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Influence of siliconizing on the oxidation behavior of plasma sprayed $MoSi_2$ coating for niobium based alloy

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ABSTRACT

Plasma spraying combined with halide activated pack cementation (HAPC) was used to deposit silicide coating on Nb-based alloy. X-ray diffraction (XRD) and energy disperse spectrum (EDS) indicate the formation of the siliconized $NbSi_2$ transition layer and the sprayed $MoSi_2$ outer layer. $NbSi_2$ layer prepared with HAPC exhibits relatively uneven surface which could promote the deposition of the sprayed $MoSi_2$. The coating specimen with 5 h siliconizing presented the best oxidation resistance with only 0.18% mass gain after 25 h oxidation at 1200 °C in air. The synergistic protection effect, depending on the continuous silica layer formed on the coating surface and the dispersal silica within the coating and interface, is responsible for the excellent oxidation resistance of the coating.

1. Introduction

Nb-based alloys are considered as the most promising candidate material for high temperature application in aeronautical and aerospace fields attributing to their excellent mechanical properties at high temperature [1–4]. However, the poor oxidation resistance seriously restricts their application at high temperature, which has received a great deal of attention in recent years [5–9]. Halide activated pack cementation (HAPC), an economic and efficient way to prepare oxidation resistant coating on substrate surface, was widely employed to resolve the poor oxidation behavior of niobium based alloy [4,10,11]. Nevertheless, the coating prepared by HAPC exhibits many cracks or defects due to its rather high preparation temperature [10,12]. In addition, the oxidation products, Nb-oxides, are not volatile and grow gradually with the oxidation prolonging [9]. Therefore, further treatment should be employed so as to improve the oxidation protective ability of the coating.

Plasma spraying has been proved as an effective surface treatment [13]. The high heat energy provided by plasma flame could melt spraying materials quickly and the solidification of the melting materials can obtain a lamellar structure coating preventing the formation of vertical cracks in the coating [14,15]. Therefore, the coating prepared with plasma spraying often exhibits good thermal shock resistance [16] and outstanding oxidation protective ability [14]. $MoSi_2$ is a kind of anti-oxidation materials attributed to the protectively sealed glassy film formed at high temperature, which can block the further inward diffusion of oxygen. $MoSi_2$ based coating system was proved to be very suitable to protect C/C composites against oxidation [17–20]. However, the overall $MoSi_2$ coating might not be thermally sprayed on the niobium based alloy due to the weak adhesion between sprayed coating and substrate [21]. Previous works often get $MoSi_2$ coating through a two-step method, namely, spraying Mo layer firstly then followed by siliconizing [22,23]. Fortunately, the siliconized diffusion zone as a result of HAPC could be considered as a transition layer in this work when taking into account the composite gradient and thermal match at interface between sprayed $MoSi_2$ coating and substrate [4,11]. Therefore, it should be effective for spraying $MoSi_2$ directly on the surface of HAPC-treat niobium based alloy to improve its oxidation resistance.

The present work combined HAPC and thermal spraying to produce a double-layer silicide protective coating on niobium based alloy. Namely, the Nb-based alloy substrate was firstly treated through HAPC with pack powder of Si, NH_4F and Al_2O_3, and then was deposited with $MoSi_2$ by supersonic plasma spraying. The effect of the $NbSi_2$ bond layer, on the microstructure and oxidation behavior of the sprayed $MoSi_2$ was analyzed.

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2. Experimental

2.1. Materials

The substrates were cut into 10 mm × 10 mm × 3 mm from a block of niobium based alloy with a nominal composition (wt. %) of W 5–6, Zr 1.5–1.7, Mo 2.1–2.5 (Bal. Nb). These specimens were grit-blasted using SiC (250 μm) to obtain rough surface to improve the adherence of the coatings. $MoSi_2$ agglomerate powders were prepared using spraying dry method. The diameter of the as-prepared $MoSi_2$ powder was 45–78 um. Such particle can be directly sprayed in thermal plasma spray technology.

2.2. Coating preparation

2.2.1. HAPC process

The substrates were firstly treated with HAPC process to obtain an inner transition layer followed by thermal spraying to produce a $MoSi_2$ outer coating. The pack composition used in HAPC process includes 20 wt. % Si, 10 wt. % NH_4F and balance Al_2O_3 filler. Each kind of the powders was weighed according to the designed ratio and then they were mixed up in a ball mill for 2 h. After filling the pack powder around the substrate specimens in an alumina crucible with a sealed cover lid, the alumina crucible was loaded in a high temperature furnace. A standard atmospheric pressure was obtained by firstly evacuating the furnace to 60 Pa then pumping within the pure Ar (99.99%) gas. After deposition for 2.5 h, 5 h and 10 h at 1200 °C, the coated samples were taken out of the furnace. The samples were ultrasonically washed for several times in alcohol and then dried at 70 °C for spraying.

2.2.2. Spraying process

The thermal spraying was employed in a high efficiency supersonic atmospheric plasma spraying system. The spraying parameter for producing the outer $MoSi_2$ coating was carried out with the current of 400 A and the voltage of 100 V. The distance between the spray nozzle and substrate was kept at 100 mm. The flow rate of the carrier gas (Ar) and second gas (H_2) was 76 and 1.3 L/min, respectively. The feedstock rate of the $MoSi_2$ powder was 4.0 r/min. The diameter of the spray nozzle was 6 mm. The designed coating structure is illustrated in Fig. 1.

2.3. Oxidation test

The static oxidation behavior of the coating samples was evaluated at 1200 °C in air. The coating specimen was placed in an alumina crucible for a certain period in an electric furnace. Subsequently, the mass of the oxidized sample was obtained by weighing the specimen in an electric balance with a sensitive of ±0.1 mg at ambient environment after taking out of the specimen from the electric furnace. Then, the coated specimens were put into the furnace again for the next cycle. Prior to the oxidation test, the crucible was heated at 1350 °C until no mass change was observed. The mass change rates of the specimens were obtained by calculating the average mass change rates of three specimens. The oxidation curves of the coated specimens were reported as a function of the oxidation time.

2.4. Characterization

The phase composition and microstructure of the as-coated and oxidized specimens were analyzed by X-ray diffraction (XRD, SHIMADZU XRD-7000) and scanning electron microscopy (SEM, Zeiss Supra-55) equipped with an energy dispersive spectroscopy (EDS, Inca X-sight). A 3D confocal laser scanning microscope (Optelics C130, Lasertec Corp., Yokohama, Japan) was used to measure the surface roughness of the HAPC treated substrate.

3. Results and discussion

3.1. Microstructure and phase composition of the as-prepared coating

The phase composition of the siliconized layer as well as the following sprayed layer was analyzed by XRD and the results are shown in Fig. 2. After HAPC process, only $NbSi_2$, with good crystallization can be observed (Fig. 2a) on the surface of the coated samples. The sprayed coating presents pure $MoSi_2$ phase (Fig. 2b), indicating that almost no oxidation of molybdenum and evaporation of silicon in $MoSi_2$ occurred attributed to the use of inert Ar gas as well as the supersonic flame in the thermally spraying process.

Fig. 3 shows the microstructure of the as-prepared coatings, in which two distinguishable layers formed on the niobium alloy substrate. Combined with the phase analysis shown in Fig. 2, the inner layer was detected as $NbSi_2$ and the outer layer should be $MoSi_2$. Several pores left by the spraying existed both in the $MoSi_2$ coating and at the interface between the inner and outer layer. This conforms to the characteristic of the thermally sprayed coatings [24,25]. Especially, from the enlarged view of 2.5 h specimens, local oxidation occurred during plasma spraying. In the EDS patterns (Fig. 4), we can find that small amount of Mo_5Si_3 formed besides $MoSi_2$. The existence of Mo_5Si_3 may result from the reaction $5/7\,MoSi_2 + O_2 = 1/7\,Mo_5Si_3 + SiO_2$. 10 h HAPC specimen shows some cracks in the inner $NbSi_2$ layer, since thick layer may introduce accumulated stress in the coating. Only the sprayed coating on 5 h HAPC treated specimen is dense and relatively free of defect.

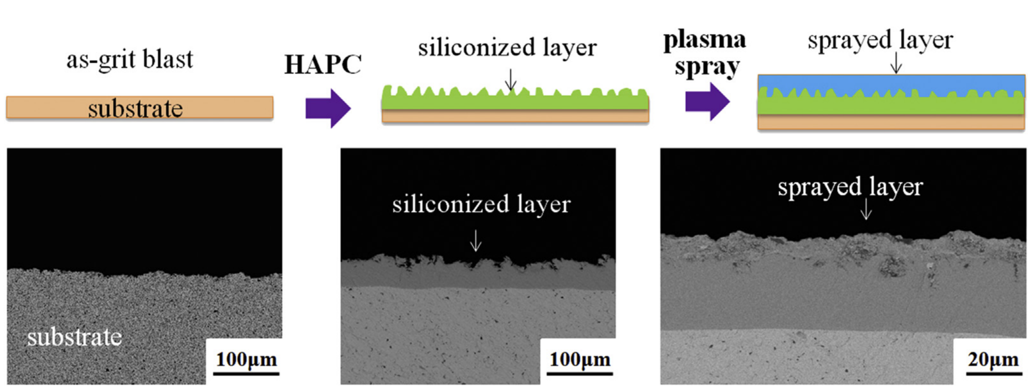

Fig. 1. Designed structure of the coating system used in this work.