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In-situ preparation, modulation and mechanism of refractory metal carbide gradient coating

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Abstract: TiC, ZrC and TaC modified layers were in-situ prepared on graphite matrix by chemical vapor infiltration method with metal salts as the activator. Taking the TiC modified layer as an example, through thermodynamic calculation and experiment, the thermal decomposition process of raw materials (Ti/K_2TiF_6) was analyzed, the formation mechanism of TiC was determined, and the distribution of TiC modified layer was modulated. The results show that activator K_2TiF_6 has higher decomposition temperature than NH₄Cl, which is conducive to improving the utilization rate of raw materials in the gas infiltration process. Increasing the content of Ti powder can increase the concentration of reaction gas and contribute to the formation of TiC modified layer. When the molar ratio of Ti to K_2TiF_6 is 3:1, the surface thickness and infiltration depth of TiC are 5.42 and 136.24 µm, respectively. Increasing the reaction temperature rises to 1600 °C, the TiC surface layer thickness increases to 20.27 µm.

Key words: graphite; TiC; in-situ reaction; gradient coating; chemical vapor infiltration; refractory metal carbide

1 Introduction

Graphite is a non-metallic multicoating material with hexagonal ring sheets between carbon atoms. Given its special structure, graphite has strong chemical stability, excellent electrical and thermal conductivities, good processability, high melting point (3700 °C), solid-state super slip and other physical properties [1-4]. Therefore, graphite materials are widely used in military, industrial and livelihood fields. However, graphite begins to oxidize when the temperature exceeds 450 °C, so its use temperature in air is only 400 °C. Furthermore, graphite is a brittle material with poor thermal shock resistance, so the application of graphite material is greatly limited [1,5]. Using the method of adding coating to graphite material can effectively protect it from chemical erosion and improve its physical properties.

are easy to combine with carbon, resulting in the high melting point, high hardness, good oxidation and ablation resistance of their carbides which are commonly used for preparing graphite surface coating. Studies show that TiC and ZrC coatings are formed on the surface of castable flake graphite through molten salt reaction to improve its wettability to water [6-8]. SUZUMURA et al [9] prepared a TaC coating on graphite crucible by the slurry sintering method. AlN and SiC single crystals prepared on the graphite crucible with TaC coating reportedly had high purity and low impurity [9–11]. MA et al [5] and TIAN et al [12] prepared HfC and ZrC coatings on a graphite surface by chemical vapor deposition. HfC and ZrC coatings can effectively improve the mechanical properties and oxidation resistance of carbon-based materials [13-15].

Chemical vapor infiltration (CVI) method is a modification method in which the precursor enters the porous preform in the reaction furnace for

The fourth and fifth sub-group metal elements

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continuous and multiple deposition to form a dense composite [16]. CVI has the following advantages over other preparation methods: simple preparation process, relatively small damage to the matrix, high-purity coating, strong binding force between the coating and the matrix and good preparation effect for materials with high porosity, such as graphite [16–19]. NH₄Cl is widely used in the solid and gas infiltration processes as a common active agent, and the decomposition temperature of NH₄Cl is approximately 300 °C [20]. Therefore, in the solid and gas infiltration processes in which the preparation temperature exceeds 1000 °C, the active gas decomposed by NH₄Cl will continue to diffuse and escape as the temperature rises, resulting in the decrease of the use efficiency of raw materials. In this study, the refractory metal carbides (i.e. TaC, ZrC and TiC) with gradient distribution were prepared on the graphite matrix by CVI with metal salts as the activator. Taking the preparation process of TiC as an example, the thermal decomposition process of the K₂ZrF₆ and Ti mixture was studied, and the formation mechanism of the TiC infiltration coating was analyzed and verified. Finally, the change in infiltration coating thickness was studied by adjusting the ratio of Ti to K_2ZrF_6 .

2 Experimental

In the experiment, refractory metal carbides (i.e. TiC, ZrC and TaC) were prepared on the graphite matrix by the CVI method. The powder used in the experiment includes refractory metal powder, refractory metal salt and metal carbide, and the matrix is graphite block. The refractory metal powders (i.e. Ti, Zr and Ta, purity not less than 99.9%) were used as reaction sources, the metal salts (i.e. K_2TiF_6 , K_2ZrF_6 and K_2TaF_7 , purity not less than 99%) were used as activators, and the

carbides (i.e. TiC, ZrC and TaC, purity not less than 99%) were used as fillers. The graphite blocks (with a density range of 1.68-1.72 g/cm³ and a porosity of approximately 7%) were ultrasonically cleaned with ethanol and dried at 100 °C for 2 h.

Taking the preparation of TiC modified layer as an example, the basic process is as follows: (1) The Ti, K_2TiF_6 , and TiC powders were weighed according to the designed proportion, and the powders were mixed in a blender for 2 h to obtain the mixture. (2) The mixture was evenly spread at the bottom of the graphite crucible as the reaction chamber, the dried graphite block was directly suspended above the graphite crucible, and a certain distance was kept between the powder and the graphite block. The graphite crucible was placed in a vacuum carbon tube furnace for heating. (3) The vacuum carbon tube pressure was reduced below 10 Pa with a mechanical pump, and then argon was injected to the room pressure. This process was repeated twice to reduce the oxygen content in the system. (4) Heating started according to the set procedure, the graphite crucible was heated from room temperature to the preset temperature T_1 at 10 °C/min, held at T_1 for 2 h, and then was cooled to room temperature with the furnace to obtain the sample. (5) The reacted graphite block was subjected to vacuum heat treatment at 1800 °C for 1 h to remove the fluoride impurities deposited on the surface of the sample. The experimental process is shown in Fig. 1.

X-ray diffraction (XRD, Panalytical Empyren type) was used to analyze the surface phase of the samples. A scanning electron microscope (Tescan Mira3 type) was used to observe and analyze the microscopic morphology of the samples after the experiment. A synchronous thermal analyzer (TG-DSC, Netzsch 449F3 type) was used to analyze the exothermic and weightless characteristics of



Fig. 1 Flow chart of experiment

some experiments. The test temperature range of differential thermal analysis was 0-1250 °C. The heating rate was 10 °C/min, the atmosphere was flowing argon, and the gas flow was 20 mL/min.

3 Results and discussion

3.1 Preparation of refractory metal carbide modified graphite

TiC, ZrC and TaC coatings were prepared on the graphite matrix by the CVI method with metal

elements (i.e. Ti, Zr and Ta) as reaction sources, the corresponding metal salts (i.e. K_2TiF_6 , k_2ZrF_6 and K_2TaF_7) as activators, and the corresponding metal carbides (i.e. TiC, ZrC and TaC) as fillers (the molar ratio of metal to activator in the three raw powders was 1:1). The surface and cross-section of the graphite modified by different refractory metal carbides are shown in Fig. 2, D_1 represents the depth of the coating infiltrating into the matrix, and D_2 represents the thickness of the coating on the matrix surface. In the measurement process, D_2



Fig. 2 SEM images of surface and cross-section of graphite modified by different refractory metal carbides: (a_1) TiC modified graphite surface; (a_2) TiC modified graphite cross-section; (b_1) ZrC modified graphite surface; (b_2) ZrC modified graphite cross-section; (c_1) TaC modified graphite surface; (c_2) TaC modified graphite cross-section

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measures the thickness of the whole surface layer, and D_1 starts from the bottom of the surface layer until there is only about 10% modifier left in the horizontal direction of the location. Phase analysis (Fig. 3) shows that TiC, ZrC and TaC are formed on the surface of graphite. Figure 2 indicates that a single uniform carbide coating is formed on the graphite surface, and a gradient infiltration coating is formed inside the matrix. The infiltration coating depths of TiC, ZrC and TaC are 64.27, 83.82 and 483.53 µm, respectively. Therefore, the refractory metal carbide coating with gradient distribution can be prepared on the graphite matrix by CVI with metal salts as the activator. Taking the formation of TiC infiltration coating as an example, the principle was analyzed and verified and the infiltration coating was modulated to explore the formation principle of refractory-metal-modified graphite and master the change law of modified graphite infiltration coating.



Fig. 3 XRD patterns of graphite surface modified by different refractory metal carbides

3.2 Mechanism of TiC coating

3.2.1 Differential thermal analysis

To understand the changes in the K_2TiF_6 powder and the Ti and K_2TiF_6 mixture in the heating process, differential thermal analysis (DTA) was performed on the two groups of powder in flowing argon atmosphere (Fig. 4). The TG and DSC curves of the K_2TiF_6 powder are Curves (1) and (2) in Fig. 4, respectively, and the TG and DSC curves of the Ti and K_2TiF_6 mixture are Curves (3) and (4) in Fig. 4, respectively. The TG–DSC curves show a group of endothermic peaks at 375 and 575 °C, which are consistent with DTA of K_2TiF_6 in Ref. [21]. PRASAD et al [21] believes that the endothermic peak at 375 °C is caused by the removal of water in salt with the increase of temperature, and the endothermic peak at 575 °C is caused by the reaction of K_2TiF_6 with water vapor to form K_3TiOF_5 .



Fig. 4 Results of thermal difference analysis

Curves (1) and (2) in Fig. 4 show that K_2TiF_6 produces an endothermic peak at approximately 690 °C and the mass loss gradually increases, implying that K₂TiF₆ reacts at approximately 700 °C. The two groups of endothermic peaks generated by the Ti and K₂TiF₆ mixture before 700 °C are similar to the DTA results of K₂TiF₆, i.e. the removal of water and the generation of K₃TiOF₅, respectively. The endothermic peak of the mixture at 762 °C is followed by the exothermic peak, and the mass loss gradually increases. The mixture reacts and results in phase state transformation at this time. The initial decomposition temperature of K₂TiF₆ is approximately 600 °C higher than that of NH₄Cl. Therefore, using K_2TiF_6 as an activator can effectively reduce the evaporation escape time of gas and improve the utilization rate of raw materials.

3.2.2 Thermodynamic simulation

The process of TiC coating formation was simulated and analyzed by the HSC Chemistry 6.0 software. Given that TiC permeation coating is generated on suspended graphite through gas phase reaction, the influence of C was excluded during calculation to better analyze the evolution process of reaction gas through thermodynamic calculation, and two groups of materials were selected: (a) 1 mol of K_2TiF_6 and (b) 1 mol each of K_2TiF_6 and Ti. The temperature range of the two groups was 0–1700 °C, and the pressure was 0.1 MPa. The following possible products were selected: F(g),

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 $F_2(g)$, K(g), $K_2(g)$, KF(g), $K_2F_2(g)$, Ti(g), $Ti_2(g)$, TiF(g), $TiF_2(g)$, $TiF_3(g)$, $TiF_4(g)$, K, KF, K_2TiF_6 , Ti, TiF₂, TiF₃ and TiF₄. The types and quantities of the components of the above reaction system at different temperature stages were calculated, and the results are shown in Fig. 5.



Fig. 5 HSC simulation results: (a) 1 mol K_2TiF_6 ; (b) 1 mol Ti + 1 mol K_2TiF_6

In the thermodynamic simulation, when the initial setting is 1 mol of K2TiF6, K2TiF6 will decompose at 600-700°C to produce KF and $TiF_4(g)$, and the KF product will gradually change into gaseous state with the increase in temperature, which is consistent with the change rule of the DSC-TG curve in the above DTA. When the initial reaction is set as 1 mol each of K₂TiF₆ and Ti, the reaction change process is relatively complex, but the key step is to produce K(g) with strong reducibility in the range of 1150-1400 °C. Therefore, combined with the two sets of thermodynamic calculation and DTA, the main reactions of the formation of TiC coating are divided into three stages: the reaction and decomposition of K₂TiF₆, the reaction of Ti and fluorine salt, and the formation of TiC gradient coating.

(1) The reaction and decomposition of $K_2 TiF_6$:

$$3K_2TiF_6 + Ti = 4TiF_3 + 6KF$$
(1)

$$K_2 TiF_6 = 2KF + TiF_4$$
(2)

(2) The reaction of Ti and fluorine salt:

$$Ti+TiF_4=2TiF_2 \tag{3}$$

$$Ti+3TiF_4=4TiF_3 \tag{4}$$

$$Ti+2KF=TiF_2(g)+2K(g)$$
(5)

$$Ti+3KF=TiF_3(g)+3K(g)$$
(6)

(3) The formation of TiC gradient coating:

 $2K(g)+TiF_2(g)+C=TiC+2KF(g)$ (7)

$$3K(g)+TiF_3(g)+C=TiC+3KF(g)$$
 (8)

In the low temperature reaction stage, K₂TiF₆ will react with Ti, but both are in solid phase and the reaction rate is slow, so the DSC curve shows a slow decline trend before 760 °C. When the temperature reaches 760 °C, the TiF₄ (with melting point of 290 °C) produced by the selfdecomposition reaction of K₂TiF₆ is liquid, which can rapidly react exothermically with Ti in the mixture to generate TiF₂ and TiF₃ (the exothermic decomposition with heat release is greater than that of K₂TiF₆). Therefore, the endothermic peak is quickly covered by the exothermic peak in the DSC curve. As the temperature continues to rise, TiF₂ and TiF₃ continue to absorb heat and slowly evaporate, resulting in a constant increase in mass loss. When the temperature is between 1150 and 1400 °C, K(g) with strong reducibility is formed. At this time, the gas mixture of K(g) and titanium fluoride diffuses to the surface of the suspended graphite and enters the pores of graphite along the direction of decreasing concentration gradient and finally reacts with the graphite matrix to form the TiC gradient coating (Reactions (7) and (8)).

Under constant pressure, the Gibbs free energy change of the above process equation changes with the temperature as shown in Fig. 6. The results indicate that Gibbs free energy changes of the decomposition of $K_2 \text{TiF}_6$ ((Reaction (2)) and the formation of K(g) ((Reactions (5) and (6)) are greater than zero in some temperature ranges, which is the key step for changing the system and controlling the reaction process. Especially, when the temperature reaches 1150 °C, the content of K(g) restricts the growth of the TiC coating,



Fig. 6 Gibbs free energy change of process reaction versus temperature curve

providing a temperature range guidance for the preparation of TiC coating.

The experiments were designed to verify the above reactions. The raw materials used were K₂TiF₆, Ti, KF and TiC (filler), and the experimental conditions were the same as those in the previous period: Experiment (a) K_2TiF_6+TiC : using K₂TiF₆ and TiC as raw materials to verify that the decomposition product of K₂TiF₆ must react with Ti to form the TiC coating; Experiment (b) KF+Ti+TiC: KF, Ti and TiC were used as raw materials to verify whether KF, the decomposition product of K₂TiF₆, can react with Ti and form the TiC coating on the surface of the suspended samples; Experiment (c) KF+TiC: KF and Ti were used as raw materials to eliminate the influence of the interaction between KF and TiC in Experiment (b).

According to the XRD analysis results of the sample surface after the test (Fig. 7), only the graphite diffraction peak exists on the sample surface after Experiment (a). DTA and thermodynamic analysis indicate that K_2TiF_6 has a self-decomposition ability, but K_2TiF_6 and its decomposition products must interact with Ti to form the target coating. In Experiment (b), the sample surface contains TiC diffraction peaks. K(g) is produced by the reaction between Ti and KF, which is the decomposition product of K_2TiF_6 (Reactions (5) and (6)), and TiC coating is formed on the surface of the graphite matrix (Reactions (7) and (8)). K(g) is considered as the key to promoting the formation of TiC coating, and K_2TiF_6 as an activator mainly plays the role of providing the K source. In addition, a series of experiments were carried out on Experiment (b), revealing that the crucible container and the sample were prone to fracture after the direct reaction of KF with Ti. A 6.89 μ m thick coating could be prepared on the surface of the graphite matrix by adjusting the molar ratio of KF to the Ti powder (Fig. 8). However, the gradient diffusion coating could not be obtained inside the graphite matrix, which may be related to the intensity of the KF reaction.



Fig. 7 XRD patterns of designed experimental samples



Fig. 8 SEM image of cross-section of sample in Experiment (b)

3.3 Modulation of TiC coating

According to the previous analysis, the K(g) generated by the reaction of Ti and KF is the key material in promoting the formation of TiC coating. In the reaction process, Ti is consumed by the reaction, while KF is generated cyclically with the formation of the TiC coating (Reactions (7) and (8)). Therefore, by increasing the ratio of Ti in the

original powder, the excessive KF in the system can react with it to form K(g) (Reactions (5) and (6)) and finally promote the formation of the TiC infiltration coating to regulate the growth of the TiC infiltration coating. To verify the above inference, two groups of experiments were performed (molar ratios of raw material are as follows: n(Ti)/ $n(K_2TiF_6)=2:1; n(Ti)/n(K_2TiF_6)=3:1)$ by controlling the total amount of powder and adjusting the molar ratio of Ti to $K_2 Ti F_6$ to study the change in infiltration coating.

The microscopic morphology of the three groups of samples after the experiment is shown in Fig. 9. When the molar ratio of Ti to K_2TiF_6 is 1:1, the surface of graphite matrix is evenly covered by a layer of coating after the experiment, the original



Fig. 9 SEM images of surface (a_1, b_1, c_1) and cross-section (a_2, b_2, c_2) of TiC modified graphite with different molar ratios of Ti to K₂TiF₆: $(a_1, a_2) n(Ti)/n(K_2TiF_6)=1:1$; $(b_1, b_2) n(Ti)/n(K_2TiF_6)=2:1$; $(c_1, c_2) n(Ti)/n(K_2TiF_6)=3:1$

pores of the graphite matrix are visible, and an infiltration layer of 64.27 µm is formed. When the molar ratio of Ti to K₂TiF₆ is 2:1, a dense and uniform coating is formed on the surface of graphite matrix after the experiment, and the coating fills the original pores of graphite. The infiltration depth of the coating into the matrix is increased to 77.65 µm and a covering layer with a thickness of 4.26 µm is produced on the surface of the matrix. When the molar ratio of Ti to K_2TiF_6 is 3:1, the coating thickness and infiltration depth on the graphite matrix increase to 5.42 and 136.24 µm, respectively. According to the XRD pattern of the sample surface (Fig. 10), the surfaces of the three groups of samples are composed of graphite and TiC. When the molar ratio of Ti to K₂TiF₆ in the raw material is greater than 2:1, the graphite diffraction peak basically disappears and the diffraction peak of TiC increases significantly, indicating that TiC basically completely covers the surface of graphite matrix, which corresponds to the results observed under electron microscope.



Fig. 10 XRD patterns of TiC modified graphite surface with different molar ratios of raw material

According to the thermodynamic analysis and experimental results, when the molar ratio of Ti to K_2TiF_6 is 1:1, the Ti content is less, which will be consumed in the reaction process, and only a small amount of K(g) will be produced. Therefore, the coating prepared on the graphite surface is thin and exposed to the original pores. When the molar ratio of Ti to K_2TiF_6 increases to 2:1, Ti can react with KF to produce a large amount of K(g). Therefore, a coating with uniform thickness is formed on the surface of graphite matrix, and the original pores of graphite can be filled. When the molar ratio of Ti to K_2TiF_6 increases to 3:1, although the Ti content further increases, it has little effect on the morphology of the whole coating, only increasing the thickness of the surface and inner coating.

Three groups of experiments were performed to explore the distribution of coating by changing the experimental preparation temperature. The highest preparation temperatures were 1400, 1500 and 1600 °C, respectively, and the molar ratio of Ti to K_2TiF_6 was 2:1. Other experimental conditions were consistent with the previous experiments. Figure 11 shows the XRD pattern of the sample surface after the experiment. From the results, it can be inferred that the coating on the surface of the three groups of samples is TiC. Figure 12 shows the microscopic morphology of the three groups of samples after the experiment, continuous complete TiC coating is formed on the three groups of sample surface, and morphology presents a grid structure. With the increase of experimental temperature, the diameter and uniformity of the grid on the sample surface increase. According to the cross-section figure, a coating with a certain thickness is formed on the surface of the three groups of samples, and a infiltration layer is formed inside the graphite matrix. The surface layer thickness of the samples prepared at 1400, 1500 and 1600 °C is 8.31, 18.04 and 20.27 µm, respectively. The corresponding infiltration depth is 79.27, 95.89 and 100.76 µm, respectively. It can be seen from the characterization results that the coating thickness on the sample surface increases obviously with the increase of temperature. In fact, the thickening of the surface coating is the result of the continuous



Fig. 11 XRD patterns of TiC modified graphite prepared at different temperatures



Fig. 12 Surface (a_1, b_1, c_1) and cross-section (a_2, b_2, c_2) morphologies of TiC modified graphite prepared at different temperatures: (a_1, a_2) 1400 °C; (b_1, b_2) 1500 °C; (c_1, c_2) 1600 °C

diffusion of carbon atoms in the matrix and the reaction with Ti to form TiC. When the experimental temperature rises to 1600 °C, the diffusion ability of matrix carbon atoms is the strongest, which leads to the thickest TiC coating on the surface of the matrix.

4 Conclusions

(1) The thermal decomposition of $K_2 TiF_6$ was investigated. The results show that the initial decomposition temperature of $K_2 TiF_6$ is about

600 °C higher than that of NH₄Cl. Therefore, using K₂TiF₆ as the reactive activator could effectively reduce the evaporation escape time of gas and improve the utilization rate of raw materials.

(2) The formation mechanism of TiC modified layer was studied. The analysis shows that K(g), TiF₂(g) and TiF₃(g) produced by raw materials are effective gases for forming TiC-modified layer. In this process, K(g) will be continuously consumed by reaction, which is the key gas restricting the growth of TiC modified layer.

(3) The growth of TiC-modified layer under different conditions was studied. The results show that increasing Ti content in the raw material or reaction temperature will promote the growth of TiC-modified layer. When the experimental temperature is 1250 °C and the molar ratio of Ti to K_2 TiF₆ is 3:1, the thickness of TiC surface layer can reach 5.42 µm, and the infiltration depth can reach 136.24 µm. When the experimental temperature reaches 1600 °C, the thickness of TiC surface layer can reach 20.27 µm, and the infiltration depth can reach 100.76 µm.

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难熔金属碳化物梯度涂层的原位制备、调制及机理

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摘 要: 以金属盐为活性剂,采用化学气相渗透法在石墨基体表面原位制备 TiC、ZrC 和 TaC 改性层。以 TiC 改 性层为例,通过热力学计算与实验,分析原料(Ti/K₂TiF₆)的热分解过程,确定 TiC 的形成机理,并对 TiC 改性层 的分布进行调制。结果表明,活性剂 K₂TiF₆比 NH₄Cl 具有更高的分解温度,有利于提高气体渗入过程中原料的 使用率。增加 Ti 粉含量能提高反应气体的浓度,有助于 TiC 改性层的形成。当 Ti 与 K₂TiF₆的摩尔比为 3:1 时, TiC 表面层厚度和渗入深度为分别为 5.42 和 136.24 μm。升高反应温度能提高原位反应速率,有助于 TiC 表面层 厚度的增加; 当实验温度升高至 1600 ℃时,TiC 表面层厚度增加至 20.27 μm。 关键词: 石墨; TiC; 原位反应;梯度涂层;化学气相渗透; 难熔金属碳化物

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