Corrosion Science 53 (2011) 3813–3820

Contents lists available at ScienceDirect

Corrosion Science

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

Short-term oxidation resistance and degradation of Cr_2AlC coating on M38G superalloy at 900–1100 °C

J.J. Li [a,b], M.S. Li [a,*], H.M. Xiang [a,b], X.P. Lu [a,b], Y.C. Zhou [a]

[a] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100039, China*

ARTICLE INFO

Article history:
Received 22 April 2011
Accepted 16 July 2011
Available online 22 July 2011

Keywords:
A. Ceramic
A. Sputtered films
C. Oxidation
C. Internal oxidation

ABSTRACT

High temperature oxidation behavior of the Cr_2AlC coating was investigated at 900–1100 °C. During the oxidation, a continuous Al_2O_3 scale formed, resulting in the improvement of the oxidation resistance of the substrate. Meanwhile, the oxidation induced depletion of Al within the Cr_2AlC coating resulted in the transformation of Cr_2AlC to Cr–C phases. Compared with bulk Cr_2AlC, the Cr_2AlC coating possessed similar oxidation behavior, but with higher oxidation rate. This is because a great number of columnar grain boundaries existed in the as-deposited coating, through which oxygen and nitrogen could diffuse inwardly, resulting in the internal oxidation and nitridation.

1. Introduction

The superior mechanical performance and good high temperature corrosion resistance of Ni-based superalloys make them favorite materials as hot components (such as blades or vanes) in industrial gas turbines [1]. However, in these working conditions, the presence of combustion gases constitutes an extreme environment, so that oxidation and hot corrosion are inevitable. Ni-based superalloys are not able to totally meet the requirements of both superior mechanical property and high temperature corrosion resistance. Therefore, it is indispensable to develop high temperature protective coatings. Generally, the high temperature oxidation resistance mainly depends on the presence of Al in the coatings to form an adherent and compact alumina scale, while the incorporation of Cr can promote the formation of Cr_2O_3 and improve the hot corrosion resistance of the coatings [2]. Thus, Cr and Al containing coatings, such as MCrAlY (M = Ni, Co or NiCo), are widely used to protect superalloys from oxidation and hot corrosion at elevated temperatures.

In recent years, Cr_2AlC has received broad attention as one of main $M_{n+1}AX_n$ phases (where M is an early transition metal, A is an A-group element, X is either C or N, and $n = 1$–6 [3–5]), due to its good oxidation and hot corrosion resistance [6–14]. Lin et al. [7,8] prepared bulk Cr_2AlC by an in situ reaction/hot pressing method and investigated its high temperature oxidation and hot corrosion behavior. They found that a protective Al_2O_3-rich scale could form during oxidation up to 1300 °C and hot corrosion in molten Na_2SO_4 salt, which endows Cr_2AlC excellent oxidation and hot corrosion resistance. In addition, compared with other kinds of oxidation resistant binary carbides or nitrides, such as SiC and Si_3N_4, Cr_2AlC possesses matched thermal expansion coefficient (TEC) to normal alloys (the TEC value of Cr_2AlC is $13.3 \times 10^{-6}\ K^{-1}$ in the range of 30–1200 °C [9]), which is beneficial for reducing the thermal stress and then improving cracking and spallation resistance of Cr_2AlC as a coating on superalloys. Meanwhile, other superior properties of Cr_2AlC also involve excellent thermal shock resistance and damage tolerance [3–5]. Therefore, aiming to develop a new high temperature corrosion resistant coating, Cr_2AlC coating has been fabricated by several researchers [15–18]. Schneider et al. [15] first deposited Cr_2AlC film by magnetron sputtering on Si (1 1 1) wafer, Walter et al. [17] successfully acquired large-scale Cr_2AlC film on steel. In our previous work [18], Cr_2AlC coating was deposited on a Ni-based superalloy (commercial brand M38G) at 370 °C and 500 °C using magnetron sputtering from a sintered Cr_2AlC target. The Cr_2AlC coating possessed a strong (1 1 0) preferential orientation and its microstructure was clearly affected by the deposition temperature. The coating deposited at 500 °C was composed of single-layered polycrystalline Cr_2AlC, but became a triple-layered structure involving an amorphous sub-layer when the deposition temperature was 370 °C. Although the preparation process and microstructure of Cr_2AlC coating have been explored, seldom work has been focused on its high temperature corrosion behavior. Recently, Wang et al. [19] deposited Cr_2AlC coating on Ti6242 alloy and investigated its oxidation behavior at 700–800 °C. Similar to bulk Cr_2AlC, Cr_2AlC coating also possessed good isothermal and cyclic oxidation resistance in this temperature range.

---

[*] Corresponding author. Tel.: +86 24 23971145; fax: +86 24 23891320.
E-mail address: mshli@imr.ac.cn (M.S. Li).

0010-938X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.corsci.2011.07.032

In the present work, the oxidation behavior of the single-layered polycrystalline Cr_2AlC coating, deposited on a Ni-based superalloy at 500 °C using magnetron sputtering, was investigated at 900–1100 °C in air. The oxidation mechanism as well as degradation of the coating was discussed based on the determination of its oxidation kinetics and the analysis of oxide phases and microstructure.

2. Experimental

M38G superalloy sample, with dimensions of 10 mm × 10 mm × 1.5 mm, was chosen as substrate in the present work. The nominal composition (wt.%) of the M38G superalloy is given as follows: Ni, bal; Cr, 15.3–16.8; Co, 8.0–9.0; W, 2.3–2.9; Mo, 1.4–2.0; Al, 3.5–4.5; Ti, 3.2–4.0; Nb, 0.4–1.0. Cr_2AlC coating was prepared using a JGP560C 14 magnetron sputtering system (SKY Technology Development Co. Ltd., China) in a D.C. mode. A piece of hot-pressed bulk Cr_2AlC was machined into a target with dimensions of Φ60 mm × 6 mm. The bulk Cr_2AlC was fabricated by an in situ reaction/hot pressing method, as described elsewhere [7]. Prior to deposition, the sputtering chamber was pumped down to a base pressure of 5×10^{-4} Pa in order to eliminate oxygen, then the samples were heated. After the samples were heated to a setting substrate temperature (i.e. 500 °C) with a 10 min hold, inert gas (Ar, 99.999%) was inlet at the rate of 15 SCCM up to the final pressure of 0.25–0.35 Pa by adjusting the valve of the sputtering chamber, whereafter the Cr_2AlC target was cleaned by Ar^+ ions sputtering for 10 min to remove surface contaminants. Consequently the sputtering deposition started. In the deposition process, the applied power on the Cr_2AlC target was kept at about 100 W, no bias voltage was applied on the samples. The deposition time was 6 h, the thickness of the coating was about 10 μm.

2.1. Oxidation test

The isothermal oxidation test was performed in a Setsys 16/18 microbalance (Setaram, Caluire, France) at 900–1100 °C in flowing air. The specimen was suspended by a Pt wire and heated to the desired temperature at a rate of 40 °C/min. The mass change was recorded continuously as a function of time once the temperature reached the target value.

2.2. Characterization of the oxidized Cr_2AlC coating

The phase compositions of the oxidized Cr_2AlC coating were identified using X-ray diffractometer and Raman spectrometer. The XRD data were collected by a step-scanning diffractometer with Cu Kα radiation (Rigaku D/mac-2400, Tokyo, Japan). Raman spectra were recorded at room temperature using a He–Ne laser with a wave length of 632.8 nm as the excitation source (Horiba LabRam HR 800, Jobin Yvon, Edison, NJ). The surface and cross-sectional microstructures of the specimen were observed in a SUPRA 35 scanning electron microscope (LEO Supra 35, Oberkochen, Germany), which is equipped with an energy dispersive spectroscopy (EDS) system. The chemical compositions of the coating were determined by employing electron-probe microanalysis (Shimadzu EPMA-1610, Kyoto, Japan). Transmission electron microscopy (TEM) analyses were also conducted to investigate the microstructural features of the oxidized coating. Specimens for TEM cross-sectional characterizations were prepared by directly gluing two oxidized samples, followed by mechanical grinding, dimpling and 5 keV Ar^+ ion milling with a Gatan PIPS apparatus. TEM observations were performed using a 300 kV Tecnai G2 F30 high-resolution transmission electron microscope (FEI, Eindhoven, Netherlands), equipped with an energy dispersive spectroscopy (EDS) detector in the STEM system.

3. Results

3.1. Oxidation kinetics

Fig. 1 shows the mass gain per unit area (Δw) as a function of oxidation time for Cr_2AlC coated sample at 900 °C, 1000 °C and 1100 °C in air for 20 h. For comparison, the data for the M38G superalloy are also presented in this figure. It is clear that, with increasing oxidation temperature, the mass gain of the Cr_2AlC coated sample increases. Compared with the M38G superalloy, the mass gain of the Cr_2AlC coated sample is lower under the same oxidation condition. For example, after the oxidation at 1100 °C for 20 h, the mass gain of the Cr_2AlC coated sample is 0.74×10^{-2} kg/m^2, the corresponding value of the M38G superalloy is 1.44×10^{-2} kg/m^2. This indicates that although M38G superalloy possesses good oxidation resistance due to the formation of Cr_2O_3-rich scale [20,21], the application of Cr_2AlC coating can further decrease its oxidation mass gain in the investigated temperature range. Fig. 2 presents the square of mass gain per unit area $(\Delta w)^2$ of the Cr_2AlC coated sample as a function of exposure time. It clearly shows that the oxidation kinetics of the Cr_2AlC coated sample follows parabolic law at 900 °C and 1000 °C in the whole period, and at 1100 °C in the initial 7 h. But its oxidation kinetics negatively deviates the initial parabolic law after 7 h at 1100 °C.

The linear relationship between $(\Delta w)^2$ and oxidation time t can be described using Eq. (1):

$$(\Delta w)^2 = k_p \cdot t \tag{1}$$

where k_p is the parabolic rate constant. The calculated values of k_p for the Cr_2AlC coated sample and the M38G superalloy are summarized in Table 1, together with those of the bulk Cr_2AlC [8] for comparison. It can be seen that, the k_p value of the Cr_2AlC coated sample is lower than that of the M38G superalloy at the same oxidation temperature, but one order of magnitude higher than that of the bulk Cr_2AlC.

The parabolic rate constant is correlated with temperature according to the Arrhenius relation:

$$k_p = k_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

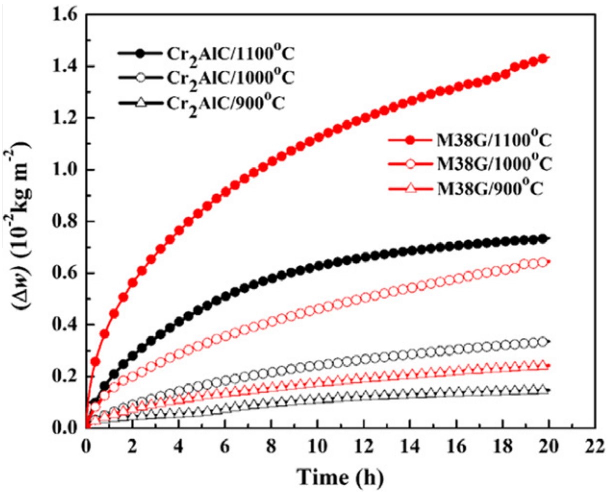

Fig. 1. Oxidation kinetics of Cr_2AlC coated sample and M38G superalloy at 900–1100 °C in air for 20 h.