth oxide doped Zirconia Yttria thermal barrier coatings. NASA UET Presentation; Cleveland, Ohio: NASA Glenn Research Center; 2004.
[19] Zhu D, Miller AR. Low conductivity and sintering-resistant thermal barrier coatings. US patent, US20060607850A1. 2001.

[20] Shannon RD. “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr A. 1976;32:751–767.

[21] Cullity BD, Weymouth JW. Elements of x-ray diffraction. Am J Phys. 1957;25:394–395.

[22] Viazzi C, Bonino J-P, Ansart F, et al. Structural study of metastable tetragonal YSZ powders produced via a sol–gel route. J Alloys Compd. 2008;452:377–383.

[23] Wang D. Design of novel thermal barrier coatings with reduced thermal conduction and thermal radiation. University in Ottawa, Ontario, Canada. 2006.

[24] Sheu TS, Tien TY, Chen IW. Cubic-to-tetragonal (t’) transformation in Zirconia containing systems. J Am Ceram Soc. 1992;75:1108–1116.

[25] Shukla S, Seal S. Mechanisms of room temperature metastable tetragonal phase stabilisation in zirconia. Int Mater Rev. 2005;50:45–64.

[26] Kröger FA. The chemistry of imperfect crystals. Amsterdam: North-Holland Pub. Co.; 1964.

[27] Brandon J, Taylor R. Phase stability of zirconia-based thermal barrier coatings part I. Zirconia-yttria alloys. Surf Coat Technol. 1991;46:75–90.

[28] Rahaman MN, Gross JR, Dutton RE, et al. Phase stability, sintering, and thermal conductivity of plasma-sprayed ZrO$_2$-Gd$_2$O$_3$ compositions for potential thermal barrier coating applications. Acta Materialia. 2006;54:1615–1621.

[29] Tsipas S. Effect of dopants on the phase stability of zirconia-based plasma sprayed thermal barrier coatings. J Eur Ceram Soc. 2010;30:61–72.

[30] Lelait L, Alperine S, Diot C, et al. Thermal barrier coatings: microstructural investigation after annealing. Mater Sci Eng A. 1989;120:475–482.

[31] Srinivasan R, De Angelis RJ, Ice G, et al. Identification of tetragonal and cubic structures of zirconia using synchrotron x-radiation source. J Mater Res. 1991;6:1287–1292.

[32] Yang H-S, Bai G-R, Thompson L, et al. Interfacial thermal resistance in nanocrystalline yttria-stabilized zirconia. Acta Materialia. 2002;50:2309–2317.

[33] Shukla S, Seal S, Vij R, et al. Reduced activation energy for grain growth in nanocrystalline yttria-stabilized zirconia. Nano Lett. 2003;3:397–401.