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Mechanical Properties and Thermal Shock Resistance of Rhenium Coating in Iridium/Rhenium/Carbon-Carbon Composites

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Abstract

Rhenium is a promising coating material for liquid rocket nozzles because of its extremely superior performance, such as high melting point, high temperature strength and excellent fatigue properties. In this work, Re coating was prepared on fabric-based pierced Carbon/Carbon composite substrate using chemical vapor deposition. Bonding strength, micro hardness and thermal shock resistance of rhenium coating on Carbon/Carbon substrate were investigated respectively. The bonding strength between the coating and the substrate was tested using different methods including tensile tests, shearing tests and micro scratch tests. Thermal shock resistance was investigated by an induction furnace from 2000°C to the room temperature. The morphologies and characteristics of the coatings were studied by scanning electron microscopy. The results indicated that the highest average value of tensile fracture strength is 20.4 MPa and shearing fracture strength is 21 MPa on Carbon/Carbon composite substrate. The rhenium coating broke up and flaked off near a crack in the scratch test. Micro hardness test suggested that C atoms diffused quickly into the rhenium coating within an hour. The thermal shock lives depended on the number of thermal shock cycles. It is also concluded that rhenium coating had good thermal shock resistant with Carbon/Carbon Composite substrate.

Keywords: Rhenium coating; Carbon/Carbon composites; Mechanical Properties; Thermal Shock Resistance;

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1. Introduction

Carbon/Carbon (C/C) composites have outstanding mechanical properties at high temperature, such as high specific strength and modulus, high creep resistance and retention of mechanical properties at temperatures above 2000°C [1-3]. In this case, they are considered as one of the most promising materials for high temperature applications in aviation and space flights. However, C/C composites are prone to be oxidized above 500°C, which limits their applications as high-temperature structural material [4].

Applying anti-oxidation coatings is considered as an effective method to prevent C/C composites from oxidation at high temperatures [5]. Iridium (Ir) has a high melting point (2440°C), excellent high-temperature oxidation and corrosion resistance due to the low oxygen permeability ($10^{-14} \text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$) and excellent chemical stability, which makes it candidate material as an anti-oxidation and thermal shock resistance coating above 1800°C [6]. Rhenium (Re) is the only refractory metal that does not form carbides, which has good combination with the C/C composites and high temperature mechanical properties [7]. Its excellent ductility can effectively release the thermal stress in the thermal shock process. Therefore, Re is an ideal transition layer used to improve the combination of Ir coating and the C/C composite.

Re transition layer have an important impact on the properties of the Iridium/Rhenium/Carbon-Carbon(Ir/Re/C-C) composites, including the mechanical properties and thermal shock resistance. Therefore, it is of great significance to study mechanical properties and thermal shock resistance of Re transition layer.

2. Experiment procedure

2.1. Preparation of the Re coating

The apparatus for chemical vapor deposition (CVD) of Re coating is shown in Fig.1. A quartz tube was fabricated as the reaction chamber, where both the chlorination of rhenium powder and CVD of Re coating took place. Rhenium powder (99.999%, Zhu Zhou Kete Industries Co., Ltd) was placed in a quartz cup and heated up to 730°C using a vertical furnace. The substrate materials were fixed on the substrate holder and heated using a high-frequency induction furnace. The temperature of the substrate materials measured using an infrared thermometer (Raytek MR1SBSF) was controlled to 1150°C. The flow rates of chlorine (99.999%) as reagent and argon (99.999%) as carrier gas determined by mass flow meter were 90 ml/min and 500 ml/min, respectively.

![Fig. 1. Schematic drawing of the CVD apparatus [8].](image-url)
2.2. Bonding strength test

The bonding strength test was measured by three methods, tensile test, shear tests and micro scratch test.

The tensile test is reference to the ASTMC633 and shear test refers to GB/T13222-91. The specimen was bonded on the stainless steel matching parts with TG205 two-component epoxy adhesive (Tiangong Material Co. Ltd.). After being positioned for 5-10 min and solidified for 24 h at room temperature, specimens were measured by a universal test machine (CTM9100). During tensile testing, the largest force of each specimen was recorded. For each group, five specimens were measured.

The micro scratch test is reference to the JB-T 8554-1997. The micro scratch test of Re coatings was conducted using a micro scratch tester (CSM Ltd., Switzerland) with a diamond stylus (120° one with a 200 μm diameter tip) under a continuously increasing load. The loading rate was 30 N/min and the scratch rate was 10 mm/min. The test was terminated at the maximum load of 30 N.

Substrates with dimensions of Φ20 mm x 4 mm were cut from a bulk of fabric-base pierced C/C composites with density of 1.80 g/cm³. Preforms used in this study were carbon fibers fabric. C/C composites were prepared by thermal gradient chemical vapor infiltration detailed in [9]. After being polished with 100, 300 and 500 grit SiC paper, the specimens were ultrasonically cleaned with acetone and dried at about 100 °C for 1 h. Define the direction vertical to the Z fiber as XY direction, parallel to the Z fiber as XZ direction.

2.3. Micro hardness test

The micro hardness test is based on Vickers micro hardness. Vickers micro hardness (Hv) of Re coating was determined by measuring the lengths of the diagonals of each indent at a magnification of 50× using an optical microscope system within the micro hardness tester. Micro hardness was evaluated by micro hardness tests (HXD-1000TC). After calibrating the system using a standard block, micro hardness tests were performed with applied load of 50 g.

2.4. Thermal shock resistance test

Thermal shock resistance tests were performed on the Ir/Re/C-C composite samples and Re/C-C composite samples. The specimens were heated to 2000 °C in a high frequency induction furnace, kept for 5 mins and then cooled to 800 °C in the air and vacuum atmosphere (10⁻⁶Pa) respectively. The temperature is measured by an infrared thermometer. The above steps were repeated. Tests stopped until the sample surface smoked, which indicated carbon and rhenium oxidation. Then record the number of thermal shock cycles and the cracks morphology on surface. It is the basis for evaluation of thermal shock resistance of rhenium transition layer. The cross-section and surface morphology of specimens were investigated by scanning electron microscopy (GSM-6360LV).

3. Results and discussion

3.1. Bonding strength test

The bonding strength of the experimental results divided into the followings: If the rupture is at the substrate, it means that the tensile strength between the coating and the substrate is higher than the rupture strength; if the rupture is at the coating – substrate interface, it means that the bonding strength is just the rupture strength.

Results of the tests are listed in Table 2. Tensile rupture strength on XY direction of C/C substrate is only 2.9 MPa, and the shear fracture strength is 11.43 Mpa, which are both lower than those of the XZ direction C/C substrate. The sample morphologies before and after the test are shown in Figure.2. The rupture is at the two kinds of C/C substrate. It is mainly because XY direction C/C substrate’s layer strength is controlled by the carbon cloth, which leads to the low surface tensile and shear strength. But the XZ direction C/C substrate’s layer strength is almost controlled by pierced fibers. It can be obtained that the tensile strength between CVD Re coating and fabric-base pierced C/C composites are larger than 21.94 Mpa, and the shear strength are larger than 24.31 MPa.
Table 1. Results of the bonding strength test.

| Substrate                  | Tensile rupture strength (MPa) | Shear rupture strength (MPa) |
|----------------------------|--------------------------------|------------------------------|
| XY direction C/C substrate | 2.94                           | 11.43                        |
| XZ direction C/C substrate | 21.92                          | 24.31                        |

Fig. 2. (a)-(d): XY direction, (a) XY direction C/C substrate, (b) As-deposited coating, (c) Sample after tensile test, (d) Sample after shear test; (e)-(f): XZ direction, (e) XZ direction C/C substrate, (f) As-deposited coating, (g) Sample after tensile test; (h) Sample after shear test.

Fig. 3 and Fig. 4 show the friction-load curve of the Re coating specimen for the scratch test and a SEM microscope image of the scratch trace respectively. The scratch track shows furrow-looking shape. The Re coating is not scraped off by diamond indenter until a load of 5 N is reached. There are fracture and chipping inside the scratch track, which may be attributed to the strong shear-resistant of the surface of C/C substrate. Also, the coating materials were squashed along the track. These phenomena suggests the excellent adhesion of the Re coating to the C/C substrate.

Fig. 3. Friction-load curve of the scratch test.
3.2. Micro hardness test

Fig. 4. SEM microscope of the scratch trace on Re coating

Fig. 5. SEM microscope of the scratch trace on Re coating

Fig. 6. Result of micro hardness test
The cross section morphologies of Re coating before and after the annealing are shown in Figure 5. It is found that the hardness of the as-deposited Re coating is location dependent. Results of Re coating annealed at 1600°C for prolonged hours at micro hardness test are shown in Fig. 6. The coating near the coating top surface was harder than the coating adjacent to the C/C substrate. After annealing at 1600°C for 1 h, the hardness in the two areas of the coating became the same, and remained unchanged with prolonged annealing. This indicates that C atoms diffuse quickly into the Re coating within an hour, reaching to the saturation and maximum hardness. Y. ISOBE [10] investigated that lattices constant a and c of Re coating on C/C substrate apparently increased after annealing an hour at 1100°C, which leads to micro hardness of Re coating increased from 254 kg/mm² to 429kg/mm². Also lattices constant and micro hardness of Re coating unchanged with prolonged annealing. C diffuses into the Re coating through both grain boundaries and lattices. Therefore, the C diffusion, on one hand, enhances the bonding between the C/C substrate and Re coating. On the other hand, decreases the ductility of the Re coating, and thus weakens its potential for relieving the thermal stress.

3.3. Thermal shock resistance test

Fig. 7. Morphology of (a) Ir/Re/C-C Composite before thermal shock test; (b) Ir/Re/C-C Composite after thermal cycles 3 times in air atmosphere; (c) Re/C-C Composite after thermal cycles 10 times in vacuum atmosphere(10⁻⁶Pa)

Figure 7(a) is morphology of Ir/Re/C-C Composite before thermal shock test. It can be seen that the surface of outer wall of tubular Ir/Re/C-C Composite sample is smooth, uniform without obvious cracks. There is a few tiny micro cracks along the axial and circular outer wall of tubular sample at the surface of inner wall, also on other obvious defects. When the high frequency induction furnace opened, the Ir/Re/C-C composite started to smoke at about 1100°C during the cooling process from 2000°C to 800°C in air. This may be due to the rhenium oxidation above 600°C in the air and the formation of highly volatile, the white smoke-like Re₂O₇ [11]. In addition, the C/C composites also have a smoke under aerobic conditions. When the sample was heated to 2000°C again, smoke phenomenon gradually disappeared causing the crack gradually healed. After thermal shock 3 times, the sample happen to crack propagation, swelling and the defect areas increased, which can be seen from Figure 7(b). In order to evaluate the impact of Re transition layer on the thermal shock lives of the Ir/Re/C-C composites, Figure 7(c)
shown that morphology of Re/C-C Composite after thermal cycles 10 times in vacuum atmosphere ($10^{-6}$Pa), no obvious cracks can be seen on the surface of outer wall and inner wall of sample. It demonstrates that Re coating has good thermal shock resistance with C/C Composite substrate.

Figure 8 is a cross-section of coating and the substrate interface of Ir/Re/C-C composite. Re coating on the C/C composite obtained by CVD is columnar grain, the grain size of which is approximately 8μm. Ir is fine equiaxed grain, and grain size is about 0.5μm. Grain size plays an important role in resistance to cracking [12]. Therefore, Re coating plays a more important role in the resistance to cracking compared with Ir coating in the entire coating system. Thermal expansion coefficient of rhenium is $6.8 \times 10^{-6} K^{-1}$, and thermal expansion coefficient of C/C composite is less than $2 \times 10^{-6} K^{-1}$ [13]. During the thermal shock cycles, the mismatch in thermal expansion coefficients of substrate and Re coating produced high thermal stresses in the whole coating system. With the increasing number of thermal shock cycles, more cracks were produced by in-plane tensile stresses (Figure 9). The cracks almost extended along the grain boundaries of Re columnar grain.

Figure 9. (a) Cracks morphology of the as-deposited Sample before thermal shock resistance test; Cracks morphology of the as-deposited Sample after thermal shock resistance test.
4. Conclusion

(1) The fracture occurred in C/C substrate in the Bonding strength tests. CVD Re coating has a good combination with C/C composites. The tensile strength of the coating is greater than 21.94MPa, and the shear strength is greater than 24.31MPa. The Re coating is scraped off by diamond indenter when the load is 5N. There exists excellent adhesion between the Re coating and C/C substrate.

(2) The hardness of the as-deposited Re coating was location dependent, the coating near the coating top surface was harder than the coating adjacent to the C/C substrate. The hardness of the coating became the same, and remained unchanged with prolonged annealing at 1600°C. C atoms diffuse quickly into the Re coating within an hour, reaching to the saturation and maximum hardness.

(3) After thermal shock 3 times in air, the Ir/Re/C-C Composite sample happen to crack propagation, swelling and the defect areas increased, cracks occurred when the samples were cooled to 1100°C. After thermal cycles 10 times in vacuum atmosphere, the Re/C-C Composite sample had no obvious cracks. The mismatch in thermal expansion coefficients layer plays an important role in thermal shock resistance of the coating system.

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