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Microstructure and oxidation resistance of a YSZ modified silicide coating for Ta-W alloy at 1800 °C

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ABSTRACT

To develop an ultra-high temperature resistant coating for a reusable thermal protection system, a YSZ-modified Si-Mo coatings were prepared on Ta-10 W alloy by slurry reaction sintering method. The coating had a $MoSi_2$-$ZrSi_2$-SiO_2 outer layer and a $TaSi_2$-WSi_2 inner layer. The coated sample remained intact after oxidation at 1800 °C for 10 h, while the untreated alloy was pulverized after 6 min. The coating withstood more than 200 shock heating cycles from room temperature to 1800 °C. Its outstanding oxidation resistance is attributed to its thermal matching with the alloy and formation of protective SiO_2 scale containing high-melting $ZrSiO_4$ and ZrO_2.

1. Introduction

Tantalum-based alloys are regarded as promising candidates for ultrahigh temperature structural materials for application in the aerospace and nuclear energy industries due to their high melting points, good corrosion resistance, and excellent mechanical properties at high temperatures [1–4]. However, the poor oxidation resistance significantly restricts their practical application at high temperatures in oxidizing environments. Ta-based alloys will be oxidized in air at temperatures above 500 °C to form porous and brittle oxides [5], such as Ta_2O_5, which are not protective and cannot stop the inward penetration of oxygen [6]. In addition, the required operating temperatures for some Ta-based alloy components are as high as 1400 °C, with short periods of service sometimes being required at 1800 °C. Sometimes such parts will also need to withstand the impact of quencher and shock heating. Therefore, it is crucial to improve the high temperature oxidation and thermal shock performance of Ta-based alloys to enable their application at high temperatures. Although the oxidation resistance of Ta-based alloys can be improved by adding alloying elements, unfortunately, the degree of improvement is not sufficient, and the additional elements may decrease the mechanical properties of the alloy. In light of this fact, applying a coating is considered a better method to improve oxidation resistance.

Aluminides, heat-resistant metals, borides, and silicides are the main effective coating materials for high-temperature anti-oxidation coatings of Ta alloys. Due to the formation of a dense oxide film mainly composed of Al_2O_3, the aluminide coatings can effectively protect the Ta alloy from oxidation at temperatures below 1650 °C [7,8]. The heat-resistant metal coatings are mainly represented by Be-Ta and Hf-Ta. The oxidation temperature of the former can reach 1500 °C, but the brittleness and toxicity of the beryllide limit its development [8]. The effective protection temperature of the latter is expected to reach 1800 °C, and the Hf-27Ta alloy can even be short-time used over 600 s at 2000 °C [9]. However, there is no public report on its successful use as a protective coating for Ta alloys. The boride coating systems are mainly represented by ultra-high temperature ceramic materials such as ZrB_2 and HfB_2, which are mainly used above 2000 °C for a short time (protection time in seconds) [10,11]. The silicide coatings are currently the most studied systems for Ta alloy. It can easily add various modified elements to improve the anti-oxidation and other properties [12–15]. The main reason for the improvement of the high temperature oxidation resistance is that it can form a layer of compact, continuous and self-repairing SiO_2 film at high temperatures. But the pure SiO_2 film is limited to melting point 1670 °C (tridymite) to 1710 °C (cristobalite) [16,17], and thus the coatings are unsuitable for the application exceeding 1600 °C. In addition, the thermal expansion coefficient of SiO_2

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($CTE_{SiO_2} = 0.55 \times 10^{-6} K^{-1}$) [18] is much lower than that of Ta alloys ($CTE_{Ta} = 6.5 \times 10^{-6} K^{-1}$) [19], and thus the coating will experience high tensile stress during the heating and cooling process [12,20], which results in easy detachment of the coating.

At present, there are many researches on silicide modification, such as adding Al, B, W, Ti, Si_3N_4, etc [21–25]. However, among the existing coating systems, few are used at temperatures greater than 1700 °C, especially in applications involving quencher and shock heating. Therefore, the aim of this work is to develop a modified silicide coating which can be applied at 1800 °C and has thermal shock resistance. Among the many candidates, the ZrO_2 modified $MoSi_2$ system was chosen. $MoSi_2$ is one of refractory metal silicide with the best high temperature oxidation resistance [26–28]. ZrO_2 has a high melting point (2715 °C), a high coefficient of thermal expansion ($CTE_{ZrO_2} = 10.6 \times 10^{-6} K^{-1}$) [29], and a good resistance to high temperature oxidation, which suggests that ZrO_2 can improve the oxidation resistance of SiO_2 films at high temperature [30]. Especially in recent years, it has been found that ZrO_2 can react with Si to produce $ZrSi_2$ [31], which indicates that it is hopeful to solve the problem of poor matching with silicide coating. Due to the occurrence of monoclinic-tetragonal-cubic crystal transformation at high temperature, Y_2O_3 is often used as an additive to modify ZrO_2 [32]. Therefore, this work has designed a novel YSZ-modified silicide coating for the Ta-10 W alloy and focuses on the microstructure and the oxidation behaviour of the coating at 1800 °C. And the coating was prepared using the method of slurry reaction sintering, which is simple, efficient, inexpensive and commonly used for the preparation of silicide coatings [33,34].

2. Experimental

2.1. Specimen preparation

An alloy with a nominal composition of Ta-10 W (wt.%) was prepared by vacuum electron beam melting, and the obtained ingot was re-melted more than five times to ensure a homogeneous composition. Specimens of 60 mm × 5 mm × 1 mm were obtained by wire-cutting from the alloy ingot. After being ground to 800-grit with silicon carbide paper, the samples were cleaned in an ultrasonic acetone bath and finally dried at 70 °C for 1 h.

2.2. Coating process

The Ta-10 W alloy substrate was coated using a slurry reaction-sintering process; the synthetic procedures are depicted in Fig. 1. Firstly, the coating powder material was prepared by adding 30Mo-10YSZ (8 wt.%)-3SiO_2-57Si (wt.%) and a small amount of halide and binder. After weighing, the powder mixtures were ground in a planetary ball mill operating at 400 r min^{-1} for 6 h using a zirconia jar and zirconia balls. Ethyl alcohol was used as the milling solvent. The mixed slurry had an irregular shape and the particle size was not uniform with an average particle size of ~1.3 μm. The slurry was then evenly sprayed onto the surface of the Ta-W alloy sample using a spray gun. After drying at 100 °C for 60 min under vacuum, the sample was placed in a molybdenum alloy crucible and was sintered at 1450 °C for 1 h under an argon atmosphere in a vacuum sintering furnace. After cooling naturally, the as-prepared coating sample was obtained with thickness of 154 ± 10 μm (in order to further ensure the complete silicidation of the coating, an additional halide activated pack cementation [27] can be carried out).

2.3. Oxidation test

The isothermal oxidation behaviour at 1800 °C and thermal shock performance of the specimens were tested from room temperature to 1800 °C using an intelligent high temperature oxidation apparatus with data display and automatic data recording functions, which was custom-built in our laboratory. As shown in Fig. 1, it can realize the heating of the sample through low voltage and high current. And the infrared radiation thermometer can help to realize the real-time temperature test (error of ± 8 °C). The isothermal oxidation and thermal shock tests were operated by setting the heating program and objective temperature (specific experimental equipment and testing process were shown in Fig. S1 of supporting information). The mass change of the specimens was measured using an electronic analytical balance with a sensitivity of ± 0.1 mg. During the cycle oxidation, the specimens were rapidly heated from room temperature to 1800 °C in 15 s, held at 1800 °C for 30 s, and then rapidly cooled to 50–60 °C in 15 s to complete one thermal cycle. This process was repeated, and when a sample exhibited obvious failure characteristics (such as smoke, fracture, etc.), this was taken as an indication of coating failure.

2.4. Microstructure characterization

The X-ray diffraction (XRD) analysis was performed on a Rigaku D/max 2500 X-ray diffractometer using a Cu Ka source (λ = 1.54178 Å). The morphologies of the samples were observed under a scanning electron microscope (SEM, FEI Sirion 200, America). Qualitative and quantitative analyses for the surface and cross-section were carried out using an electronic probe microanalyser equipped with a wave spectrometer (EPMA, JEOL JXA-8230, Japan). The structure was characterized using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20, America and HRTEM, JEOL JEM-2010, Japan). The roughness values of the coating were analysed using a 3D laser scanning confocal microscope (Carl Zeiss LSM700, Germany).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 2 shows the surface morphology and the XRD patterns of the

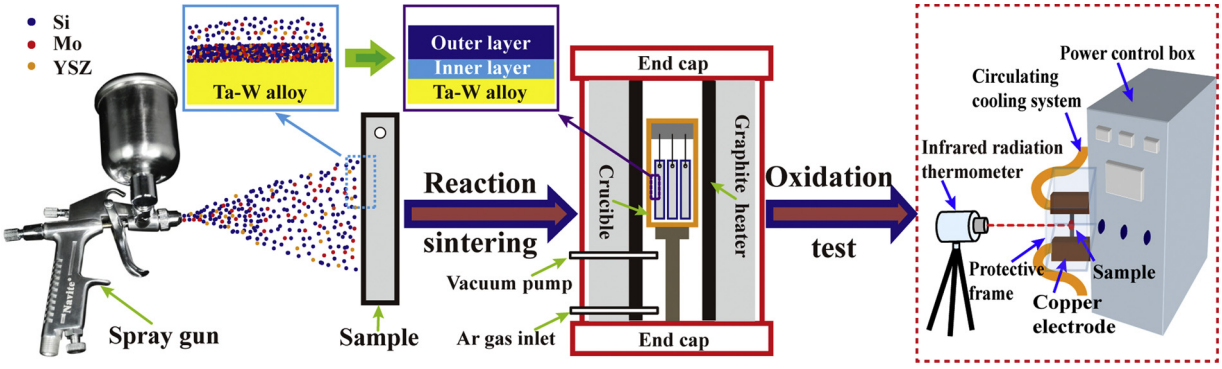

Fig. 1. Schematic diagram of coating preparation process and oxidation test.