Preparation and Properties of $K_2SiO_3/BaSO_4$ Inorganic High-Temperature Resistant Thermal Control Coating

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Abstract

In order to enhance the high-temperature-resistant performance of spacecraft in deep-space exploration, and at the same time to improve the spectral performance of inorganic thermal-control coatings, barium sulphate powder, which has a high reflectance in the whole UV/visible/near-infrared wavelength range, is used as a filler, and potassium silicate, which has a better space-resistant performance, is used as a binder, so as to research the effects of curing agent, pigment/base ratio, and thickness on the coating's thermal-control and high-temperature-resistant performance, and to prepare the inorganic The inorganic heat-controlled coatings were prepared. The experimental results show that the thermal control performance of the K2SiO3/BaSO4 coatings have excellent thermal control performance (α_S =0.12, ε =0.96), and the irradiation absorption ratio is as low as 0.125, and the appearance and spectral properties of the coating remain good after 300 ℃/24 h high-temperature test. The coating can meet the application requirements of high temperature resistance, high radiation heat dissipation and long life of future spacecraft.

Keywords

Barium Sulfate; Potassium Silicate; Thermal Control Coating; High Temperature Resistance; Solar Absorption Ratio.

1. Introduction

Spacecraft operating in the space environment mainly exchange heat with the external environment through the radiation of thermally controlled coatings. When the coating has a low absorption rate in the solar band and a high emissivity in the mid-infrared band region, it is able to achieve good radiation heat dissipation and maintain normal spacecraft operation. The paint-type thermal control coating consists of filler and binder, which can be sprayed on a large area and is inexpensive. The ambient temperature around the spacecraft will rise to 200-250 °C during deep space exploration[1]. This can lead to cracking of the coating due to thermal stresses and can also affect the surface thermal emission properties of the coating. Therefore, aerospace thermal control coatings not only need to maintain low absorption and high emissivity optical properties, but also need to be able to withstand high temperatures.

Potassium silicate (K_2SiO_3), with strong heat resistance, and hydrophilic powder can be good compatibility, excellent chemical stability, in the high temperature baking will not appear yellowing, but its brittle, high shrinkage, toughness is not enough, need to use curing agent for modification to enhance its spectral properties, high temperature resistance, water resistance[2]. Potassium silicate with an n of 2.4 modulus has less silicon oxide and more metal ions, higher bonding strength to the substrate, higher flexibility, and a lower viscosity of the binder, making it easier to spray and better film formation.

ZnO has a high absorption rate of UV light, which will cause decomposition and even yellowing, resulting in degradation of the optical properties of the coating. $BaSO_4$ is a metal oxide with a wide band gap and high whiteness, it has high mid-infrared emissivity and its reflectance in the 0.3-0.7 μm wavelength band can be as high as 0.98%[3]. The $BaSO_4$-acrylic coating prepared by Li et al. achieved a solar reflectance of 0.98 and an atmospheric window emissivity of 0.95, with high optical performance and reliability[4]. Mikhailov M M conducted electron irradiation experiments on various types of powders and found that the amount of degradation of the solar reflectance after irradiation was lower for $BaSO_4$ than for TiO_2 and ZnO[5].

In this paper, inorganic thermally controlled coatings with low solar absorption and high infrared emission are prepared by air spraying using potassium silicate and $BaSO_4$ powder as raw materials. The surface morphology and composition were studied, and performance tests such as solar reflectance, infrared emissivity, and high temperature resistance were carried out.

2. Experiment

2.1 Materials

Barium sulphate: analytically pure, Sinopharm Group Chemical Reagent Co., Ltd; Aqueous solution of potassium silicate, Unirex Refractories; Calcium hydrogen phosphate: anhydrous 98%, Shanghai Myriad Biochemical Science and Technology; Polyether-modified siloxanes: BYK349, Bickel, Germany; Deionised water: homemade.

2.2 Coating Preparation

The aluminium alloy substrate (5 cm×5 cm×2 mm) was first prepared, sandblasted and immersed in ethanol for ultrasonic cleaning, and then set aside. The filler $BaSO_4$, inorganic binder potassium silicate, deionised water, levelling agent and curing agent were weighed according to the formula proportion, and a vacuum homogeniser was used to remove air bubbles by vacuum, so as to obtain a moderately viscous and sprayable paste. Subsequently, the air spraying method was used to form a coating on the surface of aluminium alloy, and the coating was heated and dried to achieve surface drying after each spraying of a certain thickness, sprayed layer by layer to the required thickness, and finally the coating was dried at room temperature for 12~24 h, and cured at high temperature of 120 ℃ for 3 h to complete the preparation of the coating.

2.3 Sample Testing and Characterisation

The particle size of $BaSO_4$ filler was tested by laser particle sizer (Mastersizer 2000, Malvern), the thickness of the coating was tested by lacquer film thickness gauge, the solar absorption ratio of the coating was tested by UV-visible-NIR spectrophotometer (Carry500, Agilent technologies), the infrared emissivity, group analysis of the coating was tested by FTIR spectrometer (FTIRv80, Bruker) to test the infrared emissivity of the coating, group analysis; thermal analyser (STA 200, HITACHI) for thermogravimetric analysis; tube furnace (BTF-1200C, Beytec) to test the coating's high-temperature resistance; scanning electron microscope SEM (Sigma 300, ZEISS) to thermally control the surface of the coating topography analysis; the bonding grade of the inorganic coating was tested by scratching method.

3. Results and Discussion

3.1 Optical Properties of Coatings

3.1.1 Powder Particle Size Distribution

The laser particle size analyser was used to study the optimal particle size distribution to screen the particle size range of the powder with the optical performance advantages and disadvantages, and the results are shown in Table 1.

Table 1. Optical properties of $BaSO_4$ powders

Particle size range /µm	D(0.5) /µm	Solar absorption	Ultraviolet absorption	Infrared emissivity	Atmospheric window emissivity
0.3~11	6	0.03	0.08	0.93	0.95

When the particle size range is 0.3~11 µm, and the wide-scale particle size range contains the optimal particle size range of 0.3~0.5 µm for the white thermally-controlled coating[6].This band can effectively enhance the reflection of the solar band, resulting in a reduction of the absorption to 0.03 in the solar band from 0.25 to 2.5 µm, and $BaSO_4$ powder is suitable for use as a thermally controlled coating pigment due to its high infrared emissivity of 0.93 in the mid-infrared band from 2.5 to 25 µm.

3.1.2 Pigment/Binder Ratios

The ratio of pigment to binder is an important factor affecting the heat resistance, mechanical properties and spectral properties of coatings. Inorganic coatings with the same thickness but different aspect ratio were prepared on the surface of aluminum alloy substrate. For opaque coatings, solar reflectance =1- absorption rate, and the changes of optical properties with aspect ratio are shown in Figure 1.

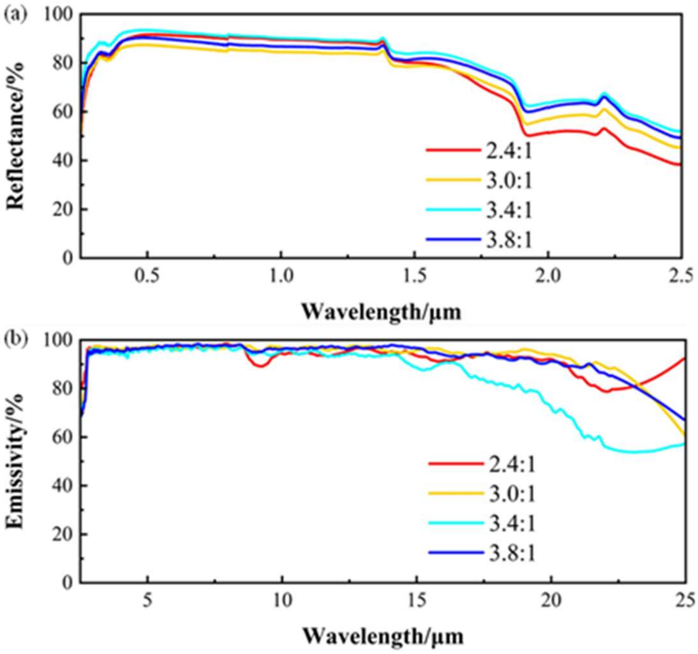

Figure 1. Comparison of optical properties of coatings with different pigment/binder ratios(a)solar reflectance(b)infrared emissivity

In the preparation process, when the pigment base is low, the powder density per unit volume of the coating is low, and the scattering of solar light is weakened, so it is difficult to obtain high solar reflectivity. When the binder ratio is high, the bonding effect of the coating is weakened, and cracking and pulverization occur, so a moderate PBR should be selected. Therefore, it is necessary to comprehensively consider the solar reflectivity and mechanical properties, so as to determine the appropriate pigment/binder ratio.

It can be seen from Figure 1(a) that the solar reflection curve of inorganic thermal control coating with 3.4:1 aspect ratio is higher than that of other aspect ratio curves. The solar reflectance in the full spectrum band (0.25~2.5 µm) is 0.9, and the reflectance in the ultraviolet band (0.25~0.38 µm) is

0.87. The solar reflection in visible light band is mainly dominated by barium sulfate powder. Potassium silicate has a great influence on the spectral properties of the coating in the near infrared band (1.5~2.5μm). The emissivity in infrared band (2.5~25 μm) and atmospheric window band of the coating with 3.4:1 aspect ratio is 0.95, and the overall spectral performance is excellent. In addition, different ratios of PBR have little effect on emissivity.

3.1.2 Curing Agent

Two curing agents, silicon tripolyphosphate and calcium hydrogen phosphate, were selected to modify potassium silicate. The purpose is to promote curing and improve water resistance, temperature resistance and spectral performance. The dosage of curing agent is 10% of the solid content of potassium silicate, and other conditions are the same. The effects of different curing agents on the spectral properties of the coating are shown in Table 2.

In the process of preparation, silicon tripolyphosphate will produce agglomerated powder clusters with the slurry, which will affect the appearance, and also cause its own solar reflectivity to be lower than that of the coating without curing agent. In the process of spraying, the inorganic coating cured by calcium hydrogen phosphate has a faster drying speed and a much shorter preparation time than the coating without curing agent. Calcium hydrogen phosphate is slightly soluble in water, and the H+ released by the curing agent in the solution is moderate, which promotes the dehydration and condensation reaction of potassium silicate and accelerates the hardening of potassium silicate solution. Whether curing agent is added or not has little effect on the infrared emissivity of the coating.

Table 2. Optical properties of coatings modified by potassium silicate with different curing agents

Particle size range /μm	/	Silicon tripolyphosphate	Calcium hydrogen phosphate
Solar absorption	0.85	0.84	0.88
Infrared emissivity	0.96	0.96	0.96

Therefore, calcium hydrogen phosphate curing agent was used for further study. The dosage of potassium silicate was 5%, 10% and 15% of the solid content of potassium silicate, and then the coating was prepared and the optical properties were tested. It was found that the effect was small.

At the same time, different curing methods were studied, such as room temperature curing for 24h, high temperature curing at 120℃ for 3h and high temperature curing at 200℃ for 3h. With the increase of temperature, the solar reflectivity further increases, while the infrared emissivity is not affected. Considering the spectral properties of the coating and the possibility of time-consuming and cracking of the coating caused by over-high temperature curing, the high temperature curing mode of the coating was determined to be 120℃ for 3 hours.

3.1.3 Thickness

Many pure high-temperature resistant coatings do not consider the solar reflectivity of the coating, and the thickness of the coating is generally 30 ~ 60 μm[7]. However, the thickness of most inorganic thermal control coatings is generally 120~180μm, which is too low to achieve high solar reflectivity. When the thickness is too high, the area density increases, the coating weight increases, and the cracking possibility increases during curing or high temperature testing. Therefore, the different thickness of inorganic coatings is 125~225 μm, and the coating thickness, area density, solar absorption ratio and infrared emissivity are shown in Table 3.

Generally speaking, with the increase of coating thickness, the solar absorption ratio gradually decreases, that is, the solar reflectivity gradually increases, and the appearance gradually changes from transparent to deeper white. The solar absorptance of the coating prepared in Table 3 increases first and then decreases with the increase of thickness, which may be because the overall hiding power is insufficient when the coating is thin, and the solar absorptance will be affected by the reflection of the metal substrate itself. When the coating reaches 200μm thick, the light transmitted to the substrate is almost zero, and the reflection enhancement effect of the substrate gradually disappears. At this time, the higher solar reflectivity mainly depends on the reflection performance of the coating itself.

It can be seen from figure 2(a) that the increase of the thickness of the inorganic coating has little effect on the improvement of solar reflectivity in visible light band. When the coating thickness reaches 200~225μm, a lower solar absorption ratio of 0.11 and a higher infrared emissivity of 0.97 can be obtained. It can be seen from Figure 2(b) that with the increase of coating thickness, the infrared emissivity increases gradually. Because potassium silicate and barium sulfate powder are both high emissivity materials, the infrared emissivity of the whole coating is high.

Table 3. Surface density and optical properties of coatings with different thicknesses

Sample	Coating thickness/μm	Surface density(g/m^2)	Solar absorption(α_S)	Emissivity(ε)
1$^\#$	125	232	0.11	0.96
2$^\#$	150	264	0.12	0.96
3$^\#$	175	284	0.13	0.96
4$^\#$	200	336	0.11	0.97
5$^\#$	225	368	0.11	0.97

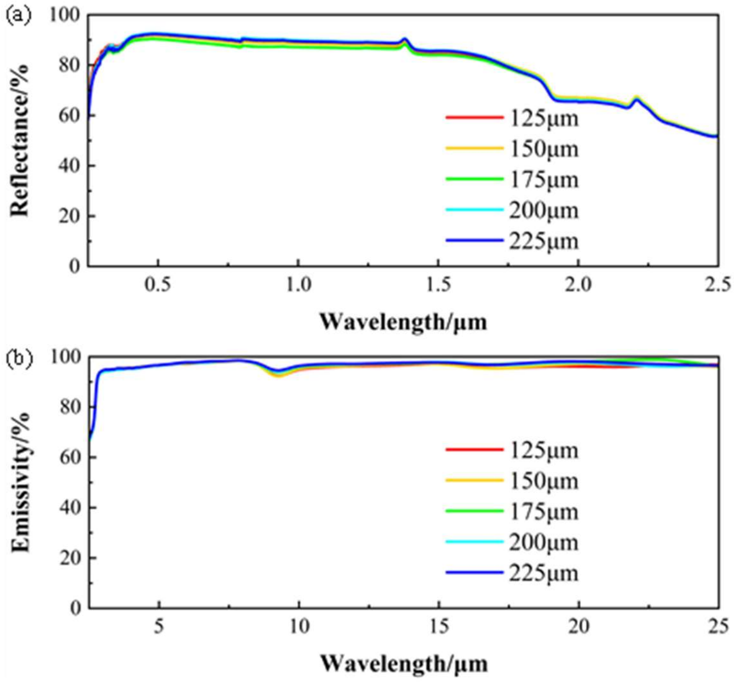

Figure 2. Comparison of optical properties of coatings with different thicknesses(a)solar reflectance(b)infrared emissivity

3.2 High Temperature Resistance of Coating

3.2.1 Actual High Temperature Resistance Test of Coating

Firstly, the coatings with the thickness of 175μm and above (modified with or without curing agent) were tested at 300°C, and all of them cracked. It may be because at high temperature, with the increase of coating thickness, the internal stress will accumulate layer by layer, which will be further aggravated at high temperature during heating and cooling, which will easily lead to coating cracking. In addition, the mismatch of thermal expansion coefficient between potassium silicate binder and aluminum alloy substrate in the coating may lead to stress surge, which will lead to coating cracking.

Because it is necessary to consider the thickness as high as possible to ensure the high solar reflectivity, the coating with a thickness of 150μm is selected for further high temperature resistance test.

The coating without curing agent and with two different curing agents (silicon tripolyphosphate and calcium hydrogen phosphate) was tested for temperature resistance at 300°C. Put the sample into a tube furnace, vacuum it, set the high temperature to 300°C and keep it for 24h, and then take it out to check its appearance, and then test the quality, solar reflectance and infrared emissivity of the sample again. The results are shown in Table 4 and Figure 3.

Table 4. Optical properties of coatings modified by potassium silicate with different curing agents

Curing agent	/		Silicon tripolyphosphate		calcium hydrogen phosphate	
High temperature test	Before	After	Before	After	Before	After
Quality retention rate	95.6%		100%		98.0%	
Solar absorption	0.85	0.87	0.84	0.84	0.88	0.88
Infrared emissivity	0.96	0.96	0.96	0.96	0.96	0.96

After 300°C high temperature, the three kinds of coatings with 150μm thickness can withstand high temperature well, with no change in appearance, no cracks and white surface. The cross-linking and polycondensation reaction of potassium silicate in the coating cured at 120°C is complete, and the coating is firmly combined with the substrate. After the high temperature test at 300°C for 24 hours, the surface of the coating is smooth and complete, and there is no macro crack.

The quality retention rate of the coating without curing modification is 95.6% at 300°C, which may be mainly caused by the thermal decomposition of siloxane leveling agent and potassium silicate binder and the evaporation of water in the coating. However, the quality retention rate of coatings with curing agent increased to some extent, probably because the curing agent promoted the dehydration and condensation reaction of potassium silicate to form a three-dimensional network of silicon-oxygen (Si-O-Si), which enhanced the degree of cross-linking, reduced the micro-cracks and pores inside the coating, and increased the thermal decomposition temperature of the coating, thus inhibiting the quality loss. However, the spectral properties of inorganic coatings with calcium hydrogen phosphate were high and stable before and after high temperature, and the infrared emissivity remained unchanged before and after high temperature. Therefore, calcium hydrogen phosphate was used to cure the modified potassium silicate coating.

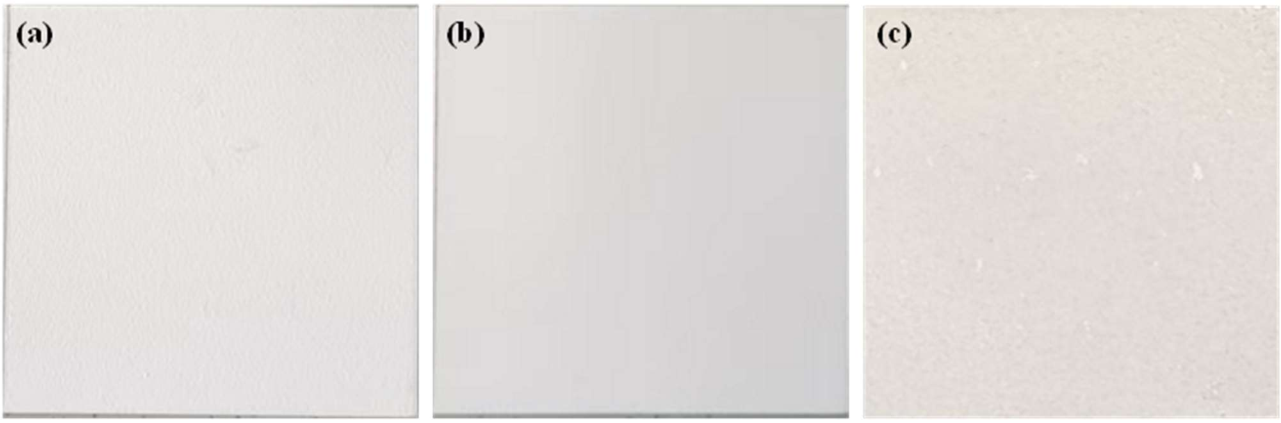

Figure 3. Appearance of potassium silicate coating modified by dicalcium phosphate (a) before high temperature test(b) after 300°C high temperature test and (c) after 400°C high temperature test

Then it was tested at a higher temperature of 400℃. The results showed that the surface of the coating was not cracked, but it was partially blackened. As shown in Figure 3(c), its spectral performance decreased: the solar reflectance decreased from 0.88 to 0.79, while the infrared emissivity remained unchanged. The analysis may be due to the incomplete oxidation of carbon residue generated by the decomposition of siloxane catalyzed by potassium silicate, thus forming carbon black, which led to the increase of solar absorption rate and the decrease of spectral performance of the coating.

3.2.2 Hermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to study the thermal stability of the coating. In nitrogen atmosphere, the temperature was gradually increased from 30℃ to 800℃ at a rate of 5℃ per minute. The thermogravimetric (TG) curve and differential curve (DTG) of the coating are shown in Figure 4.

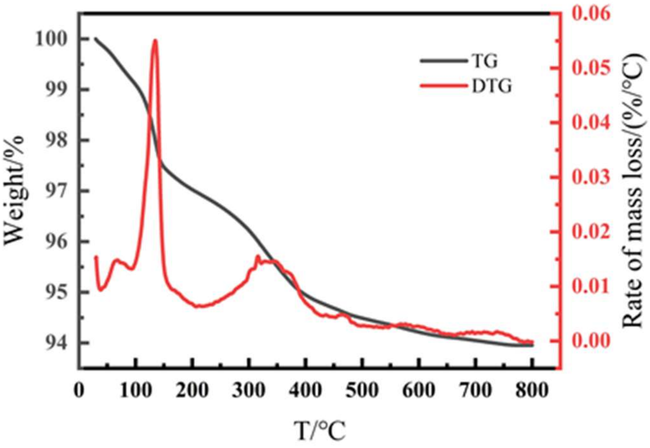

Figure 4. Thermogravimetric curve of the coating

After heating, the coating decomposes, and the temperature (Tmax) of the maximum decomposition rate is 135℃, at which time the DTG reaches the highest value of 0.055%/℃, which may correspond to the evaporation of physically adsorbed water and the decomposition of modification additives. The temperature of the next higher decomposition rate is 316℃, and the decomposition temperature (T5%) of the coating is 392℃ when the temperature is raised to 800℃.

3.2.3 Surface Morphology of Coating

Scanning electron microscope (SEM) was used to observe the surface morphology of potassium silicate coating modified by calcium hydrogen phosphate before and after high temperature of 300℃/24 h. As shown in figure 5.

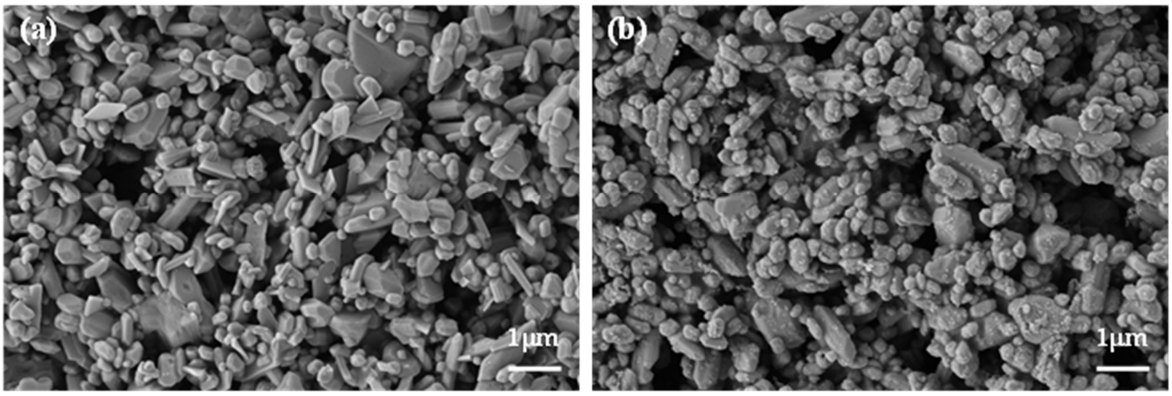

Figure 5. SEM photographs of the coating(a)before high-temperature test(b)after high-temperature test

It can be seen from Figure 5(a) that the coating cured at room temperature has a flat surface and a compact structure, in which hard $BaSO_4$ particles with different sizes are dispersed. These large particles are bonded with each other by inorganic binder potassium silicate particles with a particle size of 0.1~0.5μm, and are tightly wrapped and bonded by the surface hydroxyl. After high-temperature testing, the physical adsorption water and part of crystallization water are removed from the potassium silicate particles, and the volume shrinks slightly, which leads to stress-induced brittle fracture, resulting in more particle size distribution in 25.

3.2.4 FT-IR Analysis of Coating

The chemical structure changes and functional groups of the coating before and after baking at 300°C were analyzed by Fourier infrared spectrometer. The change curve of coating transmittance with wave number is shown in Figure 6.

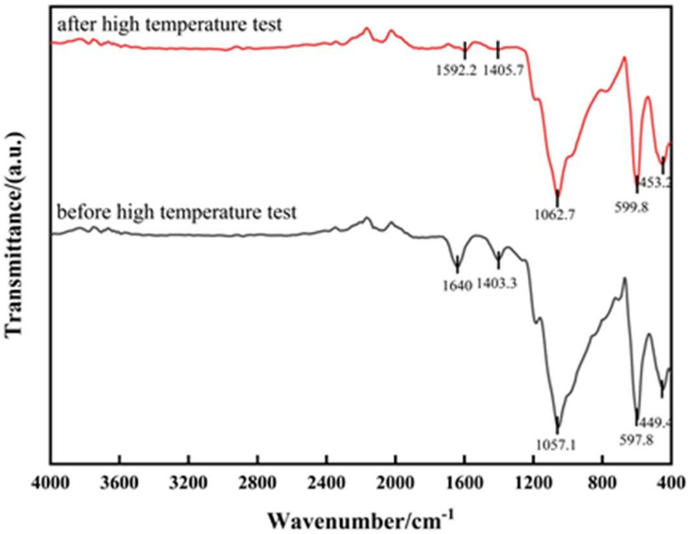

Figure 6. Fourier infrared spectrum of coating before and after high temperature test

In Figure 6, 1640cm^{-1} is related to the bending of H-O-H, suggesting that the free water in the micropores of the material evaporates after high temperature, and the absorption peak value obviously decreases. 1403.3 cm^{-1} is the symmetric stretching vibration of CO_3^{2-}, which may be caused by carbonation of potassium silicate. In addition, barium sulfate may be mixed with a little barium carbonate during the formation process, and 1057cm^{-1} is Si-of potassium silicate. S-O vibration covered with barium sulfate, 597.8 cm^{-1} is Si-O-Ba coupling vibration, which indicates that barium sulfate is chemically bonded to matrix potassium silicate, and 449.4 cm^{-1} is related to Si-O bending vibration.

To sum up, a coating with good comprehensive spectral properties and high temperature resistance at 300°C can be obtained by adding 10% potassium silicate curing agent to the coating and curing at 120°C for 3 hours, and the optimum ratio of pigment to substrate is 3.4, and the thickness is 150 μm. At this time, the ultraviolet (0.25~0.38μm) reflectivity of the coating is ≥87%, and the solar full spectrum (0.25 ~ 0.25 μm)

3.3 Basic Performance of Coating

The vacuum condensable volatility of the coating was tested according to QJ 1558B-2016. Through the mass changes before and after weighing the sample and the mass changes of the condensation collecting plate, it was calculated that the total mass loss TML was 0.821% less than 1% and the condensable volatile CVCM was 0.02% less than 0.1%, which met the quality requirements of the national standard.

The inorganic coating solidified by calcium hydrogen phosphate was selected for water resistance test. The inorganic coating was put into a beaker, immersed with proper amount of deionized water, and the water resistance of the coating was observed. After soaking in water for 10 days, the coating was taken out, and the surface moisture was absorbed by filter paper. After soaking in water, all the coatings have good appearance, and no swelling, peeling, discoloration or foaming occurred after soaking.

The volume resistivity of inorganic thermal control coating with a surface thickness of about 150μm on aluminum alloy substrate was measured by ST2643 ultra-high group micro-current tester, and the results were 2.02×10^4~2.3×10^4 Ω·m. The volume resistivity of inorganic thermal control coating meets the requirements of antistatic index less than 1×10^7 Ω·m, and it has good antistatic performance.

The hardness of the coating was tested by pencil, and the hardness of the inorganic coating after adding curing agent calcium hydrogen phosphate could reach 6 hours.

For the coating sprayed on the frosted aluminum alloy substrate, the adhesion test was carried out by the grid method: the adhesion level was grade 1, and it was not easy to fall off.

4. Summary

A new inorganic thermal control coating with high temperature resistance was developed to meet the requirements of spacecraft thermal control system. Potassium silicate binder was modified with curing agent calcium hydrogen phosphate. The method was simple and could effectively improve the spectral performance and high temperature resistance.

By air spraying, it can be quickly coated on the surface of metal substrate in a large area. After curing, the coating has good appearance, strong adhesion of Grade 1, hardness of 6H, and certain water resistance and antistatic performance. When the ratio of pigment/binder is 3.4:1 and the thickness is 150 μm, the surface density of the coating is 264 g/m^2. Under the light scattering caused by the intrinsic wide optical band gap and multi-scale particle size distribution of barium sulfate, the coating has low solar absorption ratio α_S=0.12 and high infrared emissivity ε=0.96, and meets the requirements of long-term temperature tolerance of 300°C without mass loss and optical performance degradation.

It can meet the application requirements of future spacecraft with high temperature resistance, high radiation heat dissipation, light weight and long service life. The prepared inorganic thermal control coating can be suitable for long-term space missions and has broad application prospects.

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