Study of Thermal Shock Resistance of Plasma Sprayed VW75 Alloy

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Abstract. The thermal shock resistance of T5-state VW75 Mg alloy after the plasma spraying was tested, the service process of material under the real environment was simulated, the reasons and mechanism for the coating shedding were revealed, and the comprehensive thermal shock resistance of alloy was acquired. The results showed that before the thermal shock test, the sample surface was flat with the gray color, and after the test was started, the coating surface was turned into white ZrO₂ again. As the number of thermal cycles was increased, the black brown color started appearing on the sample surface, and the coating presented the overall shedding after the 158 cycles. The microcracks and pores in the ceramic layer and bonding layer were not developed into macrocracks yet, it could be deemed that the internal bonding at each layer was rather compact, and the coating quality was very high. The failure of thermal barrier coating occurred between the Mg alloy matrix and bonding layer, the thermal expansion coefficient varied from layer to layer of the coating, thus aggravating the interlayer thermal stress and leading to the overall shedding of coating, and in addition, the thickening of thermally grown oxidation layer was also an important cause for the shedding.

1. Introduction
With the ever-increasing lightweight requirements for the aerospace[1] and weaponry[2], the research and development of high-quality and low-density materials have gradually aroused high attention. As the lightest structural metallic material, Mg alloy has been increasingly applied in high-end weaponry year by year. The high-temperature resistance and mechanical properties of Mg alloy can be considerably improved by adding rare earth elements in it[3]. At present, the pure rare earth Mg alloy systems include Mg-Gd system⁴, Mg-Y system⁵ and Mg-Nd⁶ system, with the strength generally reaching as high as above 400 MPa, being typical representatives of new-type ultrahigh-strength Mg alloy. In order to improve the heat resistance and corrosion resistance of Mg alloy, the surface treatment is usually conducted, and the present main surface treatment is micro-arc oxidation treatment⁷. Plasma spraying thermal barrier coating is a heat-resisting method of Mg alloy surface, which has been applied to aerospace and weaponry in recent years⁸, it can improve the high-temperature resistance of alloy, but
its subsequent practical application has been restricted by the frequent coating shedding phenomenon in the thermal shock test. Thermal shock test, which is a destructive test aiming to simulate the material service performance under the real environment, is used to effectively characterize the bonding performance between thermal barrier coating and matrix. Huang [9] conducted a thermal shock test by high-temperature cladding of \( \text{La}_2\text{Zr}_2\text{O}_7 \) thermal barrier coating on nickel-based matrix at the temperature of 25-1000°C, and the results showed that the thermal shock life of initial cracks was obviously lengthened, with outstanding thermal shock resistance. Feng [10] stated that the failure of thermal barrier coating was attributed to the mechanical properties of ceramic layer and the thermal stress generated by thermal mismatch. Therefore, the failure process and mechanical of thermal barrier coating under the sharp temperature changes remain to be further explored. VW75 Mg alloy is a high-strength heat-resisting Mg alloy developed in recent years, it can realize short-time service below 300°C, plasma sprayed \( \text{Y}_2\text{O}_3 \) partial stable \( \text{ZrO}_2 \) powder (YSZ) thermal barrier coating is added to its surface in order to further improve its heat resistance, but the studies regarding its thermal shock resistance have not been reported, yet. Given this, T5-state VW75 alloy was taken as the parent material in this study, suitable process parameters were used according to the existing studies [11], and the plasma spraying treatment was conducted on the surface of the parent material, in an effort to systematically study its thermal shock resistance under the cyclic thermal loads, analyze the failure mechanism of the coating, and provide effective test data for further expanding the range of application of this alloy material.

2. Experimental method

2.1. Coating material

The parent material selected in this study was VW75 Mg alloy, the components of which are listed in Table 1. The plasma spraying treatment was done after the aging treatment at 220°C for 6.5 h. The spraying materials included bonding layer material and surface course material. The NiCrAlY powders (d(0.5) = 78.5 μm) were used at the bonding layer, and the components are seen in Table 2. The YSZ powders (d(0.5) = 53.0 μm) were used at the surface course, with the components as seen in Table 3.

| Table 1. Chemical Components of VW75 Alloy (Mass Fraction, wt.%) |
|------------------|-----|-----|-----|-----|-----|
| Element | Gd  | Y   | Nd  | Zr  | Mg  |
| Content | 6.85 | 4.52 | 1.15 | 0.55 | Bal. |

| Table 2. Chemical Components of Alloy Powder (Mass Fraction, wt.%) |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Element | Ni  | Cr  | Al  | Y   | Co  | Fe  | Si  |
| NiCrAlY | Bal. | 24.51 | 8.11 | 0.42 | <0.5 | <0.25 | <0.2 |

| Table 3. Chemical Components of YSZ Powder (Mass Fraction, wt.%) |
|------------------|-----|-----|-----|-----|-----|-----|
| Component | ZrO2 | Y2O3 | HfO2 | FeO3 | SiO2 | SiO2 |
| YSZ | Bal. | 7.34 | 1.53 | <0.01 | <0.01 | <0.01 |
|            | Al2O3 |       |       |       |       |       |

2.2. Coating preparation

The sample was put into acetone for the ultrasonic concussion in order to eliminate the greasy dirt on the surface, the compressive stress was applied to its surface, and the sand blasting pretreatment was conducted on the sample surface using the AMS9080P sand blasting machine under atmospheric pressure of 0.5 MPa, sand blasting distance of 50-70 mm and sand blasting angle of 60-80°. Afterwards, the grits or dusts adhered to the coarsening surface were blown away using the dried compressed air to keep the surface clean. The plasma spraying should be carried out within 3 h after the sand blasting pretreatment. The spraying equipment was 7700 plasma spraying system produced by U.S Praxair Corporation, the manipulator system produced by Swiss ABB Corporation was selected as the spray gun, and the coating was prepared on the surface of VW75 Mg alloy sample. The spraying current,
Spraying distance, main air flow, auxiliary air flow, spraying speed and powder feeding rate were 875 A, 85 mm, 75SCFH, 45SCFH, 400 mm/s and 30 g/min, respectively.

2.3. Thermal shock test
The dried sample was placed into a 400℃ RJX-4-13 thermostatic drying oven, 5 minutes were counted after the temperature was stabilized, and then the sample was taken out and cooled with cold air to room temperature, and then one cycle was completed. The cyclic test was continued until the complete failure of the coating.

2.4. Microstructures observation
The coating morphologies were observed under an FEI Quanta 200F thermal field emission scanning electron microscope at working voltage of 200 KV.

3. Results and Analysis
The microstructure graph of plasma sprayed VW75 Mg alloy is shown in Figure 1. It could be observed from Figure 1(a) that the ceramic layer and bonding layer of the plasma sprayed sample were about 0.5 mm and 0.15 mm in thickness, respectively, with a flat surface and no bubbles or defects. As seen in Figure 1(b), the second phase could be divided into two types from its morphology: large white circular phase and white square phase. According to the early-stage study [12], the typical second phases were elemental Zr phase and rare earth phase rich in Gd and Y retained in the homogenization process.

Figure 2 shows the surface macro-morphologies of the coating sample after different thermal shock cycles in the test. By comparing the pictures, it could be seen that the sample surface was flat with gray color before the thermal shock test, mainly because the oxygen vacancies were formed after the deoxygenation of ZrO₂ in the high-temperature spraying process, generating a defective color center, which was ash black. After the thermal shock test was started, the coating surface was turned into white ZrO₂ again. As the number of thermal cycles was increased, the black brown color started appearing on the sample surface, and in the end, the coating sample experienced the overall shedding after the 158 thermal cycles, without any obvious macrocrack on the surface, manifesting its outstanding thermal shock resistance.
Figure 2. Surface Macro-morphologies of Plasma Sprayed Coating after Different Thermal Shock Cycles: (a) 0 cycle; (b) 1 cycle; (c) 25 cycles; (d) 50 cycles; (e) 100 cycles; (f) 158 cycles

In order to study the coating shedding position and failure mechanism of VW75 Mg alloy thermal barrier coating in the thermal shock test, the upper surface of matrix after the coating shedding and the ceramic layer and bonding layer of the shed coating were scanned via SEM and observed and analyzed via EDS, as shown in Figure 3.

![Figure 3. SEM Graph and Analysis of Upper Surface of Matrix](image)

From the EDS graph of upper surface of matrix, it could be found that the upper surface was mainly composed of two elements—Mg and O, accompanied by a small quantity of Ni, Al, Cr, Gd, Y, Nd and Zr, etc. The element distribution on the upper surface of matrix is shown in Figure 4. It could be observed that the elements like Mg, O, Gd, Y, Nd and Zr were dispersedly distributed on the matrix, while Ni, Al...
and Cr were aggregated on the surface, indicating that the bonding layer of coating and matrix were almost completely shed, and a small part of metals at the bonding layer were adhered onto the matrix.

From the matrix surface morphology, there were no obvious cracks on the matrix surface, but many corrosion holes existed, and the EDS analysis indicated that the atomic ratio of Mg and O was slightly greater than 2:1, so it could be preliminarily judged that the VW75 Mg alloy matrix was seriously oxidized, which might be ascribed to the large gaps between the matrix and bonding layer during the plasma spraying process. Oxygen directly contacted the matrix metal by traversing the bonding layer, while Mg alloy was of strong chemical activity and continuously experienced the thermal oxidation under the high-temperature environment in the thermal cyclic test. The difference between the layers in the thermal expansion coefficient aggravates the interlayer thermal stress, the gaps between matrix and bonding layer became larger and larger, so the bonding strength of the coating was lower and lower, and in the end, the overall shedding took place.

Figure 4. Element Surface Scanning Distribution Graph on the Matrix Surface
(a) Superposed graph of element distribution; (b) Mg; (c) O; (d) Al; (e) Y; (f) Gd; (g) Cr; (h) Zr; (i) Ni; (j) Nd
The micromorphology of sample bonding layer is shown in Figure 5. It could be seen that many gullies and pores existed on the bonding layer. This is because the oxygen diffused from the ceramic layer experiences the oxidation reaction with the metallic elements (mainly Al) in the bonding layer, and a thermally grown oxide (TGO) layer is formed between the ceramic layer and bonding layer. As the number of thermal cycles was increased, the TGO layer was continuously thickened, the metallic oxide (Al₂O₃) also started diffusing, pores started appearing in the bonding layer, and meanwhile, with the enormous consumption of Al, Ni-containing brittle intermetallic compounds would be generated, and moreover, the thermal stress was continuously increased, and the pores and cracks started propagating around. Meanwhile, Al₂O₃ might experience the phase transition in the high-temperature environment, the phase volume was changed, and some pores were formed in the bonding layer. The generation, propagation, deflection and fracture of these pores and cracks would accelerate the coating failure. The surface micromorphology of the ceramic layer of the sample is shown in Figure 5.

Figure 5. Micromorphology of Bonding Layer
(a) Scale drawing; (b) enlarged drawing

The surface micromorphology of ceramic layer of this sample is shown in Figure 6. It could be observed that densely interlaced microcracks and pores existed on the surface of ceramic layer. As the thermal shock test was carried out only at 400°C, not reaching the phase transition temperature (ZrO₂) of ZrO₂, the microcrack generation might be attributed to the damaged integrity of coating due to TGO, the cracks were propagated to the surface of the ceramic layer, and the surface microcracks accelerated the metal oxidation at the bonding layer, so the TGO layer was thicker, a vicious circle was formed, and consequently, the thermal shock resistance of this coating was degraded greatly.

Figure 6. Micromorphology of Ceramic Layer
(a) Scale drawing; (b) enlarged drawing

4. Conclusions
The service status of plasma sprayed VW75 Mg alloy in the cyclic thermal loads was systematically studied, and the thermal shock-induced alloy failure mechanism was explored by analyzing the surface state after the thermal failure. The conclusions drawn were as follows:
(1) The plasma sprayed YSZ coating was of flat surface without obvious bubbles or defects, and the processing technology was excellent.

(2) In the thermal shock test, the plasma sprayed coating went through the overall shedding after the 158 thermal cycles. The microcracks and pores in the ceramic layer and bonding layer were not developed into macrocracks, yet, so it could be thought that the internal bonding at each layer was quite compact and the coating quality was very high.

(3) The failure of thermal barrier coating took place between the Mg alloy matrix and bonding layer. The difference between coating layers in the thermal expansion coefficient aggravated the interlayer thermal stress and led to the overall coating shedding, and in addition, the thickening of TGO layer was also an important cause for the shedding phenomenon.

Acknowledgments
This research was funded by [Achievements Transformation in Jiangsu Province] grant number [BA2017044].

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