Cross-sectional oxide distribution of cast IN738 and its sputtered coating at 1000 °C

Shujiang Geng\textsuperscript{a,b,*}, Fuhui Wang\textsuperscript{b}, Sam Zhang\textsuperscript{a}

\textsuperscript{a}School of Mechanical and Production Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore  
\textsuperscript{b}State Key Laboratory for Corrosion and Protection, Institute of Metal Research, The Chinese Academy of Sciences, Wencui Road 62, Shenyang 110016, PR China

Abstract

A sputtered nanocrystalline coating of IN738 alloy was obtained by means of magnetron sputtering technique. The oxide distribution was presented of the cast IN738 and its coating after 50 h in air at 1000 °C. The results indicated that the oxide scale formed on the cast alloy consisted roughly of three sections: the top-most section being \( \text{Cr}_2\text{O}_3 \) and \( \text{TiO}_2 \) mixture, followed by internal aluminum oxide, and scattering beneath which being TiN particles. In the case of nanocrystalline coating, however, only two sections were obvious: the top \( \text{Cr}_2\text{O}_3 \), \( \text{TiO}_2 \) and NiCr\(_2\text{O}_4 \) spinel mixture layer and the inner continuous \( \text{Al}_2\text{O}_3 \) layer. No internal oxidation and nitridation occurred.

Keywords: IN738 alloy; Sputtering; Nanocrystalline coating; Oxidation

1. Introduction

Recently, nanocrystalline coatings deposited by magnetron sputtering have improved the high temperature oxidation and corrosion resistance of Ni-based superalloys [1–9]. The reason behind this improvement lies in that some of these alloys can be altered from forming a chromium oxide to forming an aluminum oxide at high temperatures through nanocrystallization. Basically, Ni-based superalloys are Ni–Cr–Al–Ti alloys that can be divided into two groups: a ‘chromia former’ giving rise to chromium oxides upon oxidation and an ‘alumina former’ producing an aluminum oxide at high temperatures [10]. The chromium/aluminum ratio (wt.%) in the alloy determines which group the alloy belongs to [11]: a chromia former if Cr/Al is greater than 4.0 and an alumina former if Cr/Al is less than 4.0. IN738 alloy has a Cr/Al ratio of 4.71, thus belongs to the group of chromia former. Will nanocrystallization change this alloy from a Chromia former into an Alumina former? The present work answers this question by revealing the oxide distribution of sputtered IN738 nanocrystalline coating and that of cast IN738 alloy.

2. Experimental

The nominal composition of cast superalloy IN738 is listed in Table 1. The substrates (∼12×8×2.5 mm\(^3\)) for nanocrystalline coating were cut from a cast IN738 ingot and ground to 600-grit on silicon-carbide paper before sandblasting and ultrasonic cleaning in acetone bath. The sputtering target of 248×124 mm\(^2\) in size was from the same ingot. The sputtering deposition was carried out at sputtering target power of 350 V and 3 A under chamber pressure of 0.1 Pa of argon for 25 h. The sample rotation was performed to ensure better uniformity. The coating was approximately 50 \( \mu \text{m} \) thick.

The oxidation was performed on a thermobalance in static air for 50 h at 1000 °C. The specimens were examined using scanning electron microscopy (SEM) with an energy-dispersive X-ray analysis attachment, X-ray diffraction analysis (XRD), scanning tunnel microscopy (STM) and electron probe microanalysis (EPMA).
Table 1
Nominal composition of IN738 and K38G alloy (wt.%)  

<table>
<thead>
<tr>
<th>Element</th>
<th>IN738</th>
<th>Cr</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>Mo</th>
<th>C</th>
<th>W</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>1.75</td>
<td>16.0</td>
<td>8.5</td>
<td>3.4</td>
<td>3.4</td>
<td>1.75</td>
<td>0.17</td>
<td>2.6</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3. Results

3.1. Microstructure

The average grain size of the cast IN738 alloy is larger than 100 μm, as shown in our earlier results [9] (cf. Fig. 1). However, in the nanocrystalline coating, the STM surface morphology shows small nodule like particles of size less than 100 nm (Fig. 2). SEM micrograph of the cross-section of the coating demonstrates a columnar structure (Fig. 3). It can be seen that each nodule in Fig. 2 is the end of a group of columnar grains. As such, the average grain size in the coating was far smaller than 100 nm, or several orders of magnitude smaller than that of the cast alloy.

3.2. Morphologies of oxide

The EPMA results are shown in Figs. 4 and 5 as cross-section morphology and elemental mapping of the oxide scale formed after 50 h at 1000 °C for cast IN738 and sputtered IN738 coating. The oxide scale formed on the cast alloy consists roughly of three sections (cross-section morphology in Fig. 4): the top-most section contains Cr and Ti elements (mapping images in Fig. 4) and XRD analysis (cf. Fig. 6) indicates Cr₂O₃ and TiO₂. The layer below that contains sporadic Al element, which is, again, identified as Al₂O₃. Further down, some Ti shows up in the elemental map and that is identified as TiN. Similar analysis on the nanocrystalline coating (Fig. 5) shows that only two sections are obvious: the top layer contains Cr₂O₃, TiO₂ and NiCr₂O₄ spinel and the inner layer is a continuous Al₂O₃. No internal oxides or nitrides are observed. In addition, the top layer appears much denser than that in the cast alloy.

4. Discussion

From the results above, it is obvious that at 1000 °C the oxide distribution of IN738 nanocrystalline coating is different from that of the cast alloy. In the sputtered coating, the grain size is a lot smaller than that in the cast alloy, therefore, there exist much more nucleation sites for Cr, Ni and Ti oxide formation at the grain boundaries, which also explains why the oxide layer in the coating is denser. TiO₂ in the coating most likely forms as a result of the high diffusivity of the positive Ti ions [12] from the coating into the Cr₂O₃ layer.
Meanwhile, NiCr$_2$O$_4$ spinel forms via solid phase reaction between NiO and Cr$_2$O$_3$, resulting in a mixture top layer of Cr$_2$O$_3$, TiO$_2$ and NiCr$_2$O$_4$ spinel. To form a continuous layer of Al$_2$O$_3$, the Al concentration in the alloy satisfy the critical concentration, $N_{Al}$, expressed in Wagner’s theory [13]:

$$N_{Al} = \left( \frac{\pi g^* N_o D_o V_M}{3 D_{Al} V_{OX}} \right)^{1/2}$$  \hspace{1cm} (1)

where $N_o D_o$ is oxygen permeability in the alloy, $D_{Al}$ is the diffusivity of aluminum, $g^*$ is a factor determined by the volume fraction of oxide required for the transition, and $V_M$ and $V_{OX}$ are the molar volumes of the alloy and oxide, respectively. As the denser mixture layer is established, the oxygen partial pressure at the coating-oxide interface decreases, the oxygen permeability $N_o D_o$ is reduced. From Eq. (1), the critical Al concentration $N_{Al}$ is lowered (threshold is lowered). On the other hand, the sputtered coating has a large amount of grain boundaries that offer short circuits for the outward diffusion of Al, giving rise to a larger $D_{Al}$. Again, from Eq. (1), larger $D_{Al}$ results in smaller $N_{Al}$. Consequently, a continuous Al$_2$O$_3$ is formed in the coating, but not in the cast alloy.

5. Conclusions

(1) The oxide distribution of the cast IN738 and its coating is different. The oxide layer formed on the cast alloy consists roughly of three sections: Cr$_2$O$_3$ and TiO$_2$ mixture top section, followed by a layer of internal aluminum oxide. Scattering beneath the internal oxidation layer exist some TiN particles. In the case of nanocrystalline coating, however, two sections form: a top mixture layer of Cr$_2$O$_3$, TiO$_2$ and NiCr$_2$O$_4$ spinel and an inner continuous Al$_2$O$_3$ layer.

(2) The oxide layers in the sputtered coating appear denser.

(3) No internal oxidation and nitridation occur in the nanocrystalline coating.
Fig. 6. Oxide XRD patterns of cast IN738 alloy and its nanocrystalline coating after oxidation for 50 h in air at 1000 °C.

Acknowledgments

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References