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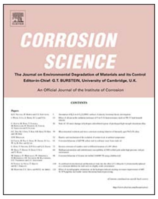

Hot corrosion behaviour of single-phase platinum-modified aluminide coatings: Effect of Pt content and pre-oxidation

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ABSTRACT

Hot corrosion behaviour of nickel-based aluminide coatings with different thicknesses of initial Pt plating was evaluated in the Na_2SO_4/NaCl (75:25, wt./wt.) salt mixture at 900 °C. Compared to plain aluminide, the Pt-modified coatings showed better hot corrosion resistance by hindering the outward diffusion of undesirable elements from the substrate alloy. Pre-oxidation was confirmed to be capable of preventing molten salt from accessing the alloy surface and reversibly dissolving the oxide scale. Oxide growth and dissolution, acting as two competitive processes, occurred simultaneously and had an important impact on the entire performance of the Pt-modified aluminide coatings in hot corrosion.

1. Introduction

Nickel-based superalloys are widely used as key structural components for high temperature applications such as airfoils and vanes [1]. However, catastrophic hot corrosion of the materials will occur when they are serviced under conditions where salts could be ingested, i.e., at coastal areas and regions with high levels of airborne pollutants. To improve high temperature oxidation and hot corrosion resistance, either a diffusion or an overlay metallic coating able to form a continuous, adherent and slow-growing oxide scale has been applied on the superalloy surfaces. Among these coatings, the diffusion coating of nickel aluminide is the most widely used owing to its advantages, such as low cost, easy processing and a satisfactory protection against high temperature oxidation and hot corrosion [2,3]. However, a conventional β-phase nickel aluminide coating will easily transform to γ'-Ni_3Al (less protective) when Al is heavily consumed by formation/reparation of alumina and inward diffusion to the substrate. Thus, improvement/modification of β-NiAl coating is necessary for survival in harsher environments.

The addition of modifying elements such as Pt, Si, Cr, and Co and reactive elements (REs) to the coating system with the purpose of either stabilising the constituent phase or enhancing the adhesion of oxide scale is a practical and efficient approach for improving the high temperature performance of NiAl [4–11]. Among these elements, synergistic effects were observed upon Pt-modification by promoting selective oxidation of Al, enhancing adhesion of the alumina scale, relieving the detrimental effects of S and preserving more Al owing to its strong affinity to Al [12–17]. Our recent works indicated that the Pt-modified β phase nickel aluminide coatings exhibited better resistance than the plain aluminide coating of β-NiAl in isothermal and cyclic oxidation tests at 1100 °C [18,19], where the advantages were mainly attributed to the alleviation of the spallation tendency of alumina scale.

Unlike for the oxidation behaviour at higher temperature, the research of Pt-modified aluminide coatings under hot corrosion circumstance has been limited, even though platinum aluminide coatings were observed to have superior resistance against Type I hot corrosion compared to the simple aluminide coatings [20–22]. Similar results for Pt in improving the hot corrosion resistance of NiAl have also been reported by Lai [8] and Task et al. [23]. However, Leyens et al. [24] showed that Pt had either little or even a detrimental effect on Type I hot corrosion resistance when the content of Pt in NiAl was 2 at.%; thus, the beneficial effect of Pt is currently controversial. It is well-accepted that hot corrosion of gas turbine material is mainly caused by the products of fuel combustion that contains considerable amounts of sulfur, sodium, vanadium, chlorine, potassium, etc. [25–27]. A mixture of these contaminants makes the environment very corrosive at temperatures above the melting point of the pollutants, further accelerating the oxidation process (namely, Type I hot corrosion).

Although Pt-modified nickel aluminide has been widely regarded as a promising coating candidate to protect gas turbine blades from

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aggressive oxidation attacks, the operation pattern and service conditions enable the occurrence of hot corrosion. Thus, it is necessary and meaningful to conduct an in-depth study on how the modification of Pt changes the hot corrosion behaviour of β-phase nickel aluminide coatings, especially the degradation mechanism of the coating samples with different Pt contents. In the present work, single phase Pt-modified aluminide coatings of (Ni,Pt)Al were prepared by Pt-electroplating and 'above-pack' aluminisation treatments. The coating specimens deposited with various thicknesses of Pt (0, 2, 5 and 8 μm) and processed under the same aluminisation manner were repeatedly examined in hot corrosion tests at 900 °C using the Na_2SO_4/NaCl (75:25, wt./wt.) salt mixture. The benefits of Pt and the effect of the Pt content on the hot corrosion behaviour of nickel-based aluminide coating were investigated. An additional effort was dedicated to clarify the influence of pre-oxidation on the subsequent hot corrosion behaviour, in which the pre-oxidation had a noticeable impact on the first contact of salt on the coating surface.

2. Experimental details

A first-generation Ni-based single-crystal superalloy (PWA1483) with the composition of 12 Cr, 9 Co, 3.7 W, 1.9 Mo, 5 Ta, 3.6 Al, 4 Ti, minor C and balance Ni (wt.%) was used as the substrate material. Disk-shape specimens with the thickness and diameter of 2 and 15 mm respectively were cut from a ⟨001⟩-orientated crystal rod using a spark discharging machine. A hole of diameter 1.7 mm was cut near the edge of the samples for the convenience of being hung during the coating preparation and the hot corrosion test. The bare samples were ground with a final 400# SiC paper finish and sand-blasted using alumina grit, followed by degreasing in boiling NaOH solution (50 g/L) for 10 min and ultrasonically cleaning in acetone and ethanol, respectively. Then, the Pt-modified aluminide coatings were prepared on the samples by depositing a thin layer of Pt followed by aluminisation on the Pt-plating.

Deposition of Pt plating on superalloy samples was achieved by electroplating in an acid solution of $K_2[Pt(NO_2)_2SO_4]$ at 65 °C with the effective Pt concentration of 10–15 g/l, while the electroplating current was set to 1 A/dm^2 to obtain the deposition rate of ~2 μm/h. The $K_2[Pt(NO_2)_2SO_4]$ solution was obtained by the following steps: (1) Pure K_2PtCl_6 powder of 5 g was loaded into a 500 ml beaker that was already filled with 200 ml deionised water, followed by heating the beaker to 80 °C with the dropwise addition of the saturated KNO_2 solution to obtain needle-like $K_2Pt(NO_2)_4$ crystals; (2) Droplets of diluted H_2SO_4 (5 mol/l) were added into the solution containing $K_2Pt(NO_2)_4$ sediments, and a clean $K_2[Pt(NO_2)_2SO_4]$ solution was obtained until all crystals were dissolved. During the preparation, the solution was kept at 200 ml and a magnetic stirrer was used at the speed of 30 r/min to accelerate the dissolving process. Prior to Pt electroplating, the pH value of the $K_2[Pt(NO_2)_2SO_4]$ solution was adjusted to 1–2 by adding more diluted H_2SO_4.

To remove the residual stress and the hydrogen gas generated by Pt-electroplating, an annealing treatment in vacuum ($< 6 \times 10^{-3}$ Pa) was conducted on the samples coated with Pt plating. Aluminisation of the samples was carried out at 1060 °C for 6 h in a gaseous aluminisation furnace (pre-vacuumed to 10 Pa and filled with high purity Ar) in the high temperature low activity (HTLA) manner (namely, "above the pack" treatment). The aluminising pack in the current study was composed of 96 wt.% commercially available Fe-50Al (wt.%) and 4 wt.% NH_4Cl (analytically pure) powders. Prior to the aluminisation, a strict dehydration treatment at 120 °C for 24 h was applied to the aluminising pack. The heating rate for the aluminisation treatment was controlled to be below 8 °C/min. Finally, single phase Pt-modified aluminide coating samples with different Pt plating thicknesses (0, 2, 5 and 8 μm) were obtained with the thicknesses ranging from 45 to 55 μm.

A salt mixture (25 wt.% NaCl + 75 wt.% Na_2SO_4) with the melting point of 645 °C was used for the corrosion test. Hot corrosion behaviour of the coating samples was tested cyclically in a muffle furnace at 900 °C in static air; for these conditions, the corrosion test was consistent with Type I hot corrosion. Each hot corrosion cycle was started by depositing 1.5 ± 0.5 mg/cm^2 salt film onto the surface of coating samples preheated on an aluminium tab, followed by hanging the samples onto a framework made of a Ni-Cr wire (3 mm in diameter). Then, the samples were loaded into a muffle furnace with the Ni-Cr framework together. To avoid a boosted corrosion attack, the saturated aqueous salt solution was painted on the surface area sufficiently far away from the hanging hole. After a time interval of 20 h (2, 5 and 10 h in initial stage), the coating samples were taken out from the furnace and cooled down to room temperature. Subsequently, a careful washing treatment was applied to the corroded samples in boiling deionised-water for 30 min. After the specimens were completely dried, the mass of each sample was measured using an electronic balance (Sartorius BP211D with sensitivity of 0.01 mg). For greater experimental accuracy, three parallel samples of each coating were used in the hot corrosion test for obtaining average values of mass change. Since the mass measurement was carried out after washing away the residual salt and the loose corrosion products, only the weight change of adherent corrosion products and oxides is reflected in these data. After weighing, a fresh salt film was recoated prior to the next hot corrosion cycle. Experimental steps of the current hot corrosion test were the same as those reported in a recent publication [28].

To investigate the effect of pre-oxidation, the coating samples of 5 and 8 μm Pt were oxidised at 1100 °C for 20 h to form a pure, continuous and dense alumina scale. Then, the pre-oxidised samples underwent identical hot corrosion tests at 900 °C for 20 h. The salt deposition manner and the steps of the hot corrosion test were the same as those of the as-received Pt-modified aluminide coating samples.

Phase constitution after hot corrosion of the coating specimens was examined using an X-ray diffractometer (XRD, X' Pert PRO, PANalytical, Almelo, Holland). Surface and cross-sectional morphologies were characterised using a field-emission scanning electron microscope (SEM, Inspect F50, FEI Co., Hillsboro, OR) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford Instruments Co., Oxford, U.K.). Unless otherwise specified, a secondary electron mode was used to examine the surface morphology, and a back-scattered electron mode was adopted to observe the cross-sectional images of the coating samples. Elemental distributions of the 5 and 8 μm Pt coating samples after hot corrosion for 300 h were carried out using an electron probe micro-analyser (EPMA-1610, Shimadzu, J.P.). For preserving the corrosion products, all samples used for cross-sectional observation were deposited with a thin layer of electroless Ni-plating and mounted in resin.

3. Results

3.1. Hot corrosion kinetics

As reported previously, all coatings deposited with 0, 2, 5 or 8 μm Pt after the sequential treatments of vacuum annealing and above-pack aluminisation were composed of an outer zone (OZ) of β- NiAl/(Ni,Pt)Al and an underlying interdiffusion zone (IDZ). Detailed microstructure of the as-received coatings was reported previously [19].

Fig. 1 shows the mass change of each coating during the hot corrosion test at 900 °C in Na_2SO_4/NaCl (75:25, wt./wt.). For the aluminide coating without Pt-modification (0 μm Pt), a rapid increase of mass change is observed until 40 h. Then, the mass change switched to a rapid mass loss owing to the occurrence of scale spallation/dissolution. Although the mass change of 0 μm Pt coating exhibited a quite negative value at 100 h, visual observation of the sample surface indicated that the hanging holes (less protected and more susceptible to corrosion attack) were stuffed by corrosion products. In comparison, the Pt-modified aluminide coatings evidently show a better corrosion

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