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Preparation and Numerical Simulation Investigation of High Reflectance Anti-laser-ablation Coating

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Abstract: An anti-laser-ablation coating using TiO_2 as pigment and potassium silicate as binder (abbreviated as KS-T) was deposited on the aluminum alloy substrate by an air spray process. Factors influencing the reflectance of KS-T coating, including particle size, pigment volume concentration and coating thickness, were investigated. The reflectance of prepared KS-T coating could be up to 96.8% at the laser wavelength of 1064 nm. A three-dimensional finite element model based on the heat-conduction equation was developed to simulate the distribution of transient temperature filed. By monitoring the temperature variation at the backside center of aluminum alloy substrate during laser irradiation and comparing with the simulation results, it is found that KS-T coating could effectively protect the substrate from laser ablation. The simulation results demonstrated reflectance decrease of samples after a period of irradiation. The possible reasons for the reflectance decrease were proposed. The calculation results also showed that an obvious temperature drop emerged at the coating/substrate interface when interface thermal resistance (ITR) was considered. Eventually heat flux was prevented from flowing to the substrate and aluminum alloy kept a low temperature.

Key words: anti-laser-ablation coating; high reflectance; finite element modeling; interface thermal resistance (ITR)

The application of laser in industry, agriculture, medical, defense and other fields has grown rapidly in recent years[1-3]. However, the improper use of laser can result in serious hazards for those materials exposed to laser irradiation. The work of laser protection has attracted researchers' attention during the past decades. Main concerns were focused on possible damages for photoelectric devices and personal safety (*e.g.* eye protection) from high-power laser beams[4-6]. Optical films are widely used in laser protection owing to their high reflectance under the application of laser with a certain wavelength[7-9]. It is usually proposed that the absorption of optical films must be minimized with the increase of laser power[10]. Laser damage research continued to focus on increasing the material's reflectance. However, optical films are difficult to be applied on the complex-shaped substrate and can be easily contaminative. One of solution methods is to apply paint coatings with high reflectance on the surface of the components to prevent from laser ablation, which is a cost-effective technique, and particularly suits for the large-scale fabrication.

Rutile TiO_2 is largely employed as reflective pigment in the reflective paint coatings because of its effective light scattering properties[11]. Zhang[12] studied K_2SiO_3-TiO_2 (KS-T) coating in the application of atomic oxygen protection with an 80% reflectance at 1064 nm. Kumar[13] developed optical reflectors by dispersing TiO_2 nanoparticles in de-ionized water solution of organic binder. They achieved a reflectance of 97.12%–96.91% in the visible spectrum. Mikhailov[14] fabricated the reflective coatings by doping TiO_2 powders with potassium peroxoborate, which obtained a 90% reflectance at 1064 nm. While this value is still lower than that of the actual demand. To our knowledge, there has been little research on the higher reflectance of paint coatings in the NIR range, especially at the laser wavelength of 1064 nm. It remains unclear that what factors will affect the final reflectance of the coating.

Generally, high-power CW lasers could produce serious heating effects in a short time[15]. It would be laborious to analyze the interaction between laser and material *via* experimental approaches. Numerical simulation is a low-cost and time-saving method to solve the related heat conduction problems[16], thus we developed a three-dimensional (3D) finite element model based on heat-conduction equation to simulate the distribution of transient temperature filed inside the sample. In order to obtain the accurate

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simulation results, the temperature-dependent parameters, such as thermal conductivity as well as heat capacity, were considered in the model. Due to the incomplete contact between the coating and substrate, the existence of interface thermal resistance (ITR) was also considered in the calculation[17].

In this work, we prepared KS-T coating by an air spray process. Influencing factors for achieving high reflectance of the coating at the wavelength of 1064 nm has been studied. Based on finite element simulation method, the decrease of coating reflectance and the significant effect of ITR played during laser irradiation were also investigated.

1 Experimental

1.1 Preparation of the paint coating

The paint coatings were prepared through an air spraying technique with rutile TiO_2 as filler and potassium silicate as binder at 0.2 MPa in air. TiO_2 slurry was stirred for 8 h with potassium silicate in a certain ratio to ensure homogeneous mixing. Enough water was used for getting good flowability of the paint. To form the reflecting layer, the paint was sprayed on the LY12 aluminum alloy substrate (20 mm×20 mm×1 mm), which was ultrasonically cleaned after sandblasting. The specific spraying process was divided into several steps in order to prevent cracking. Each intercrossing vertically painting was regarded as one step with a certain time interval to ensure surface dry. Then the sample was dried in air for 24 h at ambient temperature, followed by heating for 2 h at 80℃ to eliminate adsorbed water and 6 h at 120℃ to remove structural water. The thickness of KS-T coating was about 200 μm after curing.

1.2 Characterization

The particle size was analyzed by a BT-9300H laser scattering particle size distribution analysis meter. The thickness of the coating was measured by a thickness gauge (ElektroPhysik, Germany). The reflectance of the coating was characterized by an UV/Vis/NIR Spectrophotometer (LAMBDA950, USA) equipped with an integrating sphere. Laser irradiation experiment was carried out through a 1-on-1 method under atmospheric environment. The 1064-nm Nd:YAG laser with a power density of 281 W/cm^2, a square spot size of 11 mm×11 mm and a uniform intensity distribution was used. The CW laser was vertically irradiating on the central part of sample. The temperature at the backside center of the aluminum alloy was measured in real-time with a K-welded type thermocouple. Thermal conductivity of the coating material was measured by a laser flash thermal analyzer (TD-79A, China) and specific heat was tested by a high-temperature specific heat meter (HF DSC, MHTC96, France). The morphology was characterized by scanning electron microscopy (SEM, S-3400N, Hitachi Ltd., Japan).

1.3 Finite element modeling

Finite element simulation were performed through the commercial software package ANSYS (afflicted with ANSYS finite element code-APDL)[18]. A three-dimensional model with boundary conditions is depicted in Fig. 1. We exploited the symmetrical geometry of the sample, and then selected a quarter of the finite element model to calculate in order to reduce the computational time. The left and front side boundaries of the model were considered to be adiabatic, *i.e.* $dT/dn = 0$ (where n is the direction normal to the sample side surfaces). The model has two layers: LY12 aluminum alloy substrate with the thickness of 1mm and KS-T coating with the thickness of 200 μm, respectively. The three-dimensional equations for transient heat conduction can be expressed as[19]:

$$\frac{\partial}{\partial j}\left[k_{ij}(T_i)\frac{\partial T_i}{\partial j}\right]+q_v=\frac{\partial}{\partial t}\left[\rho_i c_i(T_i)T_i\right] \tag{1}$$

Where subscript i = 1, 2 represents the coating and substrate, $j = x, y, z$ represents the x, y and z directional vector respectively. T is transient temperature, t is time, ρ is density, k is thermal conductivity, c is heat capacity and q_v is the intensity of the internal heat source.

The initial conditions for thermal analysis is taken as

$$T_{int}=T_{amb}=30℃ \tag{2}$$

Heat source at coating surface for the laser irradiated region is expressed as:

$$k_{1y}(T_1)\frac{\partial T_1}{\partial y}=Q(1-r) \tag{3}$$

At the interface between the KS-T coating and substrate

$$k_{1y}(T_1)\frac{\partial T_1}{\partial y}=\frac{1}{R}(T_2-T_1)=k_{2y}(T_2)\frac{\partial T_2}{\partial y} \tag{4}$$

For all other surfaces, the boundary condition is

$$k_{in}(T_i)\frac{\partial T_i}{\partial n}=-h(T_i-T_{amb}) \tag{5}$$

Where T_{int} is the initial temperature of the sample, T_{amb} is ambient temperature, Q is the power density of laser beam, r is the reflectance of the coating. It can be seen from Eq.(3) that r has a significant influence on the absorbed energy. R and h represent interface thermal resistance and convection heat transfer coefficient, respectively. Besides, model assumed that the densities of the coating and substrate kept a constant, and material properties were isotropic, as well the laser irradiation heating was treated as a surface heat source[20]. The thermal conductivity and heat capacity of material were measured in this work, while h = 10 W/(m^2·K) and R = 1×10^{-3} m^2·K/W according to the Ref. [21].

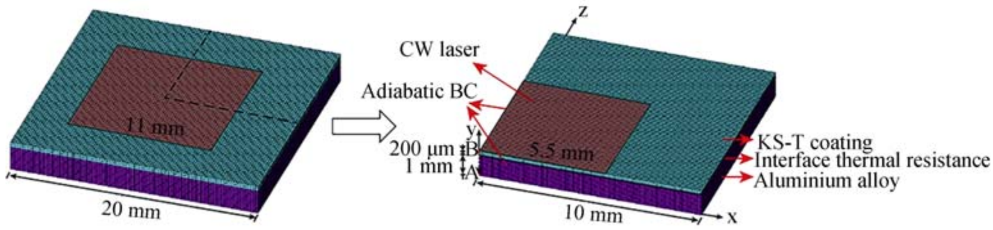

Fig. 1　The three-dimensional finite simulation model

2　Results and discussion

2.1　Factors influencing the reflectance of coating

When a laser beam irradiates on the surface of a paint coating sample, reflection, transmission and absorption will occur[22]. For opaque materials, the sum of reflectance and absorptance is unity. Therefore, a high reflectance of the coating is needed to reduce the absorption of high-power laser. The factors influencing the reflectance of KS-T coating, including particle size, pigment volume concentration and coating thickness are investigated.

2.1.1　Influence of particle size

As shown in Fig. 2, the reflectance of KS-T coating at the laser wavelength of 1064 nm increases with the increase of particle size (>200 nm). According to Kubelka-Munk (KM) theory[23], the number of reflections at the grain boundaries or interfaces increases as the particle size decreases, which leads to an increase in the reflectance. However, the particle size cannot be reduced too much (<200 nm). A strong capillary effect will make the coating easily crack, which results that light is trapped in the crackles and reflectance decreases.

2.1.2　Influence of pigment volume concentration

Pigment volume concentration (PVC) influences the reflectance of the coating as well. As seen in Fig. 3, diffraction plays a dominant role when PVC of the coating is not enough. The reflectance is at a relatively low value because the size of TiO_2 particle is less than half of the laser wavelength. With the increase of PVC, the reflectance of KS-T coating increases, attributing to the pigment particles gradually fuse together and bind into a continuous coating. However, if PVC is excessive that cracks do emerge after curing, then light will be absorbed around the crackles. Under this circumstance, reflectance decreases once again.

2.1.3　Influence of coating thickness

Coating thickness is another factor that will affect the reflectance of the coating. Measurements show that, the coating reflectance increases with the increase of thickness when KS-T coating is less than 200 μm thick. For coatings which are thicker than 200 μm, their reflectance becomes independent of the thickness. This can be explained by the fact that thicker KS-T coating makes denser coverage of the substrate for the preparation method of air spraying. A higher number of TiO_2 nanoparticles on the surface will take part in the reflection. Considering various influencing factors during the preparation of the coating, finally we fabricated KS-T coating with a reflectance up to 96.8% at the laser wavelength of 1064 nm.

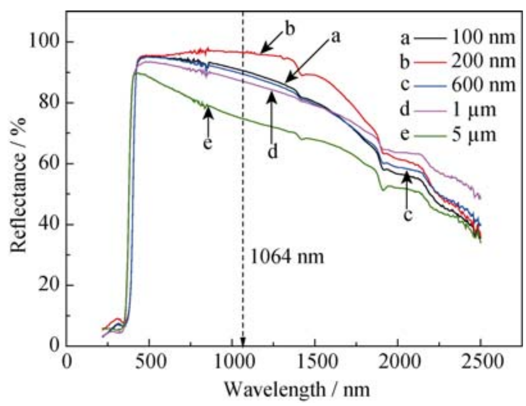

Fig. 2　Reflectance spectra of KS-T coating with different TiO_2 particle sizes

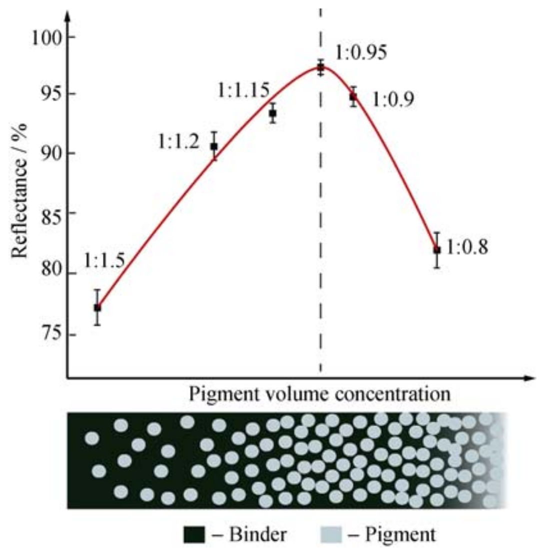

Fig. 3　The 1064-nm reflectance of KS-T coating influenced by pigment volume concentration

2.2 Experimental and numerical simulation results

For inspecting the anti-laser-ablation capability of KS-T coating, a method of monitoring the temperature change at the backside center of aluminum alloy substrate was used. The model was optimized by comparison of the experimental and simulation results. The phenomenon of the reflectance change of coating after a period of irradiation time and the effect of ITR at the coating/substrate interface were analyzed.

2.2.1 Backside center temperature

Fig. 4 presents the typical images of samples uncoated and coated KS-T coating irradiated by 1064-nm CW laser. It can be seen that the aluminum alloy could be ablated in a few seconds under laser irradiation because of its relatively low reflectance (about 85%) at the laser wavelength of 1064 nm[24], while the sample coated KS-T coating could maintain for a considerable period of time. Moreover, despite the color slightly darkened, there is no obvious ablation phenomenon of the coated sample after laser irradiation. By comparing with the measured curves of the backside center temperature of the aluminum alloy without and with KS-T coating in Fig. 5, it demonstrates that the backside center temperature of the uncoated aluminum alloy rose rapidly and could be damaged in a short time. For the coated sample, its temperature rise at the backside center was much smaller due to the high surface reflectance. It can be clearly seen that both of the curves exhibit an abrupt temperature rise during laser irradiation as marked by the circles (Fig. 5). In order to investigate the reason for the abrupt temperature rise, a three- dimensional finite element model was developed to simulate the transient temperature filed distribution. The temperature dependent parameters of KS-T coating using in the calculation were listed in Table 1. The performance parameters of aluminum alloy were taken from Ref. [25]. The reflectance of KS-T coating was taken as 96.8% at the laser wavelength of 1064 nm and considered to be unchangeable.

Fig. 6(a) shows a good agreement of the backside center temperature between the experimental and simulation results at the beginning of laser irradiation. However, the calculated temperature started to depart significantly from the experiment results after a period of irradiation time. It is considered that the abrupt temperature rise was attributed to the change of the material's reflectance. This was confirmed by the simulation results shown in Fig. 6(b) by a multi-step load method[26]. The experimental and simulation results were in accordance with each other after adjusting the reflectance of aluminum alloy from 85% to 60%, and the reflectance of KS-T coating from 96.8% to 91% at the time of abrupt temperature rise. For aluminum alloy, the rise of temperature strongly affects the electron-phonon collision frequency which affects the optical properties of the metal in turn. It will be shown that the reflectance drastically decreased with increasing temperature. Varieties of factors are associated with the reflectance decrease of KS-T coating, which probably is ascribed to

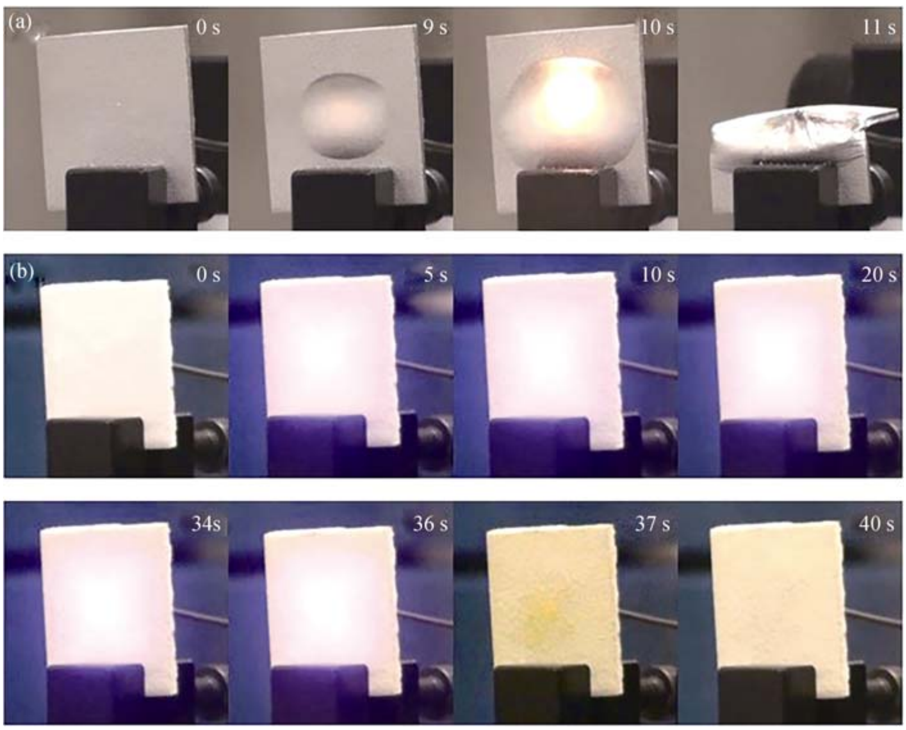

Fig. 4 Images of samples irradiated by 1064-nm CW laser
(a) Uncoated sample (laser switched off at 11 s); (b) Coated 200 μm KS-T coating (laser switched off at 36 s)

Table 1　Temperature-dependent parameters of KS-T coating

T / ℃	25	100	200	300	400	500	600	700
k/(W·m^{-1}·K^{-1})	1.145	0.943	0.883	0.805	0.790	0.746	0.727	0.727
C_p/(J·kg^{-1}·K^{-1})	699	772	844	881	907	937	967	978

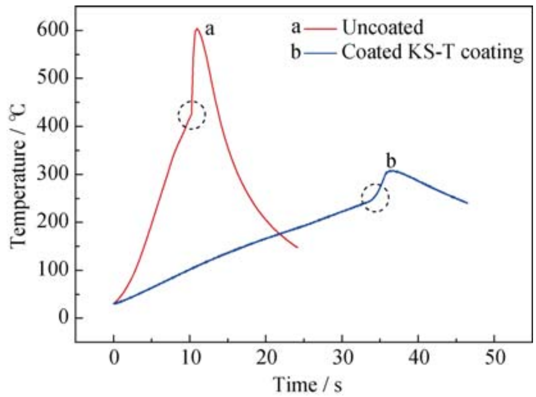

Fig. 5　Typical temperature at backside center of the aluminum alloy *vs* time

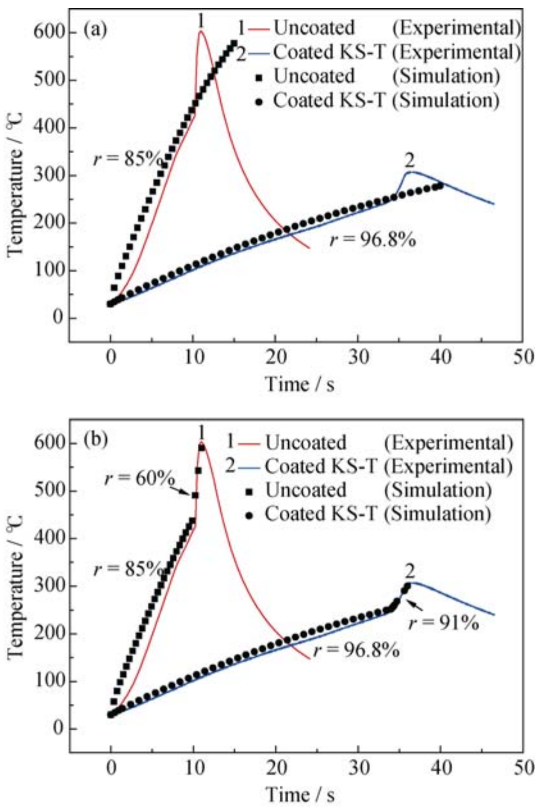

Fig. 6　Comparison of the experimental and simulation results
(a) Without considering reflectance change; (b) Considering reflectance change

the enhancement of oxygen vacancies (absorption of visible light) along with the formation of Ti^{3+} centers (absorption of IR radiation) at high temperature[27]. The color change can be clearly seen in Fig. 4(b) at the time of 37 s with the surface temperature probably rising up to 500℃.

2.2.2　Effect of ITR during laser irradiation

The highest temperature of the surface of color-changed KS-T coating was speculated probably up to 500℃ during the laser irradiation, while the aluminum alloy substrate could still keep at a low temperature near 300℃. The simulation results displayed in Fig. 7 illustrate that interface thermal resistance (ITR) at the coating/substrate interface is another important parameter that should be considered in the anti-laser-ablation coating study.

ITR is caused by imperfect contact between coating and substrate. For the substrate which is sandblasted before spaying in this work especially, heat flux will shrink in two adjacent layers[17]. The interface thermal resistance (R) is defined as:

$$R = \Delta T / q \tag{6}$$

Where q is heat flux density, ΔT is the temperature drop across the interface.

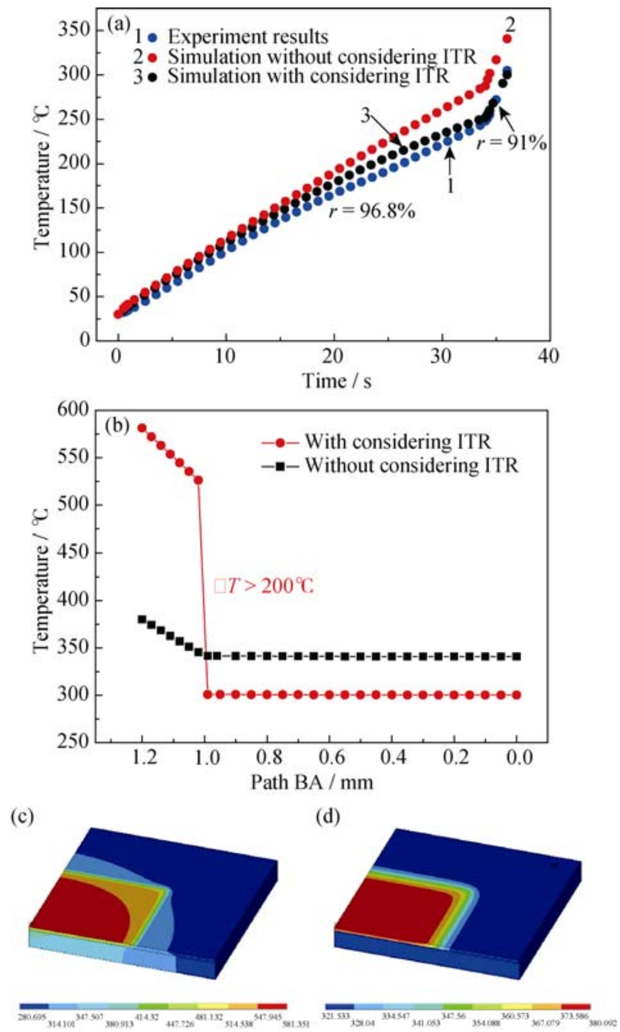

Fig. 7　The simulation results
(a) Backside center temperature of the sample coated by KS-T coating; (b) Temperature along the path B; (c) Temperature distribution plot without considering interface thermal resistance; (d) Temperature distribution plot with considering interface thermal resistance. ((b)-(d) are at the ending time of laser irradiation)

The temperature profile (along path BA in Fig. 1) in the depth direction at the central point of the sample was calculated with and without considering ITR. The simulation results in Fig. 7(b) show a large temperature drop (>200℃) across the interface when ITR was taken into account. Comparing the temperature distribution plots in Fig. 7(c) and (d) also demonstrates that the existence of ITR prevented the heat flux from flowing to the substrate, thus the surface temperature increased, meanwhile, the substrate temperature lowered.

2.2.3 Surface morphology of KS-T coating before and after laser irradiation

SEM images of surfaces of KS-T coating before and after laser irradiation are shown in Fig. 8. The surfaces of the coating are composed of TiO_2 nanoparticles fused together by the binder to form countless reflection units, which contribute to the high reflectance of the coating. The TiO_2 particle size has not grown up as expected, which indicates KS-T coating presents excellent anti-laser-ablation capacity.

3 Conclusions

In the current work, an anti-laser-ablation KS-T coating was deposited on the aluminum alloy substrate by an air spray process. The influencing factors for achieving high coating reflectance have been investigated systematically. The following conclusions can be dawned:

1) TiO_2 nanoparticles which have high refractive index were chosen for the pigment with optimized pigment volume concentration and coating thickness. The reflectance of KS-T coating at the laser wavelength of 1064 nm was measured up to 96.8%.

2) Both the experimental and simulation results indicated that KS-T coating could effectively protect the substrate from laser ablation. Although the color darkened slightly, there is no obvious ablation phenomenon of the coated sample after laser irradiation. The TiO_2 particle size of the coating has not grown up yet.

3) The simulation results showed that there was a phenomenon of samples' reflectance decrease after a period of irradiation time. For aluminum alloy, the rise of temperature strongly affects the electron-phonon collision frequency which affects the optical properties of the metal in turn. The reflectance decrease of KS-T coating is probably ascribed to the enhancement of oxygen vacancies along with the formation of Ti^{3+} centers at high temperature.

4) The numerical simulation results showed that interface thermal resistance (ITR) at the coating/substrate interface could play an important role in preventing the heat flux flowing to the substrate. The KS-T coating may have the potential application on the anti-laser-ablation for complex-shaped substrate and large-scale fabrication.

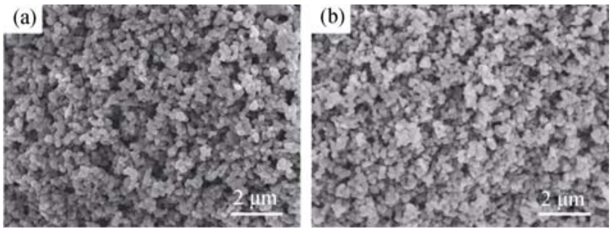

Fig. 8 SEM images of surfaces of KS-T coating
(a) Before laser irradiation; (b) After laser irradiation

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高反射率抗激光烧蚀涂层的制备及数值模拟研究

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摘 要: 以 TiO_2 为颜料, 硅酸钾为粘结剂(以下简称 KS-T), 采用空气喷涂的方法, 在铝基底上制备了一种抗激光烧蚀涂层。研究了粉体粒径大小、固含量、涂层厚度等因素对涂层反射率的影响, 获得了 1064 nm 激光波段下反射率达到 96.8%的 KS-T 涂层。基于热传导方程建立三维有限元模型模拟材料的瞬态温度场分布, 测量激光辐照过程中铝基底的背底温度变化, 与模拟结果相比较, 发现 KS-T 涂层可以有效地保护基底不被激光烧蚀。模拟结果显示, 在辐照一段时间后, 样品的反射率出现了下降的现象, 分析了反射率下降的可能原因; 计算结果还表明考虑界面热阻(ITR)后, 涂层/基底界面处出现一个明显的温降, 阻止热流向基底的传输, 从而使铝基底保持一个较低的温度。

关 键 词: 抗激光烧蚀涂层; 高反射率; 有限元模型; 界面热阻

中图分类号: TQ174 **文献标识码:** A