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Low temperature synthesis of pure phase TaB_2 powders and its oxidation protection modification behaviors for Si-based ceramic coating in dynamic oxidation environments

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ABSTRACT

To reveal the generation mechanisms of the Ta-Si-O glass ceramics layer in dynamic oxidation environments, a 40 wt% TaB_2-SiC coating was prepared by liquid phase sintering method. To obtain pure phase TaB_2 powders at lower temperature (1500 °C), excessive B_2O_3 powders were added in raw materials to eliminate the TaC by-product phase. The hexagonal pure phase TaB_2 powders own average particle size of about 386 nm. During the TGA dynamic oxidation tests, after the modification of 40 wt% TaB_2, the initial weight loss temperature of the sample delayed by about 48%, while the weight loss percentage and rate in fastest weight loss zone decreased by about 61% and 53%, respectively. During oxidation, the generated Ta-oxides were peeled and carried away by the formed fluid SiO_2 glass layer to form “Ta-oxides halation” at first, which results the dissolution of Ta-oxides in the SiO_2 glass, thus forming the Ta-Si-O glass ceramics with dendritic structure. With the spread of the SiO_2 glass layer and growth of the Ta-Si-O dendrite, the Ta-Si-O glass ceramics gradually cover on the surface of the SiO_2 glass layer, forming the structure of Ta-Si-O/SiO_2 double glass layer that is capable of sealing and arresting of microcracks.

1. Introduction

Carbon materials (graphite and carbon/carbon composites) are a kind of desirable light ultra-high temperature structure materials that are suitable for applications in aerospace and aeronautical fields [1–4], such as leading edges of reentry vehicles, rocket nozzles, and so on. Although they possess outstanding physical and mechanical properties, such as, low density, high strength-to-weight ratio, low coefficient of thermal expansion, and so on, their widespread usages are severely limited because of the oxidation sensitivity of carbon above 773 K in air [5–7]. So far, being capable of providing an oxygen shielding layer, coating technique [8–13] is thought to be the most efficient method to reduce the oxidation loss of carbon materials in ultra-high temperature aerobic environments.

Among the coatings, Si-based anti-oxidation coatings [8–13] have shown great potentials due to the generation of self-sealing silicate glass layer on the coating surface. Nevertheless, the main protective temperature of the silicate glass layer for carbon materials is limited in the range of 1200 °C – 1600 °C. Hence, facing the dynamic application environments from room temperature to 1600 °C or even high, the pure Si-based anti-oxidation coatings are not up to the applications in dynamic harsh oxidation environments.

IVB-VB-group transition metals diborides, the members of a family of the ultrahigh temperature ceramics (UHTCs) [14–18], own the high melting temperature (> 3000 °C), elevated thermal and electrical conductivity, high hardness and excellent resistance to oxidation. Hence, they are the promising materials that can be designed for use as hypersonic flight, rocket nozzle inserts, sharp leading edges, and so on [19–24]. Moreover, when they were used together with the Si-based ceramics, the oxidation resistances of the composites were significantly improved, which is owing to the formation of multi component oxides composed of B_2O_3, SiO_2 glass and oxides of transition metals [25]. The oxides of transition metals with high melting temperature are able to improve the oxidation protective ability of the silicate glass. The existence of B_2O_3 not only can react with SiO_2 glass to form borosilicate glass layer with good oxidation resistances, but also provide oxidation protection below 1100 °C through the formation of continuous B_2O_3 layer. Hence, the transition metals diborides show great potentials in the field of oxidation protection, the oxidation protective ability of which are hopeful to offset the defects of the Si-based coatings in the

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dynamic aerobic environments for carbon materials.

Due to the outstanding physical, chemical properties and excellent oxidation protective ability of TaB_2 that belongs to the family of UHTCs diborides [26–29], recently, TaB_2 was utilized to modify the oxidation protective ability of the Si-based ceramic coatings for carbon materials [30,31], which presents great potential through the formation of Ta-Si-O compound glass layer. In our previous work, to control the microstructure and contents of TaB_2 phase in Si-based coating, we have prepared 20 wt% TaB_2-SiC coating by a novel liquid phase sintering method [32]. The results showed that pure TaB_2 phase can be obtained by carbothermal reduction reaction at 1700 °C, below the temperature of which TaC phase will generate. As we know, compared with the TaB_2 phase, the TaC phase possesses worse oxidation resistance due to the formation of CO_2 and the absence of B_2O_3, and therefore, the emergence of TaC byproduct phase actually will weaken the oxidation protective ability of the TaB_2-SiC coating in dynamic environments. Thus, to pursue synthesis of pure phase TaB_2 powders at lower temperature, the TaC byproduct phase must be eliminated. In addition, after the modification of 20 wt% TaB_2, the weight loss of the SiC coating decreased from 17.7% to 11.8% after the dynamic TG tests. Although the modified coating exhibits obviously improved oxidation resistance, the oxidation protective ability of the TaB_2-SiC coating in dynamic aerobic environments still needs to be enhanced. Moreover, although we have found that the essence of the Ta-Si-O compound glass layer is a kind of glass ceramics that exhibits dendritic structure, its generation process and growth mechanisms are still unclear.

In the process of the carbothermal reduction reaction, the emergence of TaC phase is caused by the excessive C or inadequate B in raw materials. Hence, in this paper, to eliminate the TaC byproduct phase at lower temperature and take the volatility of B_2O_3 into consideration, the effect of the content of B_2O_3 on the phase compositions of the TaB_2 powders was investigated to obtain the pure TaB_2 powders at 1500 °C. Moreover, owing to the promising oxidation protective modification behaviors of TaB_2 phase on Si-based coating, it is the key material for the formation of Ta-Si-O glass ceramics. Thus, to reveal the generation mechanism of the Ta-Si-O glass ceramics as well as further enhance the oxidation protective ability of the TaB_2-SiC coating in dynamic oxidation environments, the content of TaB_2 was adjusted from 20 wt% to 40 wt% to prepare the 40 wt% TaB_2-SiC coating. The synthesized TaB_2 powders were characterized in terms of microstructure and crystal structure. Furthermore, oxidation protective ability of the 40 wt% TaB_2-SiC coating was investigated in dynamic TGA oxidation environments from room temperature to 1773 K. Finally, the generation process and growth mechanism of Ta-Si-O glass ceramics were analyzed.

2. Experimental procedures

Used as the raw materials to synthesize the TaB_2 powders, commercial powders include C (purity > 99.9%, Carbon Plant, Xi'an, China), B_2O_3 (purity > 99.9%, Tianli Chemical Reagent Co., Ltd, Tianjin, China) and Ta_2O_5 (purity > 99.9%, Guoyao Chemical Reagent Co., Ltd, Shanghai, China). The process for synthesizing TaB_2 powders is illustrated in Fig. 1(a). The TaB_2 powders were prepared through the carbothermal reduction method. Firstly, according to Reaction (1), 0.006 mol Ta_2O_5, 0.012 mol B_2O_3 and 0.066 mol C powders were weighted. To study the effect of the content of B_2O_3 on the phase compositions of the TaB_2 powders, excessive B_2O_3 powders (125%, 150%) were used separately to make comparisons. After weighing, the precursor powders were fully mixed for 2 h using a high energy planetary ball mill. Afterwards, the milled mixtures were heat treated at 1500 °C under normal argon protection atmosphere with a heating rate of ~5 °C/min. Finally, the TaB_2 powders were collected when the powders were slowly cooled down to room temperature.

$$Ta_2O_5(s) + 2B_2O_3(s) + 11C(s) \rightarrow 2\,TaB_2(s) + 11\,CO(g) \quad (1)$$

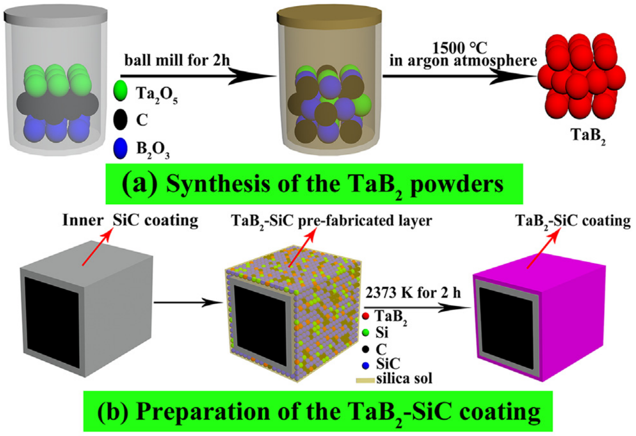

Fig. 1. Synthesis illustration of the TaB_2 powders (a) and outer 40 wt% TaB_2-SiC coating (b).

Graphite specimens (3 mm × 3 mm ×3 mm) were chosen as substrates for coating. Acting as a transition layer, the inner SiC coating was prepared by pack cementation as described previously [33]. As illustrated in Fig. 1(b), the outer 40 wt% TaB_2-SiC coating was prepared via liquid phase sintering method that consists of slurry preparation and sintering techniques. Firstly, the prepared pure phase TaB_2 powders (40 wt%), graphite (5–20 wt%) (Carbon Plant, Xi'an, China), SiC powders (10–30 wt%) (China New Metal Materials Tec. Co., Beijing, China), Si powders (5–25 wt%) (Jiuling Smelting Co., Ltd, Shanghai, China) and silica sol ($SiO_2{\cdot}nH_2O$) (the volume of silica sol to the weight of other raw materials was 0.5–1.5 ml/g) (City Fire Crystal Glass Co., Ltd, Dezhou, China) were chosen to form a homogeneous slurry by milling for 2 h. Since the coating is prepared by liquid phase sintering, the added SiC powders were used as unmelted solid skeleton in the coating to ensure the integrity of the coating structure. Afterwards, the homogeneous slurry was applied on the surface of the inner SiC coating by the method of brushing to prepare the outer pre-fabricated layer. Finally, the coated specimens were put in a graphite crucible to be heat-treated at 2373 K and held for 2 h under normal atmosphere protection. The heating rate is about 5–10 K/min. During the heat-treatment process, the reactions among Si, silica sol and C powders occur according to Eqs. (2) and (3). What is more, during the heat treatment, the Si powders and silica sol with relative low melting point (1687 K and 1923 K, respectively) would become the liquid state, which can provide a liquid phase condition for the synthesis of the outer coating through liquid phase sintering, thus speeding up the growth process of the coating.

$$Si(s) + C(s) \rightarrow SiC(s) \quad (2)$$

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \quad (3)$$

X-ray diffraction (XRD, Bruker D8 ADVANCE, BRUKER AXS, Germany) was used to analyze the phase compositions of the TaB_2 powders and the outer coating. The Laser Particle Size Analyzer (Zen 3600, Malvern, England) was used to calculate the particle size of the TaB_2 powders. Crystal microstructure of the TaB_2 powders were observed via transmission electron microscopy (TEM, JEM-3010, JEOL, Japan) and high-resolution transmission electron microscope. The microstructure and elemental analyses of the TaB_2 powders and the coating were conducted by Field Emission Scanning Electron Microscopy (FE-SEM, JSM-6700F, JEOL, Japan) equipped with an energy dispersive spectroscopy (EDS). Thermogravimetric analyzer (TGA, STA 449 F3, Netzsch, Germany) was used to evaluate the oxidation protective ability of the coating in dynamic TGA oxidation environments from room temperature to 1773 K with a heating speed of 10 K/min. TGA tests were implemented in synthetic air, which consists of argon and oxygen with a volume ratio of 78:22. Weight changes of the