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Effect of the $MoSi_2$ coating on operational reliability of bipropellant rocket engine

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Abstract. This present study investigated the $MoSi_2$ coating and its effect on reliability of bipropellant rocket engine. This coating is developed to protect the chamber substrate material form oxidization under high-temperature oxidative circumstance as bipropellant engine works. The multilayer structure of the $MoSi_2$ coating shows excellent high-temperature and thermal-cycle resistance. Its characteristic of self-healing leads to the good performance under the long-time steady working condition for rocket engines. A 25000-seconds firing test was conducted to testify the performance of $MoSi_2$ coating under high temperature above 1400℃. In addition, the influence of coating surface morphology on liquid film cooling was fully discussed in experiment and simulation. High-speed microscopy camera was used to study the effects of Weber number on the spreading and lasting of cooling liquid-film. the simulative comparison was conducted by OpenFOAM to present different transfer-heat modes, when a droplet impinges on the high-temperature surface of $MoSi_2$ coating. All results show that higher smoothness of the coating is suitable for liquid-film cooling, strengthening liquid film spread and heat transfer. Moreover, scanning electron microscope (SEM) was used to study the effect of Mo layer residue on the coating thermal-cycle profermance. The test results indicates that Mo layer residue significantly cause penetrating cracks of the coating and then weaken the self-healing of the coating at downstream of throat. Therefore, it is important to strictly control the thickness of Mo layer by means of matching Mo target in ion plating. Thus after properly prolonging the infiltration time, Mo layer can be silicified completely without residue.

Keywords: Bipropellant rocket engine; $MoSi_2$ coating; Liquid film cooling; Mo Layer residue.

1 Introduction

The bipropellant propulsion system has been widely used in lots of satellites since the 1980s and has achieved great success in service. Meanwhile, the bipropellant engine plays the most important role in the bipropellant propulsion system, influencing the capability

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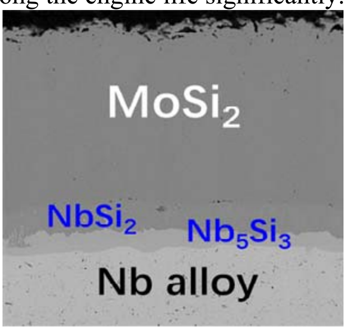
and reliability of spacecrafts. After atomization, mixing, and combustion, methylhydrazine (MMH) and nitrogen tetroxide (NTO) react by spontaneous combustion to form high-temperature gas to power the satellite. In combustion chamber, the gas temperature is usually up to 3000K [1]. So combustion chamber material and its coating are in the demanding requirement for reliable working at high temperature. The coating is needed to resist high-temperature flame eroding [2]. The allowable working temperature of chamber material and its oxidation-resistant is one of the most important factors that determines the specific impulse of engine. Through plasma-sprayed method and siliconizing annealing [3], $MoSi_2$ coating covering the surface of the Niobium-tungsten alloy can be very uniform and dense. The processing method and its structure are very different from traditional coating. This coating has obvious advantages in high-temperature and thermol-cycle resistance. However, the firing test results show that the thickness of Mo layer need to be strictly controlled, which strongly correlates the reliability of engine .

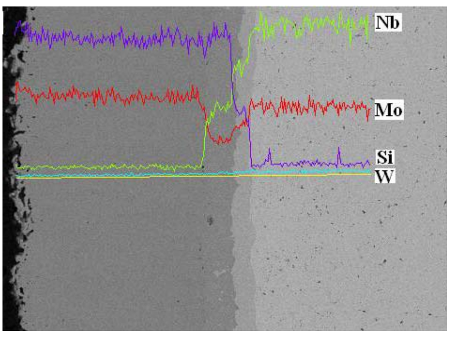
In this paper, the protection mechanism of $MoSi_2$ coating under the high-temperature oxidative circumstance and its influence on liquid cooling film were deeply studied. These aspects all determine the operational reliability of bipropellant rocket engine. Moreover, the failure analysis of the abnormal thickness of Mo layer residue was also investigated. The control method to eliminate Mo layer residue was proposed with the latest test results.

2 $MoSi_2$ coating structure

The substrate of combustion chamber is a high-melting niobium-tungsten alloy. The Mo coating is deposited on chamber surfaces in ion plating. After the siliconizing annealing process, dense and smooth $MoSi_2$ coating can be formed[4]. The structure of $MoSi_2$ coating can be divided into outer layer ($MoSi_2$), intermediate layer ($NbSi_2$) and transition layer (Nb_5Si_3) from the outside to the inside, as shown in Fig. 1. Generally, the coating thickness is approximately about 160μm. The outer layer of the coating is $MoSi_2$, with a thickness of about 110μm, which is an anti-oxidation layer to generate a protective self-healing SiO_2 film. The middle layer is $NbSi_2$ with a thickness of 25μm, which makes the outer layer and substrate more firmly bonded. This layer ameliorates the coating damage caused by thermal stress, and improves the thermal-cycle resistance. The third layer is Nb_5Si_3 with a thickness of only 16μm, which is the thinnest. But it is a transition layer that blocks the inward diffusion of O and Si elements and the outward diffusion of Ni elements. Thereby it can prolong the engine life significantly.



(a) Diffusion layer structure

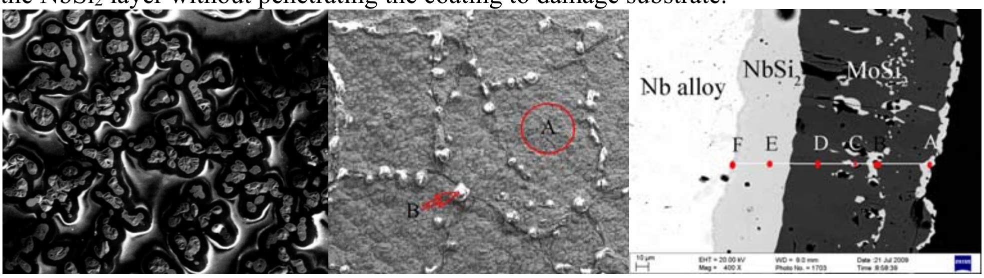


(b) Elements distribution in different layers

Fig. 1. The structure of the diffusion layer inside $MoSi_2$ coating.

The test data shows that the Niobium-tungsten alloy samples coverd with $MoSi_2$ coating can keep intact at 1800℃ for 20 hours, and at 1700℃ for 30 hours in the atmosphere. It is already obviously better than the traditional SiCrTiZr coating [5-7]. Furthermore, this coating can pass the 1000 thermal-cycle test from 1700°C to room temperature, and pass the 9-hour scouring test with high-speed airflow at 1600°C.

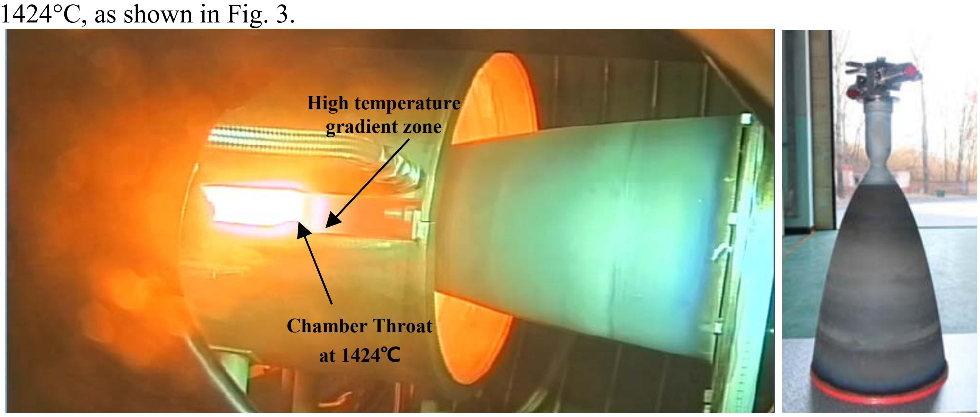
Through the microscopic observation of morphology, a SiO_2 layer of molten glass glaze can be formed on the coating surface after tests. This dense oxide layer can effectively block the diffusion of outside O elements. Especially in the thermal-cycle process, the oxides of Mo and Si diffuse into the coating along cracks on the coating, as shown in the white island-shaped area in Fig. 2(c). Two points A and B in Fig. 2 (b) are the coating surface and silicon enrichment area after thermal-cycle test. These cracks commonly end in the $NbSi_2$ layer without penetrating the coating to damage substrate.



(a) Glass glaze layer (b) morphology after thermal cycles (c) Section layered morphology

Fig. 2. The dense oxide film formed on the surface after test.

The above tests indicate that $MoSi_2$ coating has excellent high-temperature resistance with self-healing capability. It is suitable for orbit engines to work in the longtime mode. During the firing-test runs, the engine coated with $MoSi_2$ coating can pass the lifetime test of 25,000 seconds, and the measured maximum temperature of throat can reach about 1424°C, as shown in Fig. 3.



(a) Engine firing test with $MoSi_2$ coating (b) The coating after test

Fig. 3. Engine coated with $MoSi_2$ coating can reliably work over 1400°C.

3 $MoSi_2$ coating influence on engine

3.1 Influence on liquid-film cooling

When spray injection from engine injector impinges on combustion chamber wall, droplets can form liquid cooling film. $MoSi_2$ coating is not only proved with oxidation resistance at high temperature, but also has a certain influence on liquid-film cooling [8].
The surface of traditional silicide coating prepared by slurry-spray processing is very rough. Even though there are silicide protrusions formed in the siliconizing process, but more than

90% of $MoSi_2$ coating surface is very smooth. The roughness of SiCrTiZr coating was about 4.5μm and that of $MoSi_2$ coating was only 2μm.

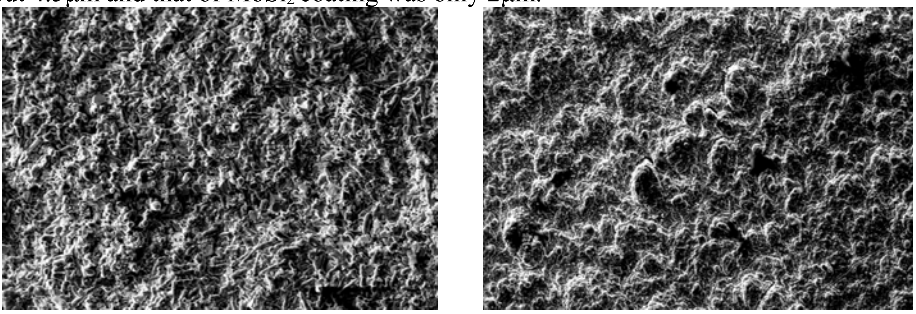
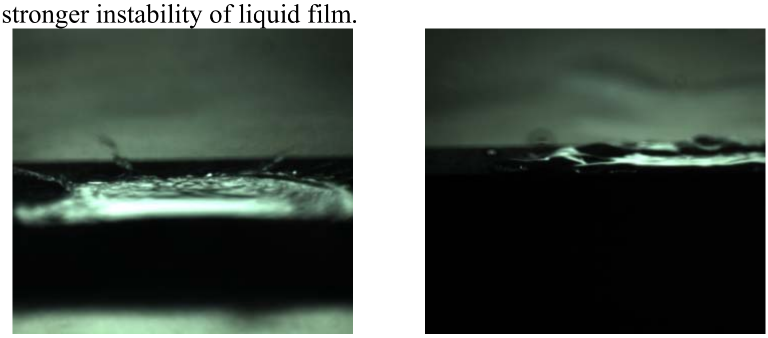


Fig. 4. The difference in surface morphology of SiCrTiZr coating (Left) and $MoSi_2$ coating (Right).

High-speed photography and microscopy were used to record the entire process of single droplet impingement on the coating wall. The droplet generator triggers small droplets with a certain incident We number, then impinging on the heated coating wall. According to the test results, the critical We number of the splash/spreading mechanism of SiCrTiZr coating is significantly lower than that of $MoSi_2$ coating. That means that droplets are more easily broken when impinging on $MoSi_2$ coating. The splash and breakup of droplets on heated wall is violent, because the liquid film is strongly disturbed under boiling condition. The surface tension of liquid decreases as temperature increases, which results in stronger instability of liquid film.



(a) Droplet splash on SiCrTiZr coating (b) Droplet spreading on $MoSi_2$ coating

Fig. 5. Comparison of droplets impacting the coating wall when the incident We is 700.

Fig. 6 shows the classification of the droplet/wall impinging mechanism based on the experimental results. The verticle axis is the We number of the droplet incident, the horizontal axis is the wall temperature T. T_B and T_L are the boiling temperature and the Leidenfrost temperature under wall conditions, respectively.

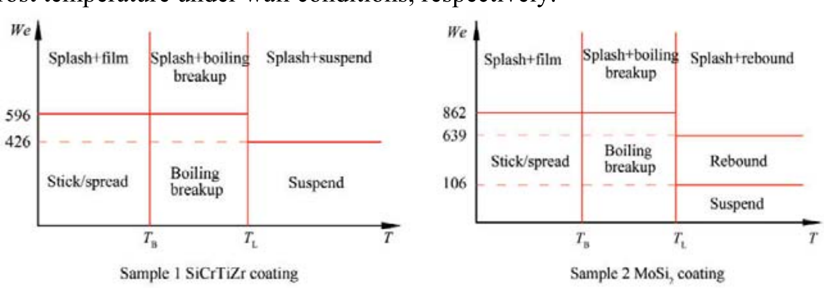


Fig. 6. The droplet impingement mechanism of SiCrTiZr coating (Left) and $MoSi_2$ coating (Right) [1].

It can be analyzed from Fig. 6 that when wall temperature is low, it is easier to form a liquid film after impingment. As the kinetic energy of the droplets increases, they can gradually splash with bouncing back in further combustion. The smoother $MoSi_2$ coating surface tends to keep the low-velocity droplets spreading on the wall as liquid cooling film, and bounce the high-velocity droplets to the central combustion zone. That makes the gas flame reacted in the central area and away from the wall of combustion chamber.

3.2 Influence on heat transfer

When wall temperature exceeds the Leidenfrost temperature, the heat transfer between the droplets and wall causes droplets evaporation. CFD simulation conducted by OpenFOAM can quantitatively analyze the influence of wall smoothness. The droplet evaporation is simulated by the VOF method of gas-liquid two-phase flow. The pure diffusion control model was used to study the evaporation process. This model assumes that the vapor-liquid interface is in a state of phase equilibrium, and the evaporation rate is calculated by Fick's diffusion law. Based on the N-S equation, the turbulent large eddy simulation (LES) is used to analyze the development of fluids, and the filtering function is used to filter the original N-S equation. Therefore, the LES governing equation is obtained by filtering the small-scale vortices. Two kinds of wall were set up in the simulation. The roughness of smooth surface and rough surface are 0μm and 4.8μm, respectively. And the incident velocity of a 1.5mm diameter droplet is 5m/s. The surface roughness of rough surface is constructed with an ideal groove.

When a droplet impinges on the smooth wall at high temperature, this droplet can get three stages: spreading, rolling, and coronal splashing. When the droplet is in contact with the smooth wall, the resistance of liquid spreading is small, and evaporation occurs. Eventually the liquid spreading terminates under aerodynamic interaction, and then evolves into a rolling and splashing.

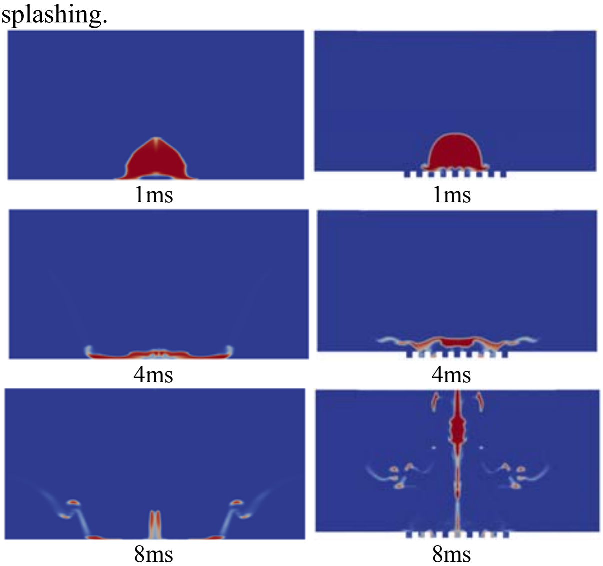


Fig. 7. Development comparison between impingement on a smooth wall (Left) and a rough wall (Right)

When a droplet impinges on a rough wall at high temperature, a violent "coronal splash + central jet" mode can be formed. Compared with the smooth surface, the rough wall cannot limit liquid spreading in the early stage of impinging process, but promotes droplet splashing. The reason is that a vapor layer is formed between droplet/wall interface, which weaken the influence of wall roughness on liuqid spreading. Meanwhile, the groove shape increases the area of heat transfer between liquid and high-temperature wall. It can improve the heat-flux density of droplets, strengthening the evaporation. Nevertheless, compared with the smooth wall, its capacity of heat transfer is significantly lower.

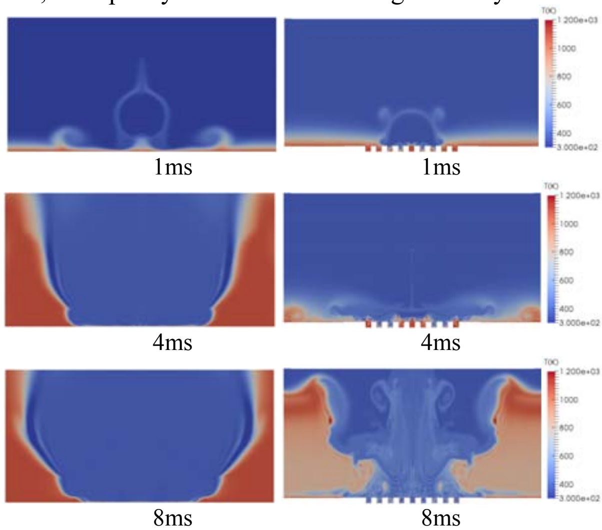


Fig. 8. Thermal comparison between impingment on a smooth wall (Left) and a rough wall (Right) [9].

3.3 The influence of the Mo layer residue

In the process of $MoSi_2$ coating preparation, the thickness and uniformity of Mo layer has an significant influence on the reliability of engine. Once the pure Mo layer unexpectedly remains inside the coating, the structure of coating diffusion layer will be abnormal, as shown in Fig. 9. The existence of Mo layer residue not only weakens the bond strength between coating and substrate, but also has a negative effect on the thermal matching of coating structure. The thermal expansion coefficient of niobium-tungsten alloy is 7.7×10^{-6} K^{-1} [10], $MoSi_2$ is 7.8×10^{-6} K^{-1} [11], and the diffusion layer Nb_5Si_3 is 6.1×10^{-6} K^{-1} [12]. However, the thermal expansion coefficient of Mo layer is only 4.9×10^{-6} K^{-1} [13], which is greatly different from other layers, resulting in the thermal mismatch. It is very risky to produce penetrating cracks as engine works.

As for cracks, $MoSi_2$ coating has a certain self-healing ability to block these cracks, and SiO_2 glassy protective film can be formed on its surface in the high-temperature and oxidative circumstance. The glassy protective film of SiO_2 is dense with fluidity. The fluidity of this SiO_2 film can fill micro-cracks and holes, effectively blocking the O diffusion into the Nb substrate. However, the self-healing of $MoSi_2$ coating will decrease under certain conditions. As shown in Fig. 10, cracks are concentrated downstream of the throat for two reasons. Firstly, as shown in Fig. 3, the temperature gradient there is the largest, which fully enhance the tremendous thermal stress with Mo layer residue. So a number of penetrating cracks are generated, and cannot be healed by SiO_2 film. (2) $MoSi_2$ coating cannot form pure dense film of SiO_2 under high-temperature and low-pressure condition. The temperature and pressure at the downstream throat exactly match this characteristic. So even if SiO_2 film is formed on the coating surface, it will be blown away quickly in the gas scouring. The XRD (X-ray diffraction) scan confirmed that the SiO_2 spectrum reaction at downstream throat was far less than that at upstream location.

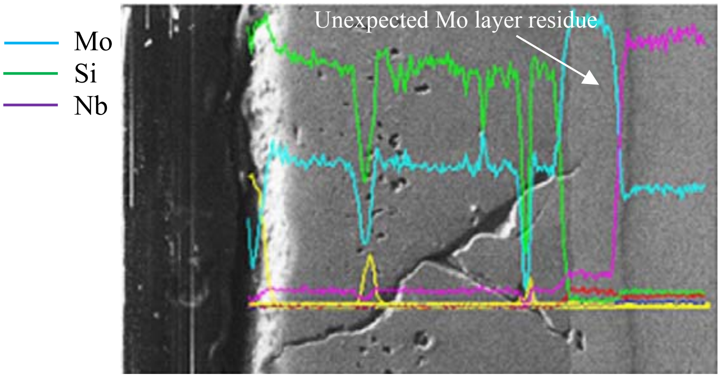


Fig. 9. Mo layer residue affects the structure of coating, leading to the unhealed penetrating crack.

Therefore, $MoSi_2$ coating must completely eliminate the residue of Mo layer, to ensure that Mo layer can be completely converted into $MoSi_2$ through the following siliconizing process. Firstly, the thickness of the molybdenum layer needs to be strictly controlled, and the uniformity could be improved by ensuring the purity and dimensional accuracy of the Mo target in the arc deposit processing. Secondly, the thickness of Mo layer is tested by means of measuring and weighing. It is also necessary to adjust the siliconizing time to match Mo layer thickness, and then calculate the Si-Mo atomic ratio. When the Si-Mo atomic ratio is greater than 2.3, Mo layer could be silicified into $MoSi_2$ coating completely. Through a large number of tests, quantitative preparation has been summarized. For this purpose, researchers prepared a number of coating test pieces to verify this method.

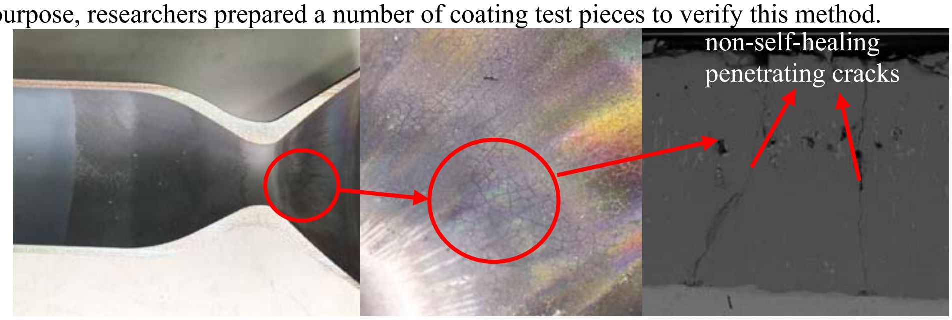


Fig. 10. A big number of non-self-healing penetrating cracks were formed in the large temperature gradient region at downstream of the throat.

The thickness of the Mo layer at chamber throat is required to be 40μm -55μm, and many test pieces in large range were prepared as shown in Table 1. The data from line No. 1-3 are the results with different thicknesses in static high-temperature test at 1800℃. After siliconizing annealing process, the thickness of the $MoSi_2$ coating are 2.6-3.2 times of the thickness of Mo layer (completely silicified). Through 30h at 1800℃, all of the $MoSi_2$ coating with different thicknesses can be still well with the glass glaze surface, as shown in Fig. 11.

Fig. 11. Static high-temperature test sample after 30h at 1800℃.

Table 1. The performance of different thickness of the molybdenum layer samples.

No.	**Thickness of Mo layer (μm)**	**Thickness of $MoSi_2$ coating (μm)**	**1800℃≥10h or 1700℃≥1000 times**
1	24	77	> 30h
2	61	180	> 30h
3	97	254	> 30h
4	23	74	> 1050 times
5	62	182	> 1050 times
6	93	243	> 1050 times

The data from line No. 4-6 in Table 1 are the results for thermal-cycle test ranging from 1700℃ to room temperature. The thickness of Mo layer ranges from 23μm -93μm. After siliconizing annealing process, the thickness of the coating are 2.6-3.2 times of Mo layer thickness too. After thermal-cycle tests of 1050 times, some cracks were generated but the surface was covered with SiO_2 glass glaze, and the test piece substrate was fully protected as shown in Fig. 12.

Fig. 12. Thermal-cycle test sample after 1050 times ranging from 1700℃ to room temperature.

According to the samples observation in Fig. 11 and Fig. 12 , it can be concluded that no matter how thick or thin the coating is, as long as the Mo layer can be completely silicified, the coating sample could remain intact in the high-temperature and thermal-cycle tests.

4 Conclusion

In this paper, the effects of $MoSi_2$ coating on the reliability of bipropellant rocket engine was studied with following conclusions:

(1) $MoSi_2$ coating is prepared with composite gradient layers, showing its outstanding resistance against high temperature and thermal cycle with good self-healing ability.

(2) The coating effects on liquid film formation and its heat transfer efficiency are investigated experimentally and simulatively. The surface of $MoSi_2$ coating is relatively smooth, and it is easier to form liquid cooling film. The vapor layer formed between $MoSi_2$ coating surface and propellant has a stronger heat transfer effect, which can strengthen the liquid-film cooling.

(3) Any Mo layer residue in the preparation process of $MoSi_2$ coating is not acceptable. Thermal cracks at downstream throat unexpectedly causes the engine failure with strong possibility. Therefore, it is necessary to strictly control the thickness of Mo layer and match silicification time to completely eliminate Mo layer residue.

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