Computational Materials Science 153 (2018) 208–216

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Understanding the improved stability and reduced thermal conductivity of yttria stabilized zirconia: A combined experimental and atomistic modeling study

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ARTICLE INFO

Keywords:
8YSZ
Density functional theory
Oxygen vacancy
Thermal conductivity
Thermal stability

ABSTRACT

Y_2O_3 is often utilized to stabilize zirconia and reduce the thermal conductivity. However, the phenomena of improved stability and thermal insulation properties are not clarified yet. In this paper, different compensated and non-compensated 8YSZ systems are modeled and simulated using density functional theory (DFT). 8YSZ coatings with different processing parameters are prepared by atmospheric plasma spray (APS) technique to verify the theoretical findings. Moreover, a qualitative and quantitative relationship between the microstructure and thermal conductivity is developed. Based on the phonon scattering, the substitutional point defect (Y^{3+} dopant) plus oxygen vacancies are responsible for the improved stability and reduced thermal conductivity. Electron back scattered diffraction analysis verifies the molecular dynamics simulations results. Thermal conductivity values estimated from the calculations are consistent with the experimental observations.

1. Introduction

To improve the performance and increase the operating temperature of gas turbine engine, thermal barrier coating (TBC) is widely used as a tool for lowering the engine component operating temperature. For effective temperature drop across the coating, a suitable material should be selected for the ceramic top coat of TBC [1–4]. Zirconia (ZrO_2) based ceramic materials are found to be state of the art materials to address the required features for TBC. Zirconia possesses high thermal stability, low coefficient of thermal expansion and thermal conductivity making it different from the other prospective materials. However, in pure form, it is not suitable for wide range of applications due to its intrinsic problems. The thermal conductivity of pure ZrO_2 is not sufficiently low for achieving ideal thermal insulation and the volume expansion during the phase transformation (tetragonal to monoclinic) leads to the TBC failure in the form of cracking. Introducing substitutional point defects in ZrO_2 by mixing it with metal oxides can overcome the disadvantages of ZrO_2 [5,6].

To stabilize the high temperature tetragonal and cubic phases and reduce the thermal conductivity of ZrO_2, mixing of Y_2O_3 with ZrO_2 is a suitable solution and widely investigated [7–9]. Both the substitutional point defect and oxygen vacancy are the sources of phonon scattering and its creation in the ZrO_2 lattice can reduce the thermal conductivity. The size mismatch between the host ion and the vacancy generate intensive electric field. Moreover, the mass loss and linkage loss make the vacancies a strong phonon scatterer compared to the substitutional point defect [5]. Effective reduction in the thermal conductivity of ZrO_2 is expected for a substitutional dopant that could also lead to the creation of oxygen vacancy. Yttrium exits in (Y^{3+}) oxidation state and replacing Zr^{4+} would create the charge imbalance in the ZrO_2 network. Due to the low formation energy of oxygen vacancies compared to the metal ions, the probability for the creation of oxygen vacancy for charge compensation is very high [10,11]. The substitutional dopant and oxygen vacancy strongly scatters the phonons thereby reducing the thermal conductivity.

With the advancement in theory and experiments, now it is possible to locate the position of dopants/vacancies in the lattice of ZrO_2 and measure the movement of particles during spraying [12,13]. Different processing parameters lead to various crystal defects and varied phase contents that influence the microstructure and thermal conductivity of YSZ coatings. YSZ coatings with different grain boundaries, pores, cracks and monoclinic phase contents demonstrate varied thermal conductivities [14–16]. Qualitative relationship has been reported lacking the quantitative relationship [17]. Various factors influencing

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https://doi.org/10.1016/j.commatsci.2018.06.045
Received 30 March 2018; Received in revised form 28 June 2018; Accepted 29 June 2018

the thermal conductivity of YSZ are studied in the literature. Nicholls et al. [18] found that the thermal conductivity of the coating could be altered by the phonon transport. Influence of pores, cracks and splat interface on the thermal conductivity of YSZ is revealed [19,20]. With the finite element models, the influence of pores on the thermal properties is elucidated [21]. A quantitative relationship can batter describe the relationship between the spraying parameters, microstructure and thermal conductivity. Structure and defect formation in YSZ coatings are very much important and it influence the thermal conductivity. Therefore 8YSZ coating with different spray parameters should be prepared. Moreover, it would be interesting to model the YSZ system and simulate the system using density functional theory for making possible agreement between the theoretical results and experimental findings. To elucidate the effect of oxygen vacancy on the thermal conductivity, YSZ models with and without oxygen vacancy should be modeled.

This manuscript report a detail analysis about the structure of YSZ coating modeled in the Materials Studio 8.0 and then simulated using density functional theory. In parallel, 8YSZ coating was deposited using atmospheric plasma spray technique with different spraying parameters. Finally, the theoretical findings and experimental data and compared and critically discussed.

2. Methodologies

2.1. Computational details

Electronic band structure calculations are performed using density functional theory (DFT) with generalized gradient approximation (GGA) as an exchange correlation potential [22]. The $4s^2$ $4p^6$ $4d^2$ $5s^2$, $2s^2$ $2p^4$, $4d^1$ $5s^2$ electrons are considered as valence electrons for Zr, O and Y, respectively. The Perdew-Burke-Ernzerhof potential (PBEsol) implemented in CASTEP code of Materials Studio is adopted for plane wave calculations with the ultrasoft pseudopotential [23]. The PBEsol provided consistent results with the PBE potential [24]. Energy of 380 eV is used as a cutoff limit for the structure optimization and energy calculations. Defect induced and pure models are relaxed (using BFGS algorithm) for making good comparison with the experimental findings. The relaxation constraints in the form of maximum force, stress and displacement were 0.01 eV/Å, 0.02 GPa and 0.01 Å, respectively [25,26].

Using molecular dynamics (MD), as implemented in the General Utility Lattice Program (GULP) [27,28] was used to predict the thermodynamic properties of the models. Being as an essential part of the atomic simulations, the LEWIS and Buckingham were utilized as forcefields. The LEWIS forcefield [29] is a collection of oxide potentials based on the Catlow oxygen-oxygen shell model potential. The findings of utilizing LEWIS forcefield are found consistent with the experimental results [29]. To evaluate the heat transport though the material, the thermal conductivity (k) is calculated using Eq. (1) [30]

$$k = \frac{1}{V}\sum_{i=1}^{modes} C_i(T)D_i \quad (1)$$

The terms V, $C_i(T)$ and D_i represent the cell volume, heat capacity of mode i at temperature T, and the mode diffusivity, respectively. The thermal conductivity parameters were: Frequency from 1000 to 1.0×10^4 1/cm; cutoff frequency = 60 1/cm, DOS broadening = 5.0, lorentzian tolerance = 0.01, and Debye model constant = 0.0 s/km^2.

Cubic ZrO_2 unitcell with the replication of $2 \times 2 \times 1$ make a supercell of 48 atoms. Table 1 summarizes the detail of defect induced models created for explaining the experimental findings. Different defects are introduced in the supercell of ZrO_2 and the defect state and doping concentration is elaborated. Models YSZ-1(theo) and YSZ-2(theo) possess only yttrium dopant at Ti sites. The corresponding Y doping concentration for YSZ-1(theo) and YSZ-2(theo) is 2.08 and 4.16 at.%, respectively. Yttrium normally exits in Y^{3+} state and replacing one or two host Zr^{4+} atoms by Y^{3+} may disturb the charge neutrality of the host network. To maintain the charge neutrality, the structure may prefer some defects. The possible compensation may be done by creating oxygen vacancy (O^{2-}). In YSZ-3(theo) and YSZ-4(theo) systems, an oxygen vacancy was created along with replacing one Zr^{4+}, and two Zr^{4+} ions by Y^{3+} ions, respectively. Yttria stabilized zirconia models with charge compensation could be satisfactorily explained by YSZ-4(theo). In YSZ-4(theo), the charge imbalance due to replacing two Zr^{4+} ions by Y^{3+} ions is neutralized by the creation of one oxygen vacancy (O^{2-}). Fig. 1a display the defect state of model YSZ-4(theo). Feeding powders of ZrO_2–8 wt.% Y_2O_3 with the morphology shown in Fig. 1b were obtained from Shenyang Shihua Weifen Materials Co. Ltd., Shenyang, China.

Table 1
YSZ simulated models and the corresponding defect state and doping concentration.

System	Y dopant	Y doping concentration (%)	O vacancy
ZrO_2	0	0	0
YSZ-1(theo)	1	2.08	0
YSZ-2(theo)	2	4.16	0
YSZ-3(theo)	1	2.08	1
YSZ-4(theo)	2	4.16	1

2.2. Experimental details

The YSZ coatings with different processing parameters are deposited using atmospheric plasma spray equipment (Metco A-2000) with a F4-MB plasma gun (Sulzer Metco AG, Switzerland) on aluminum substrate having dimensions of 130 mm × 85 mm × 3 mm. After grit blasting and degreasing in acetone, the YSZ coatings were deposited on the substrate. To maintain similar temperature conditions, compressed air is applied on both side of the substrate. Table 2 summarizes the processing conditions and the corresponding velocity and temperature of the particles. The data about the velocity and temperature of particles were obtained using and an online monitoring system (Spray Watch 2i, OSEIR, Tampere, Finland).

Images obtained from scanning electron microscope (SEM) were analyzed by the Image Pro Plus (IPP, Image Pro Plus 6.0). More detailed information about the microstructure of the coatings are obtained using Electron back scattered diffraction (EBSD) system (INCA SERIES, Oxford Instrument, Oxford, UK) along with SEM system (Magellan 400, FEI, Hillsboro, OR, USA). For EBSD analysis, samples were shaped into 3 mm × 3 mm × 1 mm followed by polishing by ion milling system (Leica EM TIC 3X, Wetzlar, Germany).

From EBSD analysis, the phase composition and grain size are evaluated. Using the Kikuchi patterns, the different phases were differentiated from each other. Contents of any particular phase can be obtained from its area fraction in EBSD images. With the magnification of 1500×, 10 images (for each sample) were analyzed to calculate the phase contents of any particular phase.

To calculate the thermal conductivity, initially the thermal diffusivity and specific heat were calculated. Using Eq. (2), the thermal conductivity (λ) is calculated.

$$\lambda = \alpha\rho C_p \quad (2)$$

The terms used in the equation are referred as; α = thermal diffusivity; ρ = density; C_p = Specific heat. Thermal diffusivity in the range 25–1200 °C was calculated using commercial laser flash equipment (TD-79A, SIC, Shanghai, China). With the diamond DSC (SIC) (Perkin Elmer, Waltham, MA, USA), the specific heat (25–1200 °C) of YSZ is calculated according to the ASTME 1269-05 standard [31]. The Neumann-Kopp law [32] is utilized to evaluate the specific heat above 500 °C.