Hot corrosion behavior of NbSi$_2$/SiO$_2$-Nb$_2$O$_5$ multilayer coating on Nb alloy

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ABSTRACT

A NbSi$_2$-SiO$_2$-Nb$_2$O$_5$ multilayer coating, consisting of a NbSi$_2$ inner layer and a SiO$_2$-Nb$_2$O$_5$ outer layer, was prepared on Nb alloy through halide activated pack cementation (HAPC) and microarc oxidation (MAO). The hot corrosion behaviors of the single NbSi$_2$ coated and the NbSi$_2$/SiO$_2$-Nb$_2$O$_5$ coated Nb alloys were comparatively investigated with a mixture of Na$_2$SO$_4$/NaCl (3:1 wt.%) salt at 900 °C. The growth kinetics of the corroded scales follow the parabolic laws, and the parabolic rate constants of the NbSi$_2$ coated and the NbSi$_2$/SiO$_2$-Nb$_2$O$_5$ coated specimens were 2.16×10^{-3} mm s^{-2} and 1.04×10^{-3} mm s^{-2}, respectively. During the corroding process, the SiO$_2$-Nb$_2$O$_5$ outer layer that serves as a barrier promotes the formation of continuous SiO$_2$ scale, and isolates the NbSi$_2$ layer from the corrosion salt. The lower corrosion rate of the NbSi$_2$/SiO$_2$-Nb$_2$O$_5$ coated specimens is attributed to the formation of the protective SiO$_2$ corroded scale.

1. Introduction

Nb-based alloys have been considered to be candidate materials to meet the increased inlet temperature of advanced turbine engines [1—3] due to its high melting point, low density and high temperature strength [4,5]. However, Nb-based alloys are subjected to the devastating oxidation at high temperature [6]. Thus, the protective coatings are always necessary for impeding the oxygen penetration. Among various coating systems, silicide coatings fabricated by halide activated pack cementation (HAPC) has been proved with better oxidation resistance performance [7—9]. Despite the recent attempts in improving the oxidation resistance, the combined hot corrosion against molten salts such as Na$_2$SO$_4$, K$_2$SO$_4$, NaCl, KCl etc still remains a challenge.

The hot corrosion accompanied with oxidation degradation has been recognized as a serious problem, in connection with the accelerated attack by the molten salt depositing on the service applications, such as turbine blades [10—12] and combustion chambers [13,14]. It has been demonstrated by Wan Wang et al. that the hot corrosion of Nb-Ti-Si alloy leads to a porous oxide scale in the mixture of Na$_2$SO$_4$ and NaCl melts [15,16]. By contrast, a NbSi$_2$ coating fabricated by HAPC improves the oxidation resistance and retards the corrosion rate compared to the bare alloy [17]. However, the protective property is restricted because a protective corroded scale fails to form in the hot corrosion condition.

It is well known that the hot corrosion of Nb alloy is mainly caused by the alkaline fusion of Na$_2$O, which is decomposed from the mixed molten salt. Furthermore, the formation of the low melting point halide aggravates the corrosion process. We suppose that a ceramic layer is preset on the NbSi$_2$ HAPC layer as a barrier to isolate the molten salt from the NbSi$_2$ layer. It is expected to make some of the corrosion reactions lazy. Microarc oxidation (MAO) process is a good way to fabricate a ceramic coating on Nb based alloy, during which the coating composition is controlled by regulating electrical parameters and types of electrolyte [18—21]. So, it is desirable to fabricate a MAO ceramic coating with compounds which are thermodynamics stable against corrosion salts. It has been reported that employing aluminate-based electrolyte leads to the formation of Al$_2$O$_3$ or aluminate [22], and using silicate-based electrolyte increases the content of Si in MAO coatings [23]. Our recent exploration shows that a compact lamellar MAO coating

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with the components of SiO_2-Nb_2O_5 can be formed in a specially designed silicate-based electrolyte. The lamellar structure, without any micropores across the coating section, might be helpful in providing a good barrier from being corroded during hot corrosion [24].

Therefore, in this work, a multilayer coating, consisting of a $NbSi_2$ inner layer and a lamellar SiO_2-Nb_2O_5 outer layer, was fabricated on Nb alloy through a duplex process of HAPC followed by MAO. The hot corrosion behaviors of the single $NbSi_2$ coated and the $NbSi_2$/SiO_2-Nb_2O_5 coated Nb alloys were comparatively investigated with a mixture of Na_2SO_4/NaCl (3:1 wt.%) salt at 900 °C, and the possible hot corrosion mechanism was proposed.

2. Experimental procedures

2.1. Coating fabrication

The niobium-based alloy (Nb-8.9Hf-1.2Zr) was prepared by vacuum arc-melting. Specimens were machined to the dimensions of 10 mm × 10 mm × 0.5 mm. All the sharp corners and edges of the specimens were chamfered. The specimens were polished with SiC paper up to 1000 grit, and then ultrasonically cleaned in ethanol and dried by a hot air stream.

A multilayer coating, consisting of a $NbSi_2$ inner layer and a SiO_2-Nb_2O_5 outer layer, was prepared on Nb alloy through a duplex process of HAPC followed by MAO. Firstly, the $NbSi_2$ layer was coated by HAPC with the following steps. The chemically pure Si, Al_2O_3 and NaF powders were mixed up at the ratio of 16Si:79Al$_2O_3$:5NaF (wt.%) by tumbling in a ball mill for 4 h. The pack powders were filled in a cylindrical alumina crucible, and then the cleaned specimens were embedded in the pack powders. The crucible was sealed with aluminum phosphate binder, and placed into a tube furnace. The furnace was heated under argon atmosphere with a heating rate of 8 °C min^{-1} up to 1300 °C, held for 8 h at 1300 °C, and then cooled down to room temperature with a rate of 5 °C min^{-1}. The $NbSi_2$ coated specimens were retrieved from the pack powders and ultrasonically cleaned in ethanol. To obtain a multilayer coating with a SiO_2-Nb_2O_5 ceramic barrier layer on the top of the $NbSi_2$ layer, the $NbSi_2$ coated specimens were subjected to MAO treatment in an electrolyte bath of 15 g L^{-1} Na_2SiO_3. The specimens worked as anode, and a steel plate was used as cathode. A 500 V square wave voltage with 600 Hz frequency and 8% duty cycle was applied between the two electrodes for 5 min by a 65 kW MAO device, and the device details can be found in our previous literature [25].

2.2. Hot corrosion testing

The hot corrosion tests were conducted in static air at 900 °C for 100 h. Before the tests, Na_2SO_4 and NaCl with 3:1 wt ratio were firstly mixed in distilled water to obtain a homogeneous salt solution. The single $NbSi_2$ coated and the $NbSi_2$/SiO_2-Nb_2O_5 coated specimens were sprayed with the as-prepared salt solution, and then dried at 200 °C to remove crystal water. Then, repeat spraying and drying of the salt solution on the other side of the specimens. Each specimen was weighed carefully before and after salting by precision analytical balance (CPA225D, Sartorius, Germany) with an accuracy of 10^{-5} g, thus to ensure a salt supplement of 4 mg cm^{-2} on each side of the specimens. The specimens were heated to 900 °C in a muffle furnace with a heating rate of 7 °C min^{-1}. After holding at 900 °C for 2, 5, 10, 20, 50 and 100 h, the specimens were moved out from the furnace respectively. The mass of the salt coated specimens was recorded before and after the hot corrosion test.

2.3. Microstructure characterization

Scanning electron microscopy (SEM; Helios Nanolab600i, FEI, U.S.A.) equipped with an energy dispersive spectroscopy (EDS) was used to characterize the surface and cross-section morphologies. The phase compositions of the coated specimens before and after the coatings were investigated using an X-ray diffractometer (XRD; Empyrean, PANalytical, Netherlands) with a Cu K_α radiation working at 30 mA and 40 kV.

3. Results and discussion

3.1. Characterization of the multilayer coating

Fig. 1 shows the morphology and the XRD pattern of HAPC treated Nb specimen. According to the XRD pattern in Fig. 1 (a), the coating mainly consists of $NbSi_2$ (ICDD PDF No.8-450). The coating surface is smooth. The average grain dimension of the coating is 6.5 μm (Fig. 1 (b)). The white particles on the $NbSi_2$ surface are Al_2O_3 according to the weak characteristic peaks of Al_2O_3 (ICDD PDF No.10-414), which comes from the pack powders by adhesion or the reaction products of the deposited Al atoms with the residual O_2 in the crucible [26].

Fig. 2 shows the surface, cross-section BSE morphologies and XRD pattern of the $NbSi_2$/SiO_2-Nb_2O_5 multilayer coating. The multilayer coating consists of a $NbSi_2$ inner layer (90 μm in thickness) and a MAO outer barrier layer (5 μm in thickness). In addition,
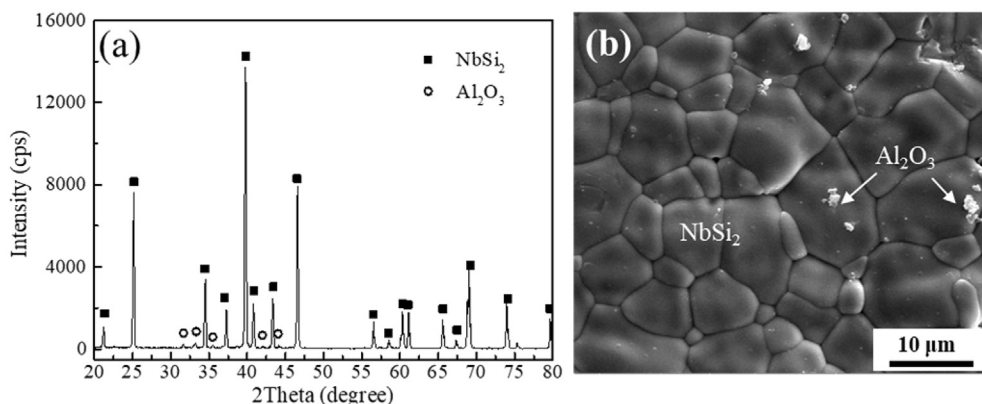
Fig. 1. (a) The XRD pattern and (b) the surface morphology of the $NbSi_2$ coating.