Hot corrosion behavior of NbSi₂/SiO₂-Nb₂O₅ multilayer coating on Nb alloy

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Abstract

A NbSi₂/SiO₂-Nb₂O₅ multilayer coating, consisting of a NbSi₂ inner layer and a SiO₂-Nb₂O₅ outer layer, was prepared on Nb alloy through halide activated pack cementation (HAPC) and microarc oxidation (MAO). The hot corrosion behaviors of the single NbSi₂ coated and the NbSi₂/SiO₂-Nb₂O₅ coated Nb alloys were comparatively investigated with a mixture of Na₂SO₄/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 NbSi₂ coated and the NbSi₂/SiO₂-Nb₂O₅ coated specimens were 2.16 × 10⁻³ mm s⁻² and 1.04 × 10⁻³ mm s⁻², respectively. During the corroding process, the SiO₂-Nb₂O₅ outer layer that serves as a barrier promotes the formation of continuous SiO₂ scale, and isolates the NbSi₂ layer from the corrosion salt. The lower corrosion rate of the NbSi₂/SiO₂-Nb₂O₅ coated specimens is attributed to the formation of the protective SiO₂ corroded scale.

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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 Na₂SO₄, K₂SO₄, 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 Na₂SO₄ and NaCl melts [15,16]. By contrast, a NbSi₂ 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 Na₂O, 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 NbSi₂ HAPC layer as a barrier to isolate the molten salt from the NbSi₂ 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 Al₂O₃ 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 SiO2–Nb2O5 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 NbSi2 inner layer and a lamellar SiO2–Nb2O5 outer layer, was fabricated on Nb alloy through a duplex process of HAPC followed by MAO. The hot corrosion behaviors of the single NbSi2 coated and the NbSi2/SiO2–Nb2O5 coated Nb alloys were comparatively investigated with a mixture of Na2SO4/NaCl (3:1 wt.%). 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 NbSi2 inner layer and a SiO2–Nb2O5 outer layer, was prepared on Nb alloy through a duplex process of HAPC followed by MAO. Firstly, the NbSi2 layer was coated by HAPC with the following steps. The chemically pure Si, Al2O3 and NaF powders were mixed up at the ratio of 16Si:79Al2O3:5NaF (wt.%), tumbled in a ball mill for 4 h. The pack powders were mixed in distilled water to obtain a homogeneous salt solution. To obtain a multilayer coating with a SiO2–Nb2O5 ceramic barrier layer on the top of the NbSi2 layer, the NbSi2 coated specimens were subjected to MAO treatment in an electrolyte bath of 15 g L−1 Na2SiO3. 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, Na2SO4 and NaCl with 3:1 wt ratio were firstly mixed in distilled water to obtain a homogeneous salt solution. The single NbSi2 coated and the NbSi2/SiO2–Nb2O5 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.

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 NbSi2 (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 NbSi2 surface are Al2O3 according to the weak characteristic peaks of Al2O3 (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 O2 in the crucible [26].

Fig. 2 shows the surface, cross-section BSE morphologies and XRD pattern of the NbSi2/SiO2–Nb2O5 multilayer coating. The multilayer coating consists of a NbSi2 inner layer (90 μm in thickness) and a MAO outer barrier layer (5 μm in thickness). In addition,