Corrosion Science 80 (2014) 19–27

Contents lists available at ScienceDirect

Corrosion Science

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

High-temperature oxidation resistance of (Al_2O_3–Y_2O_3)/(Y_2O_3-stabilized ZrO_2) laminated coating on 8Nb–TiAl alloy prepared by a novel spray pyrolysis

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ARTICLE INFO

Article history:
Received 22 February 2013
Accepted 30 August 2013
Available online 7 September 2013

Keywords:
A. Titanium
B. Thermal cycling
B. SEM
C. Oxidation
C. Oxide coatings

ABSTRACT

A novel spray pyrolysis with two-step cycles has been developed to fabricate (Al_2O_3–Y_2O_3)/(Y_2O_3-stabilized ZrO_2) (YSZ) laminated coating on 8Nb–TiAl alloy for resisting high-temperature oxidation. And a crack-free structure, except in the top sub-layer, has been established ultimately, with interlocking adhesion between the layers of coating. It is shown, from cyclic oxidation at 1000 °C, that 8Nb–TiAl alloy with laminated coating exhibits superior oxidation and spallation resistance. These beneficial effects can be attributed to the compact structure, the suppression of oxygen diffusion in Al_2O_3–Y_2O_3 layers, the decrease of thermal stresses and the increase of fracture toughness in such laminated coating.

1. Introduction

TiAl alloys have been considered of growing interest as high-temperature structural materials due to their numerous attractive comprehensive properties including low density, high specific strength, high elastic modulus and good creep resistance up to high temperature. With the development of aerospace and power generation, high-temperature structural materials require lower density or higher service temperature, which bring about more research values for TiAl alloys [1–7]. Nevertheless, poor high-temperature oxidation resistance over 800 °C may become a limiting factor for the practical applications of TiAl alloys largely [8]. Generally, metallic materials are protected against high-temperature oxidation by the formation of protective oxide scales such as Cr_2O_3, SiO_2 or Al_2O_3. However, at elevated temperatures, TiAl generally cannot form continuous Al_2O_3 scale, but a mixed scale consisting of TiO_2 and Al_2O_3 [9]. Therefore, extensive studies on improving the high-temperature oxidation resistance of TiAl alloy have been carried out within the past decades. Adding different beneficial alloy elements such as Nb, Mo and W to the alloy is one of the commonly accepted solutions [10,11]. Besides, coatings such as alloy coatings and ceramic coatings, have been applied on TiAl alloy to ensure long-term stable application at high temperature [12–14].

For alloy coatings on TiAl alloy, an Al_2O_3 scale is normally formed on the surface of alloy coating. However, the elements interdiffusion must take place at the interface between the coating and TiAl alloy. This could lead to the degradation failure of alloy coatings ultimately. While, for ceramic coatings, they can protect the alloy effectively against the inward diffusion of oxygen at elevated temperatures. And there is no interdiffusion at the interface between the coating and alloy, which is beneficial to maintain the mechanical properties of TiAl alloy. However, cracking and spallation of ceramic coating with a single phase cannot be avoided completely due to the excessive stresses generated at high temperature [15].

Composite ceramics, especially multilayered composite ceramics, have been demonstrated to improve their fracture toughness effectively by means of energy release mechanism, such as crack deflection or crack bifurcation [16,17]. Thus, multilayered composite ceramics have been developed as an alternative choice for the design of structural ceramics with high stresses tolerance [18]. Given this tendency, the multilayered ceramic coatings have been considered of growing interest for the high-temperature protection of alloy [19,20]. In recent years, multilayered Al_2O_3/ZrO_2 composite coatings have been well developed to improve their mechanical properties and exhibit good resistance to cracking and spallation [21–23].

So far, numerous techniques have been developed to fabricate ceramic coating, including chemical vapor deposition (CVD) [24,25], evaporation and sputtering [26], electrophoretic deposition [27], sol–gel [28], electro-deposition [29] and spray

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0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.08.029

pyrolysis [30]. Among these techniques, spray pyrolysis is well-acknowledged as one of the simplest techniques for coating fabrication. It requires only a liquid source, atomization device, air supply, conduit tube, and heated substrate surface [31]. Many studies have been done over about half century on spray pyrolysis processing and fabrication of thin films, since the pioneering work of Chamberlin and Skarman [32] in 1966 on cadmium sulfide (CdS) films for solar cells. But generally, it is difficult to obtain a compact coating with enough thickness using spray pyrolysis method [33]. The porous and cracking structure of such coatings may limits their application in the fields of high-temperature protection of alloys [34].

The spray pyrolysis process can be divided into three main procedures including the atomization of precursor solution, the transport of droplets onto the heated sample by carrier gas and the pyrolysis of coating on heated substrate, although they are performed at the same time approximately. In order to obtain good property of coating fabricated by the spray pyrolysis technique, increasing attention has been paid to improve the above-mentioned procedures. For the atomization of precursor solution, various atomization modes have been developed, including pressure atomization, ultrasonic atomization, electrostatic atomization and so on [35,36]. For the transport of droplets, an electrostatic field with high voltage can be applied to assist this process [37]. And many influence factors on the pyrolysis of coating have been also studied, such as substrate temperature, type of metal salt, salt saturation and organic solvent in the precursor [38–40]. However, in all of the above-mentioned spray pyrolysis techniques, both spray and pyrolysis are carried out at the same time and little attention is paid on the change of such procedures.

It has been known that, in spray pyrolysis, intensive cracking and delaminating are induced by the stress in the coating caused by the dehydration and decomposition of large amount of reactants [41]. In order to fabricate compact and thick coating, the spray pyrolysis process is assumed to be divided into numerous cycles, so that the defects formed in every cycle can be healed up well in the next cycle. In this work, a novel ultrasonic spray pyrolysis with such cycles is proposed to fabricate compact (Al_2O_3–Y_2O_3)/(Y_2O_3-stabilized ZrO_2) (YSZ) laminated coating. Every cycle in this process includes two steps: firstly spraying at a low temperature, then pyrolysis and sintering at a high temperature. The defects formed in pyrolysis process could be infiltrated by the wet spreading droplets in the spraying process. Consequently, a compact structure with some micro-cracks on the surface could be obtained in the laminated coating. And, the effect of such laminated coating on high-temperature oxidation resistance of 8Nb–TiAl alloy will be investigated and the mechanisms accounting for such effects will be discussed.

2. Experimental procedure

2.1. Substrate pre-treatment

8Nb–TiAl alloy (8% Nb, 45% Al, 0.1% Y, 0.2% W, balance Ti, wt.%) was used as the substrate. The plate samples (15 mm × 10 mm × 2 mm) were ground using SiC paper up to a grit of #2000, and ultra-precision polished (Ra = 0.03 μm). Then the substrates were ultrasonic cleaned in acetone and ethanol, respectively, and cleaned by ionized water at last.

2.2. Preparation of the coatings

Al_2O_3–Y_2O_3 coating, YSZ coating and (Al_2O_3–Y_2O_3)/YSZ laminated coating were fabricated on 8Nb–TiAl alloy respectively by the ultrasonic spray pyrolysis with two-step cycles. The apparatus used for preparing such coatings consists of an ultrasonic atomization chamber with a transport nozzle and a resistance furnace. The precursor solution for preparing Al_2O_3–Y_2O_3 layers was $Al(NO_3)_3$ and $Y(NO_3)_3$ aqueous solution, with a molar ratio of 1:0.01 for Al^{3+}/Y^{3+} and a total concentration of 0.05 mol/L. The precursor solution for preparing YSZ layers was $Zr(NO_3)_4$ and $Y(NO_3)_3$ aqueous solution, with a molar ratio of 1:0.16 for Zr^{4+}/Y^{3+} and a total concentration of 0.05 mol/L.

Before the cycles begin, the sample was heated to 480 °C on resistance furnace and then removed from the furnace. In the first step, the hot sample was placed opposite the transport nozzle of an ultrasonic atomization chamber for depositing coating, with the distance of 30 mm and a spraying flow of 5 L/min. When the temperature of sample was decreased to 100 °C (measured by K-type thermocouple) by natural cooling, the spray process stopped. In the second step, the sample was replaced on the resistance furnace for heat treatment. The times of these two steps in one cycle were 30 s and 120 s respectively. The thickness of coating was estimated by the weight gain. With repeated cycles of these two steps, Al_2O_3–Y_2O_3 coating, YSZ coating and (Al_2O_3–Y_2O_3)/YSZ laminated coating were fabricated ultimately. At last, the coatings were sintered at 850 °C for 2 h.

2.3. High-temperature cyclic oxidation test

Cyclic oxidation test was carried out in a tube type resistance furnace at 1000 °C in air for 200 h. After a certain oxidation period of 10 h, samples were taken out and rapidly cooled down to room temperature. And then the weight gain (crucible with sample) and spallation (crucible without the sample) of samples were weighed by an electronic balance with an accuracy of 10^{-5} g. After that, the samples were put back to the furnace again for another cycle. The test providing 20 times thermal cycles was applied to evaluate the oxidation resistance and mechanical properties of the coatings.

2.4. Characterization

The surface and cross-section morphologies of coatings and elements maps were observed by a scanning electron microscope (SEM, JSM-6510) equipped with an energy dispersive spectroscopy (EDS) system. Phases in the coatings were characterized by X-ray diffraction (XRD, Cu Kα, PW 3710, Philips, step wise of 0.02°, continuous scanning) in the 2θ range of 20–80°.

3. Results

3.1. Microstructure of the as-prepared coatings

Fig. 1 shows the surface and cross-section morphologies of the as-prepared Al_2O_3–Y_2O_3 coating, YSZ coating and (Al_2O_3–Y_2O_3)/YSZ laminated coating. From Fig. 1a and c, it can be seen that there are many micro-cracks on the surfaces of coatings which are induced by the volume decrease of the as-deposited sub-layer in last cycles during the dehydration and decomposition. While, no obvious micro-cracks can be observed in Fig. 1e. This can be attributed to the wide cracks openings which may be formed along with the dehydration and decomposition of thin sub-layer, resulting in the slightly rough surface as shown in Fig. 1e. However, from Fig. 1b, d and f, it is demonstrated that the cross-section morphologies of three coatings show a compact and crack-free structure in these coatings. Based on these results, it can be supposed that the micro-cracks only formed in the top sub-layers of such coatings. Furthermore, all the coatings have good adhesion with 8Nb–TiAl alloy since no delaminating or cracks have been detected at the coating–substrate interfaces. It can be observed in Fig. 1f that there