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Feature article

Defect engineering in development of low thermal conductivity materials: A review

Meng Zhao [a], Wei Pan [a,*], Chunlei Wan [a], Zhixue Qu [b], Zheng Li [a], Jun Yang [a]

[a] State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China
[b] College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, PR China

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ABSTRACT

Low thermal conductivity is the key property dominating the heat insulation ability of thermal barrier coatings (TBC). Reducing the intrinsic thermal conductivity is the major topic for developing advanced TBCs. Defect engineering has attracted much attention in seeking better TBC materials since lattice defects play a crucial role in phonon scattering and thermal conductivity reduction. Oxygen vacancies and substitutions are proven to be the most effective, while the accompanying lattice distortion is also of great importance. In this paper, recent advances of reducing the thermal conductivity of potential thermal barrier coating materials by defect engineering are comprehensively reviewed. Effects of the mass and size mismatch between the defects and the host lattice are quantitatively estimated and unconventional thermal conductivity reduction caused by the lattice distortions is also discussed. Finally, challenges and potential opportunities are briefly assessed to further minimize the thermal conductivity of TBC materials in the future.

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1. Introduction

Promoting the thermal efficiency and reducing emissions require gas turbine designers to further increase the operating temperature, which leads to more rigorous conditions faced by the superalloy components in the hot section, such as blades and vanes [1]. Therefore, it is urgently demanded to develop new ceramic materials with low thermal conductivity, high stability and durability at high temperature as candidates for thermal barrier coatings (TBCs) [2]. The state-of-the-art TBC material is 7 wt% yttria stabilized zirconia (7YSZ) with a low thermal conductivity about 2.5 W/m K for the fully dense bulks and less than 2 W/m K for the sprayed coatings at high temperature [3]. It may allow a 100–200 °C operating temperature increase without exceeding the limits of the superalloy components and the internal cooling system, which significantly benefits the output power and energy efficiency of the turbines [4]. Fig. 1 shows a sectional view of typical air plasma sprayed TBCs. A great deal of effort has been conducted to optimize the fabrication technologies of 7YSZ coatings during the last decade

[5–7]. Better mechanical properties and cycling lifetime have been achieved by controlling the porosity and microstructure of the coatings [8]. Yet, relatively high thermal conductivity and the t′ phase degradation restrict the application of 7YSZ coatings at temperatures above 1200 °C [9,10]. In order to further improve the heat insulation ability, $Ln_2Zr_2O_7$-type rare earth zirconates with either pyrochlore or fluorite structure have been developed as alternative candidates of TBCs and already been applied in some J-class gas turbines (operating temperature ~1600 °C) due to their lower thermal conductivity (less than 2 W/m K for fully dense bulks at high temperature, which is 20% lower than that of 7YSZ) [11–13]. Increasing the thickness of TBCs will certainly improve the thermal insulating ability, the temperature gradient in the top-coat and retard the TGO growth. However, the increasing of thickness is strictly limited by the enhanced thermal stress produced during the thermal cycling in an oxidation environment, the thermal expansion mismatch between the top-coat and bond coat. Thicker coatings may fail to bond with bond coat alloy and may pile off the surface. Currently, the optimum thickness of TBCs for gas turbine is usually within 100–400 μm [1]. Thus, there is a consensus that even lower thermal conductivity is needed to achieve still higher gas temperature for increased energy conversion efficiency of turbines. Indeed, it has been estimated that a 50% further decrease in the thermal conductivity of TBC materials will reduce the temperature at the surface of hot section components by about 55 °C, which corresponds to the improvement of single crystal Ni-based

* Corresponding author.
E-mail addresses: zhao-m07@mails.tsinghua.edu.cn (M. Zhao),
panw@mail.tsinghua.edu.cn (W. Pan), wancl@mail.tsinghua.edu.cn (C. Wan),
quzhixue@bjut.edu.cn (Z. Qu), lizheng13@mails.tsinghua.edu.cn (Z. Li),
yangjun13@mails.tsinghua.edu.cn (J. Yang).
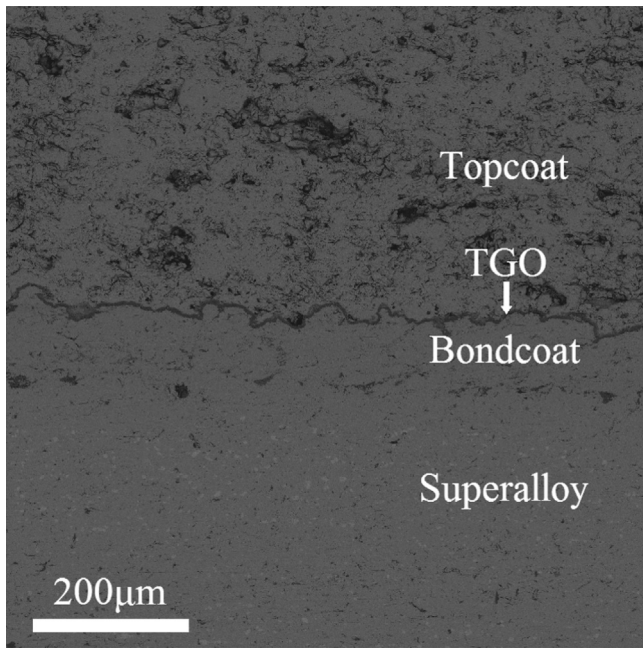
Fig. 1. A sectional view of typical air plasma sprayed thermal barrier coatings. Heat insulation is mainly provided by the ceramic topcoat. Generation of the thermally grown oxide (TGO) layer is the major failure mechanism of TBCs.

superalloy over the last 20 years [14]. Therefore, new TBC materials with even lower thermal conductivity are definitely required and a deeper fundamental understanding of the underlying heat transfer mechanisms is also necessary as the scientific guideline of future development.

As illustrated in some previous researches, some significant progress in identifying promising TBC materials has been made during the last decade. The development mainly focuses on two aspects: (1) further decrease the thermal conductivity of 7YSZ and $Ln_2Zr_2O_7$, for example designing multicomponent solid solutions based on them; (2) develop totally new material systems with low thermal conductivity, such as perovskite zirconates, rare earth hexaaluminates, orthophosphates and silicates [15–20]. In both directions, solid state heat transfer mechanism is always the theoretical foundation and defect engineering is acknowledged as the most systematic perspective and effective approach. Lattice defects, such as vacancies and substitutions, have an extremely important impact in the thermal conductivity reduction. The accompanying lattice distortion also plays a considerable role. In this paper, recent researches on the thermal conductivity of promising TBC materials have been reviewed and effects of various lattice defects on the thermal conductivity reduction are summarized and discussed in consideration of the point defect phonon scattering and lattice distortions.

2. Fundamentals of heat conduction in solid state materials

Generally, phonon propagation dominates the heat conduction in non-magnetic insulating ceramic materials [21]. However, fundamentals of understanding the phonon heat conduction in solid state materials have not been updated much from the Debye model for gas heat transfer since the 1960s due to the lack of motivation, except for some normalization on the mathematic symbols and notations. According to that, thermal conductivity of ceramic materials can be expressed as [22]:

$$\kappa = \frac{1}{3}\int_\omega C_V v l \tag{1}$$

where C_V is the specific heat, v is the average sound velocity and l is the phonon mean free path, which is the most important factor controlling the phonon thermal conductivity. The integration is over all the practical phonon frequencies of a certain material.

Ideal materials with defect-free lattice and perfectly harmonic vibration express infinite thermal conductivity because of the free phonon propagation and unlimited phonon mean free path. However, in real materials with defective lattice structure, phonon mean free path and thermal conductivity are limited by phonon scattering effects caused by other phonons, defects, boundaries, etc. [23]. Callaway has derived the expression of thermal conductivity on the assumption that all the phonon scattering processes can be represented by relaxation times (τ_C), as [24]:

$$\kappa = \frac{k_B}{2\pi^2 v_s}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_C(x)\frac{x^4 e^x}{(e^x - 1)^2}\mathrm{d}x \tag{2}$$

where $x = \hbar\omega/k_B T$, k_B is the Boltzmann constant, θ_D is the Debye temperature, and v_s is the average sound velocity. Then the combined relaxation time τ_C is defined as [25]:

$$\tau_C^{-1} = \tau_P^{-1} + \tau_D^{-1} + \tau_B^{-1} \tag{3}$$

where τ_P, τ_D and τ_B respectively correspond to the relaxation time of phonon–phonon scattering, phonon-defect scattering and phonon-boundary scattering.

Generally, the phonon-boundary scattering can be omitted since the grain size is much bigger than the phonon mean free path, which is limited by the phonon–phonon and phonon-defect scatterings in bulk materials within the whole temperature range. As for the phonon-defect scattering, Klemens provided the expressions [26]:

$$\tau_D^{-1} = A\omega^4 \tag{4}$$

$$A = \frac{\Omega\Gamma}{4\pi v_s^3} \tag{5}$$

where ω is the phonon frequency and Ω is the average volume per atom. Γ is the phonon scattering coefficient, which will be further defined below. In particular, defects here refer to the point lattice defects, such as vacancies and substitutions.

In addition, the relaxation time of phonon–phonon scattering (Umklapp scattering) can be estimated as:

$$\tau_P^{-1} = S(T)\omega^2 \tag{6}$$

where $S(T)$ is proportional to the temperature ($S(T) = CT$) when $T > \theta_D$. Combining all the three aspects mentioned above, the thermal conductivity of materials can therefore be expressed as [27]:

$$\kappa = \frac{k_B}{2\pi^2 v_s \sqrt{(ACT)}}\tan^{-1}\left[\frac{k_B\theta_D}{\hbar}\left(\frac{A}{CT}\right)^{\frac{1}{2}}\right] \tag{7}$$

For "perfect crystal materials" without "intrinsic lattice defects", the scattering coefficient Γ is approximately zero, then the thermal conductivity (κ_p) is mainly controlled by the phonon–phonon scattering:

$$\kappa_p = \frac{k_B^2\theta_D}{2\pi^2 v_s \hbar CT} \tag{8}$$

Therefore, phonon–phonon scattering will lead to a thermal conductivity inversely proportional to the temperature, that is $\kappa_p \propto 1/T$. This is usually correct for ceramic materials without "intrinsic lattice defects".

On the other hand, the thermal conductivity of a "real material" with lattice defects is related to that of the corresponding "perfect crystal material" by [28]:

$$\frac{\kappa}{\kappa_p} = \frac{\tan^{-1}(u)}{u} \tag{9}$$