Thin Solid Films 517 (2009) 5120–5129

Contents lists available at ScienceDirect

Thin Solid Films

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

High emissivity coatings for high temperature application: Progress and prospect

Xiaodong He [a,*], Yibin Li [a], Lidong Wang [a,b], Yue Sun [a], Sam Zhang [c]

[a] Center for Composite Materials, School of Astronautics, Harbin Institute of Technology, P.O. Box 3010, Harbin 150080, PR China
[b] School Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 405, Harbin 150001, PR China
[c] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Available online 22 April 2009

Keywords:
Emissivity
Coatings
Review

ABSTRACT

High emissivity coatings are widely used in many cases where heat transfers through electromagnetic radiation that arises due to the temperature of a body. Extensive theoretical and experimental efforts have been made to synthesize and investigate high emissivity coatings. The emissivity can be improved through various or combined mechanisms. The characterization of the emissivity is still a fully open problem. In this paper, we review the various mechanisms associated with the emissivity enhancement and emissivity characterization techniques. Based on these literature reviews, the prospect will be presented in the concluding remarks.

1. Introduction

High emissivity coatings are widely used in many high temperature applications to effectively transfer the heat by radiation [1–4]. For example, the surface of Ni-, Fe-, Co-based alloys applied in metal thermal protection systems (MTPS) [5,6] in third generation of reused space vehicles involves high friction heat from acute friction between space vehicle surface and atmosphere, which causes obvious increase of surface temperature up to 1000 °C during hypervelocity flight [7–9]. As a result, the lifetime and performance of MTPS will be seriously degraded. Therefore, the high emissivity coating is intentionally deposited on MTPS to decrease the surface temperature by radiation.

When a radiation falls on a body it may be partially reflected, transmitted, or absorbed, which is associated with reflection (R), absorption (A), transmission (T), and emission (ε). The principle of conservation of energy ties together these radiation characteristics as $A+R+T=1$. According to Kirchhoff's law, at equilibrium for a given wavelength λ and temperature T, the emissivity of any body is equal to its absorption [10], i.e. $\varepsilon(\nu, T, \theta)=A(\nu,T,\theta)$, where ε is the emissivity, ν the frequency, and the angle θ specifies the observer angle. This indicates that the emissivity of an object can be indirectly obtained by measuring its absorptivity. For a uniform and isotropic opaque surface in thermal equilibrium, the transmission is zero, the relationship between the emissivity and the reflectivity is: $\varepsilon(\nu,T,\theta)=A(\nu,T,\theta)=1-R(\nu,T,\theta)$. Many materials can be considered as opaque body. The emissivity here is characterized to describe the surface radiative property which involves the transfer of heat by electromagnetic radiation arising due to the temperature of a body. The emissivity is defined as the ratio of energy radiated by the material to energy radiated by a black body (A body that emits the maximum amount of heat for its absolute temperature is called a black body, meaning that a blackbody completely absorbs all radiation incident upon it, and at the same time it emits all the energy that it absorbs with the same absorbing spectrum. That is to say, $\varepsilon=1$) at the same temperature, which is described by Eq. (1):

$$\varepsilon(T)=\frac{\int_0^\infty \varepsilon(\lambda)E_\lambda d_\lambda}{\sigma T^4} \tag{1}$$

Where E is radiant heat of gray body to its surroundings, ε hemispherical emissivity of the gray body (dimensionless), σ Stefan–Boltzman constant (5.67×10^{-8} W/(m$^2\times$K^4)), T temperature (K). The emittance is dependent on direction and wavelength, thus the radiance ability can also be evaluated by the spectral emissivity and directional emissivity, described as Eqs. (2) and (3) respectively:

$$\varepsilon_\lambda(\lambda,T)=\frac{E_{\lambda,\text{actual emitted}}(\lambda,T)}{E_{\lambda,\text{black body}}(\lambda,T)}=\frac{E_\lambda(\lambda,T)}{E_{b\lambda}(\lambda,T)} \tag{2}$$

$$\varepsilon_\theta(\theta,\phi,T)=\frac{\int_0^\infty L_{\lambda,\text{actual emitted}}(\lambda,\theta,\phi,T)d\lambda}{\int_0^\infty L_{\lambda,\text{black body}}(\lambda,T)d\lambda}=\frac{L(\theta,T)}{L_b(T)} \tag{3}$$

A real object does not radiate as much as a perfect black body, which radiates less heat than a black body and is called gray body ($\varepsilon<1$).

Thermally emitted radiance from any surface mainly depends on two factors. (1) the surface temperature, which is an indication of the equilibrium thermodynamic state resulting from the energy balance of the fluxes between the gray body surface and its surroundings; and (2) the surface emissivity, which is the efficiency of the surface for transmitting the radiant energy generated in the surface into its surroundings. The latter depends on the temperature (but the relationship between emissivity and temperature is not definite,

* Correspondence author.
E-mail address: hexd@hit.edu.cn (X. He).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.03.175

depending on material nature, surface parameters and wavelength), composition, surface roughness, coating thickness, wavelength, and physical parameters of the surface. Here we review recent progress with emphasis on the discussion of the design methodology, followed by briefing the emissivity characterization. Lastly, the prospects for research and technology in high emissivity coatings will be summarized.

2. Design methodology

2.1. Doping

According to Wien's displacement law and Planck's law [11], most energy of the black body at high temperature is radiated in the wavelength range of 1–5 μm, however it happens that many materials have the weak intrinsic absorption within this range. As a result, the emissivity in this region is quite low since the object's absorptivity and emissivity spectra are identical in thermal equilibrium state. Extensive work proves that total emissivity or spectral emissivity could be effectively enhanced via doping (doping refers to the process of intentionally introducing impurities into an extremely pure material). Several mechanisms for doping enhanced emissivity in the wavelength range of 1–5 μm were proposed for different materials, namely, free carrier absorption mechanism (the phenomenon whereby an electron within a band absorbs radiation by transferring from a low-energy level to an empty high-energy level) [12], d–d transitions in octahedral coordination [13,14], distortion of the crystal lattice [15]. For semiconductor material, free carrier absorption mechanism generally dominates the emissivity enhancement in the wavelength region of 1–5 μm. Fig. 1 shows the absorption coefficient as a function of wavelength for three different SiC specimens with different impurity (dopant) concentrations [16]. It is obvious that increase in impurity concentration strengthens the absorption in the wavelength range of 1–5 μm. As higher impurity concentration causes more free electrons, more electrons within a band absorb more radiation by transferring from a low-energy level to an empty high-energy level, leading to more absorption. As such, the emissivity is accordingly enhanced within this wavelength range as the impurity concentration increases since the object's absorptivity and emissivity spectra are identical in thermal equilibrium state.

In glassy oxide coatings, different excitations are responsible for the absorption of electromagnetic radiation [17]. It is suggested that suitable dopants with transition metal oxides diluted in silicate glasses may yield emissivity as high as 0.9 in the whole temperature range. For example, the d–d transitions of Cr^{3+} in octahedral coordination play an important role on the absorption [13,14]. The

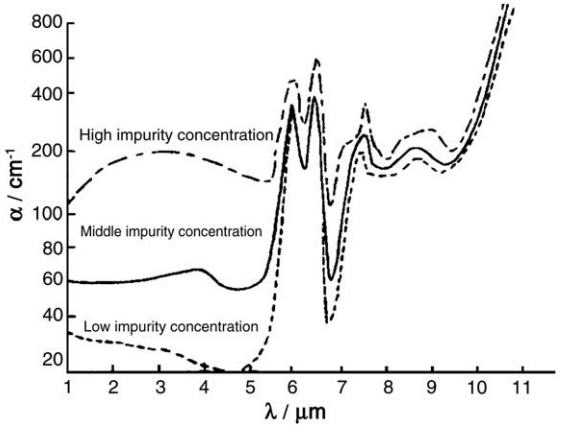

Fig. 1. Absorption coefficient as a function of wavelength of SiC. The three curves are for SiC specimens with different impurity concentrations [16].

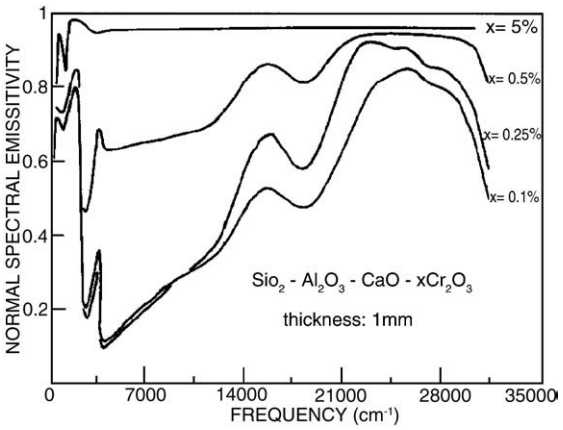

Fig. 2. The emissivity spectra at room temperature for 0.1%, 0.25% and 0.5% Cr_2O_3 doped compounds [17].

emissivity spectra at room temperature for 0.1%, 0.25% and 0.5% Cr_2O_3 doped compounds as shown in Fig. 2 indicates that the concentration of Cr_2O_3 dramatically enhanced the normal spectral emissivity between 1 and 5 μm (i.e. 2000–10,000 cm^{-1}). This enhancement is related to formation or precipitation of new phases on the grain boundary due to substitution, which will change the grain boundary area. But the mechanism still needs to be further digested.

Another consequence caused by dopant is the crystal distortion due to different ion radii, which also has the contribution to radiation. Pratt et al. incorporated NiO into $MgO–Al_2O_3–SiO_2$ system glasses heated at 1020 °C for 2 h and the whole-band normal direction emissivity changes from 0.82 to 0.90 by doping NiO [18]. When the Ni^{2+} is incorporated into cordierite structure and substituted with Mg^{2+}, the order degree of Al/Si in crystal structure of cordierite is decreased due to different radii of Ni^{2+} and Mg^{2+}, leading to the crystal structure distortion. This in turn decreases the symmetry of lattice vibration, thus enhances the effects of anharmonic vibration of polar lattice, the coupled action of phonon, and phonon combination radiation. Therefore, the infrared radiance of this material is enhanced by NiO doping.

Moreover, the dopant (rare-earth oxides and transition elements) could tune the spectral emissivity thus change the emissive power [19,20]. Incorporation of 2–4 wt.% Co_3O_4 or NiO into MgO host (a low infrared emissivity) produced “matched emitters”, which means its emissive power spectrum is matched very efficiently to the response of GaSb photovoltaic cells that convert the infrared radiation into electricity. Fig. 3 shows the continuous, strong radiant emissions which is up to 0.9 in the optimal energy range between 1 and 2 μm and minimal radiation at higher wavelengths [21,22]. The total emissive power between 1 and 9 μm is calculated by integrating the area under each curve. Interestingly, both the blackbody emitter and the NiO-doped MgO emitter have the same total emissive power of 144,000 W cm^{-2}. However, it is noticeable that the NiO-doped MgO emitter emits most of power at wavelengths less than 2 μm, instead of 1–5 μm in theoretical blackbody. The phenomenon results from intra-atomic electronic transitions determined by the electronic configuration of the dopant ions and interactions with the coordinating crystal field of the host oxide [23].

2.2. Surface roughness

The correlation between emissivity and surface roughness has been explored both theoretically [24,25] and experimentally[26,27]. Wen et al. [24] modeled the effect of surface roughness on emissivity of aluminum alloys. Normally the surface involves two broad categories: optically smooth (ideal) and rough (real) surfaces. For