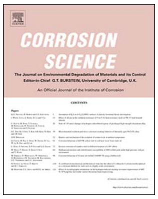
Corrosion Science 133 (2018) 112–119

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Cyclic oxidation behaviour of Co/Si co-doped β-NiAl coating on nickel based superalloys

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ARTICLE INFO

Keywords:
A. Metal coatings
A. Superalloys
B. Thermal cycling
B. TEM
C. Oxidation

ABSTRACT

Co/Si co-doped β-NiAl coating on nickel based superalloys was prepared using pack cementation method. Microstructure and cyclic oxidation behaviour of the coating were investigated. The weight loss of the coating is less than 3 mg/cm^2 after 3200 cycles at 1050 °C. The coating exhibits a good cyclic oxidation resistance. The addition of Si decreases the growth stress in the oxide scale by inhibiting the formation of harmful NiO. The formation of SiO_2 particles at the scale/coating interface decreases the growth rate of the Al_2O_3 scale. Moreover, Si addition promotes the formation of the high Al-content phase β-NiAl.

1. Introduction

For decades, nickel based superalloys have been applied in key hot end components (such as blades and vanes) of modern aeroplane engines and marine turbine engines owing to its attractive mechanical properties at high temperatures [1–7]. The life extension of gas turbine blade is mainly limited by the durability of the materials applied in severely oxidative and corrosive environments [8–13]. As the superalloy substrate does not possess good resistance to oxidation and corrosion, it is necessary that coatings be utilized to protect metallic components used at high temperatures in order to extend their lifetime. Aluminide diffusion coatings have been deemed as the most desirable materials due to the continuous formation of protective Al_2O_3 scales [14–17]. However, cracks and premature spallation of oxide scales could occur in aluminide coatings during cyclic oxidation process at elevated temperatures [18].

Recently, aluminide coatings which were modified by adding some elements such as Co, Cr, Si, Pt or Hf [19–29] have been achieved to enhance the oxidation and hot corrosion resistance in brutal environments. It has been reported that Co modified aluminide coating exhibited good isothermal oxidation and hot corrosion resistance at high temperatures because the addition of Co increased the adhesion of oxide scale and restrained the internal diffusion of sulfur in the coating [22,30,31]. However, the cyclic oxidation resistance of single Co modified aluminide coating was proved poor owing to the spallation of the oxide scale at high temperatures [32]. Therefore, some researchers considered co-doping of Co and other elements such as Y, Ce, Si and Hf or their oxides, which could contribute to the formation of protective oxide scale and the improvement of oxide scale adherence [33–36].

It has been reported that the addition of Si into Ni-Al coatings or nickel based alloys could improve both the cyclic oxidation and hot corrosion resistance [37–39]. Gong [37] et al. prepared two-layer structural TBCs with MCrAlYSi and MCrAlY bi-layer bond coat on Ni_3Al based alloy IC6 and found that the thermal cycling behaviour of the TBCs was greatly improved. The reason was that by using MCrAlYSi layer with the addition of 0.5 wt.% Si into MCrAlY, the diffusion of Mo into the protective coating was effectively suppressed and no Si was found at the interface of bond coat and top coat. Li et al. [40] found that the cyclic oxidation resistance of the nickel based alloy 45TM was improved significantly with Si addition. The mechanism was that a discontinuous distribution of SiO_2 precipitates in the vicinity of the alloy/scale interface not only caused a decrease in the growth rate of the Cr_2O_3 scale, but contributed to good scale adherence during cyclic oxidation. The work done by Dai [41] et al. showed that the Si addition retarded the inter-diffusion of elements between NiAlHf coating and the substrate due to a barrier diffusion effect. As a result, the oxidation resistance of the NiAlHf coating was improved obviously. The addition of Si could boost the cyclic oxidation resistance of NiCrAlY coating after a long exposure time, as Si had a beneficial effect on oxide scale adherence and suppressed the formation of metastable Al_2O_3 [42]. He [43] et al. investigated the hot corrosion behaviour of the Co/Si co-doped β-NiAl coating exposed to the mixed molten salt (75 wt.% Na_2SO_4 + 25 wt.% NaCl) at 900 °C for 100 h. The result demonstrated that Si could enhance the hot corrosion resistance by improving the

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https://doi.org/10.1016/j.corsci.2018.01.032
Received 21 April 2017; Received in revised form 30 December 2017; Accepted 19 January 2018

formation of Al_2O_3 scale and preventing the rapid corrosion attack of the mixed salt. However, the cyclic oxidation behaviour of the Co/Si co-doped β-NiAl coating prepared by pack cementation method on nickel based superalloy DZ125 has not been studied so far. The motivation of the present study is to explore the role of Si during the cyclic oxidation of the Co/Si doped β-NiAl coatings.

In this paper, the Co/Si co-doped β-NiAl coating was prepared on nickel based superalloy DZ125 using a pack cementation method and cyclic oxidation behaviour of the coating was studied. The effects of Si addition on Co-modified aluminide coating microstructure, the cyclic oxidation product and the cyclic oxidation dynamics curve were investigated. Besides, the influence mechanism of Si addition on the cyclic oxidation resistance was discussed.

2. Experiment

2.1. Materials

The nickel based superalloy DZ125 provided by Beijing Institute of Aeronautical Materials was used as the substrate material in the present study and its nominal alloy composition was 63.5Ni, 6.2Co, 8.9Cr, 7.0W, 6.1Al, 3.8Ta, 2.0Mo, 1.5Hf and 1.0Ti (in wt.%). Samples were cut into small coupons with the dimensions of 12 mm in diameter and 3 mm in thickness by wire-electrode cutting. Then all the surfaces of the samples were ground with SiC abrasive papers to 800-grit. Before the coating deposition, the specimens were ultrasonically cleaned in acetone and alcohol for 20 min.

2.2. Coating preparation

The pack cementation method was used to deposit the Co/Si co-doped β-NiAl coating on the surface of nickel based superalloy. For comparison, the Co doped β-NiAl coating was prepared using the same process. In this process, the compositions of the pack powder used for co-deposition were listed in Table 1.

The halide salt NH_4Cl acted as the activator, and the alumina powder was used as the inert filler. Each powder used for co-deposition was accurately weighed by an analytical balance according to the proportion listed in Table 1 and then ground with a mortar and pestle for 30 min. Subsequently, the specimens were buried in the well-mixed pack powder in a cylindrical alumina retort of 20 mm in diameter and 35 mm in length. After that, the retorts containing the mixed powders and specimens were placed in a tubular resistance furnace, which was flushed with argon gas in order to protect the specimens from being oxidized during the whole process. The prepared samples were heated to 1050 °C with a heating rate of 5 °C min^{-1}. After holding for 10 h at 1050 °C, the samples were slowly cooled down in the furnace to room temperature. The coated specimens were removed from the retorts and ultrasonically cleaned in alcohol solution for later use. All the detailed experimental procedures were also presented in the previous papers [33–36,44,45].

2.3. Cyclic oxidation test

An open-ended tube furnace with an automatic discontinuation procedure was used under atmospheric pressure to evaluate the cyclic oxidation behaviour of the Co/Si co-doped β-NiAl coating. In order to reduce experimental error, three parallel specimens were used in each cyclic oxidation test. Before the test, the original weight of each sample was measured by an analytical balance (Model BS 224S Sartorious, Germany) with an accuracy of 0.1 mg. Each specimen was placed in a small square alumina crucible separately and then all the small square alumina crucibles were put into a big square alumina crucible so that the specimens could be taken out easily. During the test, each cycle consisted of heating the samples at 1050 °C in the furnace for 50 min and cooling outside the furnace with a cooling fan at room temperature for 10 min. Weight changes were measured without the alumina crucible after each cooling period because of the possible spallation of loose oxide scale during the cooling process. For comparison, the cyclic oxidation test for the Co doped β-NiAl coating was also performed simultaneously.

Table 1
Compositions of compound pack mixtures used for co-deposition.

Samples	Pack (wt.%)				
	Co	Al	Si	NH_4Cl	Al_2O_3
Co doped β-NiAl coating	20	7.6	–	4	68.4
Co/Si co-doped β-NiAl coating	20	7.6	2	4	66.4

2.4. Analyzing methods

The surface phase constitutions of the coated samples and oxidized samples were examined by X-ray diffraction in the range 2θ = 20–90° with a step size of 0.02° (XRD, Model D/Max 2500PC Rigaku, Japan: Cu Kα radiation). Scanning electron microscopy (SEM) (Model FEI Quanta 600, USA) with energy dispersive spectrometer (EDS) system and electron probe micro-analyzer (EPMA) (Model JEOL JXA-8230) with wavelength dispersive spectrometer (WDS) system were utilized to characterize the chemical compositions and microstructures of the coatings and the oxide scales. A transmission electron microscope (TEM, JEOL 2010) equipped with a tracer EDS detector was used to analyze the precipitates in the coating.

3. Results and discussion

3.1. Coating characterization

Fig. 1 shows the cross-sectional images Cross-sectional SEM images and major elemental concentration profiles of the coatings. From Fig. 1(a) and (b), it can be observed that both of the coatings consist of two layers, including an outer layer and a diffusion zone. Fig. 1(a) shows that the depths of the outer layer and the diffusion zone of the Co doped β-NiAl coating are approximately 20.8 μm and 16.7 μm, respectively. Fig. 1(c) illustrates that the element distribution of the outer layer is 28.80Al, 1.77Cr, 13.68Co, 55.75Ni (in wt.%) and that of the diffusion zone is 12.62Al, 18.01W, 10.66Cr, 10.91Co, 47.80Ni (in wt.%) as analysed by WDS. Fig. 1(b) indicates that the depths of the outer layer and the diffusion zone of the Co/Si co-doped β-NiAl coating are approximately 21.1 μm and 19.3 μm, respectively. According to the results of WDS, the element distribution of the outer layer is 22.34Al, 0.85Si, 3.76Cr, 9.33Co, 62.69Ni (in wt.%) and that of the diffusion zone is 14.21Al, 0.98Si, 8.24W, 8.98Cr, 12.18Co, 55.41Ni (in wt.%) as seen in Fig. 1(d). It can be seen that the thickness of the outer layer for the Co/Si co-doped β-NiAl coating is larger than that for the Co doped β-NiAl coating and the thicknesses of the diffusion zone for the two coatings are similar.

Cross-section TEM image of the outer layer of the Co/Si co-doped β-NiAl coating is shown in Fig. 2(a). The corresponding EDS analysis reveals that the chemical composition of area A is 52.42Ni-12.81Co-7.83Si-26.93Al (at.%). Fig. 2(b) presents SAED pattern of the outer layer of the Co/Si co-doped β-NiAl coating. According to the SAED pattern, it can be calculated that the space group of the area A is Pm–3 m (221) with cell parameters of a = b = c = 2.907 nm, which is consistent with the space group and cell parameters of $Al_{0.9}Ni_{1.1}$ (PDF-44-1185. The standard cell parameters of $Al_{0.9}Ni_{1.1}$ are a = b = c = 2.877 nm). The result suggests that no Co-containing phases and Si-containing phases exist, indicating that some of the Ni atoms are replaced by Si and Co in the $Al_{0.9}Ni_{1.1}$ phase.