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Research on ZrO_2 Thermal Barrier Coatings Modified by High-Intensity Pulsed Ion Beam *

WU Di(吴迪)[1,2], LIU Chen(刘臣)[1], ZHU Xiao-Peng(朱小鹏)[1], LEI Ming-Kai(雷明凯)[1**]

[1]*Surface Engineering Laboratory, School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024*

[2]*College of Physical Science and Technology, Dalian University, Dalian 116622*

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We report a modification method for ZrO_2 thermal barrier coatings (TBCs) by high-intensity pulsed ion beam (HIPIB) irradiation. Based on the temporal and spatial distribution models of the ion beam density detected by Faraday cup in the chamber and the ions accelerating voltage, the energy deposition of the beam ions in ZrO_2 is calculated by Monte Carlo method. Taking this time-dependent nonlinear deposited energy as the source term of two-dimensional thermal conduction equation, we obtain the temporal and spatial ablation process of ZrO_2 thermal barrier coatings during a pulse time. The top-layer TBC material in thickness of about 0.2 μm is ablated by vaporization and the coating in thickness of 1 μm is melted after one shot at the ion current density of 200 A/cm^2. This calculation is in reasonable agreement with those measured by HIPIB irradiation experiments. The melted top coat becoming a dense modification layer due to HIPIB irradiation seals the gaps among ZrO_2 crystal clusters, and hence barrels the direct tunnel of oxygen.

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High-intensity pulsed ion beam (HIPIB) interacts with thermal barrier coatings (TBCs), leading to the top surface layer of TBCs melted and the properties of the surface changing dramatically. The energy of a single ion among HIPIB is as high as several tens of keV to a few of MeV. High energy of the beam is efficiently deposited into TBC materials in the ion range 0.1–10 μm in a short pulse width usually less than 1 μs to rapidly melt and strongly vaporize the near-surface layer. Therefore, the chemical and physical properties of surfaces can be changed[1−3] due to the melted surface re-solidify by thermal conduction.

TBCs are of complex coating structures consisting a ceramic top coat on a metallic bond layer by electron beam physical vapour deposition (EB-PVD).[4,5] TBCs play an important role in aero- and land-based gas turbines.[6] The top coat commonly applied material is yttria partially stabilized zirconia, with a very low thermal conductivity as well as high thermal expansion properties. However, it still exhibits some shortcomings resulting in the oxidation of a bond layer,[7] crack formation on the surface or inside the TBCs[8] and even spallation-failure of the coatings,[9] etc. Great effort has been made to improve some properties of the coatings by the art of generation like gradient coatings[10] or hybrid spraying technique,[11] and by the modification of the deposited coatings with laser or focused sun light beam.[12−15] In our previous study, we found that the properties of the surface of the coatings can be changed when irradiated by HIPIB.[16] The difference of HIPIB from laser beam irradiation is that the ions stop the inner TBCs, so both the heating and melting processes are under the surface. In this Letter, a time-dependent nonlinear model is proposed to model the heat transfer in TBCs under HIPIB irradiation to investigate the ablation behaviour of irradiated TBC materials and the subsequent dynamical effects.

The irradiation process of ZrO_2 ceramic TBCs by HIPIB was carried out on a TEMP-6 type apparatus[17] mainly consisting of two parts, one is a pulse power system that includes a Marx generator and a double coaxial pulse-forming line (PFL), and the other is an ion diode system that includes a magnetically insulated ion diode (MID) with external-magnetic field installed in a vacuum chamber.

In the TEMP-type ion source, the main ion species of ion beam for the anode of MID coated by polyethylene were approximately 70% H^+ and 30% C^+.[17] The accelerating voltage of ions generated by MID of TEMP-type accelerator in the experiment was typically 300 kV. The ion current density with full pulse duration 120 ns has a radial distribution with a maximal value of 200 A/cm^2 in the centre of beam spot. The TBC specimens prepared for this study were ZrO_2 stabilized by 7%Y_2O_3 fabricated by EB-PVD on the NiCoCrAlY bond layer, 180 μm in thickness, and irradiated by HIPIB with one shot.

A JSM-5600LV scanning electron microscope (SEM) was used to observe the structure and mor-

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** Email: surfeng@dlut.edu.cn

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phology of the irradiated surface before and after the irradiation in the experiments.

Based on HIPIB irradiation, the profile of voltage of MID fits can be expressed by[18]

$$U(t) = A \exp\Big[-\frac{(t-t_{0U})^2}{2\sigma_1^2}\Big], \tag{1}$$

the ion current density detected by Faraday cup reads[18]

$$J(y,t) = B \exp\Big[-\frac{(y-y_0)^2}{2\sigma^2}\Big] \exp\Big[-\frac{(t-t_{0J})^2}{2\sigma_2^2}\Big], \tag{2}$$

where y_0 represents the coordinate of central position of the ion beam bombarding spot along the TBCs target surface, A and B represent the maximal value of MID voltage and HIPIB current density respectively, t_{0U} and t_{0J} correspond to the time when voltage and ion current density reach the maximal values, and $\sigma_1, \sigma, \sigma_2$ are the standard deviation for voltage and ion current density respectively. The total deposition energy versus time t at position (x, y) is given by[18]

$$E_S(x,y,t) = \int_0^T \frac{dE(x)}{dx} \frac{J(y,t)\cos\theta}{q} dt. \tag{3}$$

The energy deposition term $dE(x)/dx$ can be calculated by the TRIM code which is commonly used to simulate the interactions of ions with target materials, θ is the incident angle of the ion beam. In the calculation, we take $\theta = 45°$, q represents the charge of a single ion.

$E_S(x, y, t)$ is used as a thermal source term in the two-dimensional transient heat transfer equation in specimens irradiated by HIPIB:

$$\rho C(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\Big(\kappa(T)\frac{\partial T}{\partial x}\Big) + \frac{\partial}{\partial y}\Big(\kappa(T)\frac{\partial T}{\partial y}\Big) + E_S(x,y,t), \tag{4}$$

where ρ, $C(T)$ and $\kappa(T)$ are the mass density, specific heat and thermal conductivity, respectively. The initial condition is $T(x, y, 0) = T_0$ and the boundary conditions at the exterior surface are treated to be adiabatic. In the calculation, we take the TBCs specimens in size $50 \times 50\,\mathrm{mm}^2$, thickness $50\,\mu$m and the initial temperature $T_0 = 20°$C. A finite difference method is used to solve the non-linear heat transfer equations (1)–(4).

After a shot, the microstructure of the ZrO_2 surface changes dramatically. This can be seen from Figs. 1(a) and 1(b), i.e. the SEM images of the original ZrO_2 TBC surface and the surface irradiated by HIPIB with one shot under ion current density of $200\,\mathrm{A/cm}^2$. The original surface morphology looks to be roughness, with gaps among the crystal clusters. However, after the irradiation by HIPIB, the raised parts disappear and form a melting style.

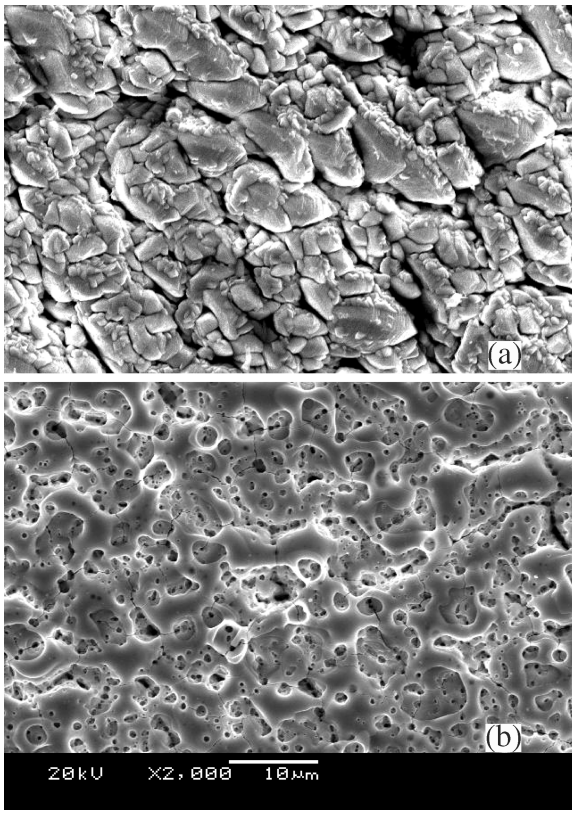

Fig. 1. SEM images of surface morphology of EB-PVD ZrO_2-7% Y_2O_3 coatings: (a) original, (b) irradiated by HIPIB under beam current density of $200\,\mathrm{A/cm}^2$ per shot.

According to the calculation results based on the models of MID voltage, ion current density and the heat transfer equations, we obtain the temporal and spatial evolution profile of temperature in the irradiation centre during a pulse of HIPIB, as is shown in Fig. 2. The surface of specimens at the irradiation centre reaches melting point at about 40 ns from the beginning of a pulse under the ion current density of $200\,\mathrm{A/cm}^2$. After 60 ns, about 0.3-μm-thickness top surface materials at the irradiation centre are melted. When a pulse finished, about 0.2-μm-thickness top layer material is removed due to the vaporized ablation, about 1.2-μm-thick TBC materials are melted. Except for the vaporized layer, there is an about 1-μm-thick top layer re-solidified after melting. This is in reasonable agreement with the measured result as shown in Fig. 3, in which we present the SEM image of cross section of ZrO_2 irradiated by HIPIB under the ion current density of $200\,\mathrm{A/cm}^2$. The melting phenomenon on the top layer of the sample can be seen clearly from the figure, about a 1-μm-thick ZrO_2 TBC top layer is densified, and the gaps among the ZrO_2 crystal cluster have been filled. This barrels the direct tunnel of oxygen while TBCs work in the high

temperature environments, and certainly protects the bond coating layer and the bulk metal under ZrO_2.

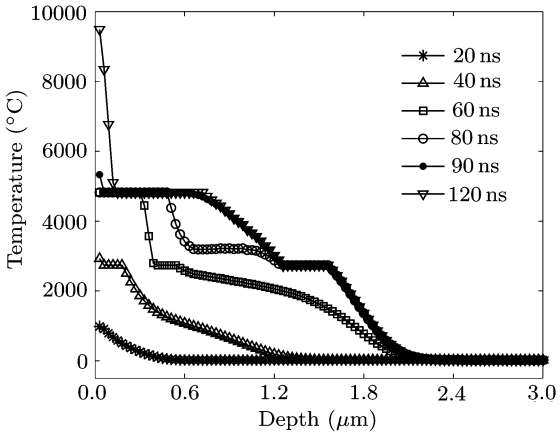

Fig. 2. Temporal-spatial evolution of temperature of ZrO_2 surface irradiating by HIPIB under the ion beam density of 200 A/cm^2 and the oblique angle of 45°.

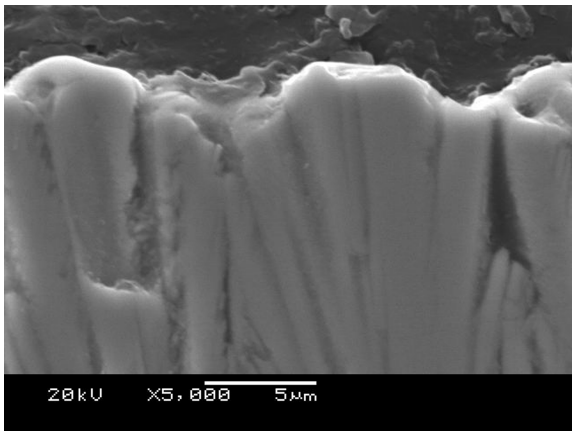

Fig. 3. SEM image of cross-sectional morphology of EB-PVD ZrO_2-7% Y_2O_3 coatings irradiated by 200 A/cm^2 HIPIB with 1 shot.

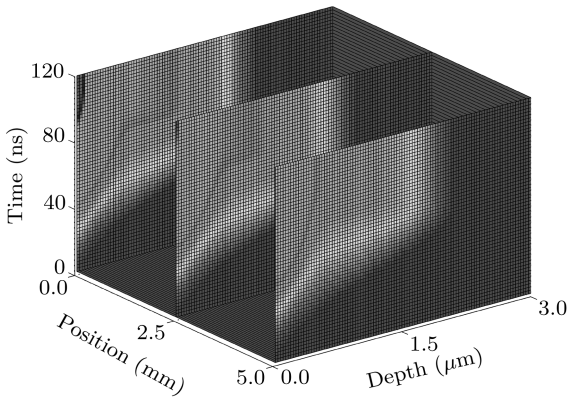

Fig. 4. Evolution profile of sample material melting ablation in the irradiation centre with 2.5 mm and 5 mm deviations.

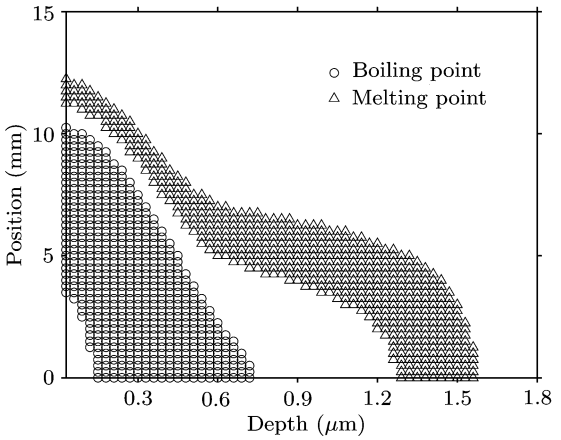

Fig. 5. Sample material ablation distribution profile in TBCs at the end of a pulse.

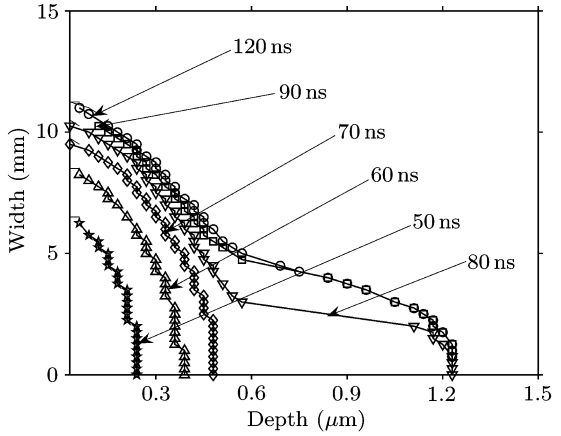

Fig. 6. Sample material melting ablation curve in the TBCs as a function of time during a pulse.

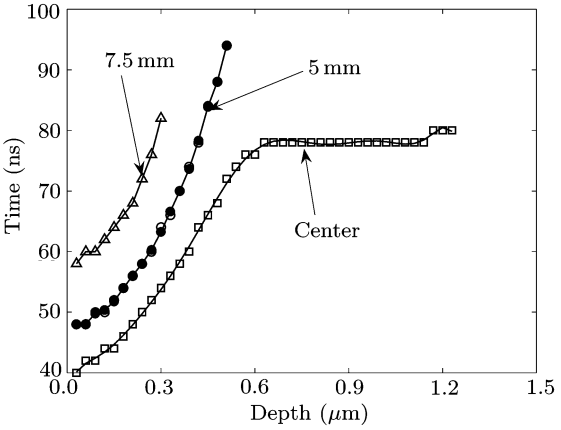

Fig. 7. Ablation depth of sample in the shooting centre of TBCs with 5 mm and 7.5 mm deviations as a function of time during a pulse.

The melting ablation evolution curves of the ZrO_2 materials in the irradiation centre and with 2.5 mm and 5.0 mm deviations are shown in Fig. 4. We can see that the melting thickness decreases with the in-

creasing distance from the irradiation centre. Figure 5 gives the ablation distribution profile of the ZrO_2 materials on the surface and in the body of TBCs at the end of an irradiation pulse. Only a little area of material is ablated off due to the vaporization compared with the melting ablation area on the surface after a shot. The most deep melting depth is in the irradiation centre. Figure 6 shows the ZrO_2 melting ablation curve inside the target. The melted region becomes wider and deeper on the surface and inside the body of TBC target with the irradiation time, respectively. Figure 7 shows the temporal evolution profile of the sample in the centre and with 5.0 mm and 7.5 mm deviations during a pulse. We can see from the image that some region inner the sample with some deviations from the irradiation centre will never be melting ablated. The temperature contour is drawn in Fig. 8 at the end of a shot. The temperature distribution after a pulse can be seen clearly. For the small value of the conductivity of ZrO_2, the thermal transportation along the longitudinal depth in the specimens is less than 3.0 μm when a pulse finishes.

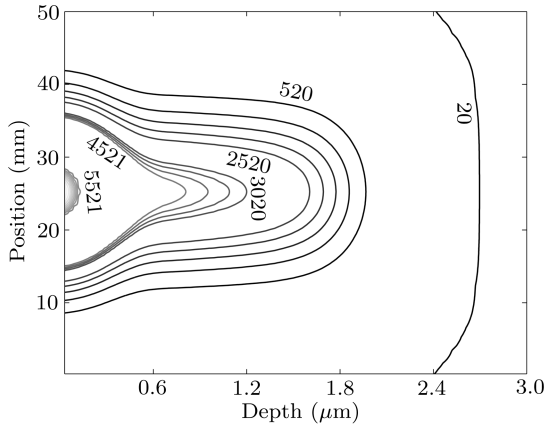

Fig. 8. Temperature contour of ZrO_2 TBCs after the irradiation of HIPIB under the ion beam current density of 200 A/cm^2.

In summary, a two-dimensional model of transient heat transmission in TBC materials irradiated by HIPIB has been constructed based on the nonlinear temporal and spatial distribution of HIPIB. The modification behaviour on the surface of a ZrO_2 TBC material irradiated by HIPIB during a full pulse width 120 ns has been investigated based on the models. The evolution of temperature field and the ablation process of ZrO_2 TBCs are obtained during a pulse according to the models. The melting longitudinal thickness induced by HIPIB irradiation is only about 1 μm with one shot under the ion beam current density of 200 A/cm^2. It is far less than the thickness of TBCs (often over 100 μm). A fully dense top layer can be formed and the gaps among the crystal clusters on the surface can be sealed after the irradiation.

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