High-temperature corrosion behavior of sputtered K38 nanocrystalline coatings with and without yttrium addition in molten sulfate at 900 °C

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Abstract

The high temperature corrosion behavior of sputtered Ni-based superalloy K38 nanocrystalline coatings with and without yttrium addition in molten sulfate (75 wt.% Na2SO4 + 25 wt.% K2SO4) was investigated at 900 °C in air. The results indicated that nanocrystallization significantly increased the corrosion resistance through the rapid formation of a protective oxide scale. The addition of yttrium in the nanocrystalline coating furthermore improved the corrosion resistance of the coating.

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1. Introduction

Ni-based superalloy is designed for turbine blades in engines. There are often salts, such as Na2SO4 and NaCl, to deposit on its surface in some working environments, which lead to hot corrosion of the alloys. Therefore, protective coatings, such as aluminides and MCrAlY coatings have been developed to provide corrosion resistance against the salt attacks. It has been shown that the nanocrystalline coatings exhibited excellent high temperature oxidation resistance compared to the conventional protective coatings [1–4]. Geng’s work [5] revealed that nanocrystallization improved the high temperature corrosion resistance in molten sulfate by the formation of continuous alumina scale on the surface of the coating.

It is well known that addition of reactive elements (RE) significantly improves the high temperature oxidation resistance of Al2O3- and Cr2O3-formers, the mechanisms of reactive-element effects (REE) have been reviewed by several authors [6–8]. In our previous work [9], the isothermal oxidation behavior of nanocrystalline K38 coating with yttrium additions was investigated. The results showed that additions of 0.05 and 0.1 wt.% yttrium had beneficial effect on the oxidation resistance of the coating, however, the addition of 0.5 wt.% yttrium had negative effect. In order to reveal the effect of yttrium on the high temperature corrosion resistance of sputtered nanocrystalline coating, the corrosion behavior of sputtered K38 coating with and without yttrium addition in molten sulfate was investigated in this work.

2. Experimental procedures

The nominal chemical composition of K38 superalloy, which was chosen as the substrate for coating deposition, is listed in Table 1. The sputtering targets of K38 alloy with 0, 0.5% (in weight percent) yttrium additions were melted in a vacuum-induction furnace and then machined into dimension of 380 × 126 × 10 mm. The coatings with grain size less than 100 nm [5] were deposited by magnetron sputtering and the detailed sputtering parameters were described in previous work [10]. Coated samples were denoted as K38-0Y and K38-0.5Y corresponding to the yttrium additions of 0 and 0.5 wt.% (nominal content) respectively. The uncoated samples were also tested as reference, denoted as K38 and K38Y, corresponding to the cast alloys with 0 and 0.5 wt.% yttrium addition respectively. The chemical compositions of the sputtered coatings are almost same to that of the cast alloys.

Corrosion test was carried out in molten salt of 75 wt.% Na2SO4 + 25 wt.% K2SO4 at 900 °C in air. The samples were completely immersed in the molten sulfate and taken out at certain intervals. After cooling to room temperature, removing sulfate by boiling water and drying, the samples were weighted. Then, the samples were re-immersed in fresh molten sulfate to repeat the above procedures.

After corrosion, samples were characterized using scanning-electron microscopy (SEM) with energy-dispersive X-ray analysis.
(EDS), X-ray diffraction analysis (XRD), and electron-probe micro-analysis (EPMA).

3. Results

3.1. Corrosion kinetics

The corrosion kinetics of the coated and uncoated samples in molten sulfate at 900 °C is shown in Fig. 1. It can be seen that the cast K38 exhibited the greatest weight gain among the samples. The addition of 0.5 wt.% yttrium significantly reduced the weight gain of cast alloy, especially the weight gain of K38Y was slightly greater than that of coating K38-0Y during the initial 20 h. The coating K38-0.5Y had the lower weight gain than the coating without yttrium addition throughout the test. During the test, a porous yellow green corrosion product was apparently observed on the surface of the samples except coating K38-0.5Y, as shown in Fig. 2. Most of the porous corrosion product was detached from the sample during the salt removing procedure prior to sample weighting and SEM examinations. Therefore, it is reasonable that the actual weight gains of cast K38, K38Y and coating K38-0Y resulted from corrosion are greater than the measured value in Fig. 1.

3.2. Characterization of corrosion products

Fig. 2 shows the macro-morphology of the samples after 100 h immersion in molten sulfate at 900 °C. It is indicated that the amount of the yellow green corrosion products was reduced due to the crystallization, and the further addition of yttrium in the coating inhibited the formation of the product. The SEM observation and EDS analysis demonstrated that the product was a Ti- and Cr-rich fibroform compound (Fig. 3). A small amount of fibroform, enriched in Ti and Cr, was also observed on the surface of samples except the coating K38-0.5Y, which was supposed to be the yellow green product retained on sample surface after salt removing procedure.

The X-ray maps of the cast alloys after 100 h corrosion at 900 °C are shown in Figs. 4 and 5. For the cast K38 alloy (Fig. 4), an external scale, enriched in Cr, Ti and O, formed on the surface. XRD analysis indicated that the scale consisted mainly of Cr2O3 and Cr2TiO5. Meanwhile, remarkable internal oxidation and sulfidation were observed. EDS analysis revealed that the internal sulfide and oxide were enriched in Al. The addition of yttrium to the cast alloy led to the formation of a thin discontinuous oxide scale rich in Al and Cr (Fig. 5). The formation of alumina in the scale was evidenced by XRD analysis. Nodular corrosion products, enriched in Ti and Cr, locally formed on the surface of K38Y. And internal oxidation and sulfidation occurred beneath them. In Fig. 5, it can also be seen that the yttrium was prone to react with sulfur to form internal sulfide, which was enveloped in the Al-rich oxide.

Fig. 6 shows the surface morphologies of the coatings after 100 h immersion in molten sulfate at 900 °C. It can be seen that some scattered Ti-rich particles were observed on the surface of the coating K38-0Y (Fig. 6a). XRD analysis indicated the scale consisted mainly of Al2O3 and Cr2O3, TiO2 peaks were identified even though the intensity of the peaks was quite weak. On the contrast, no such corrosion product formed on the surface of K38-0.5Y coating and the original sputtering morphology of the coating was remained.

### Table 1

Nominal chemical composition of K38 superalloy (wt.%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Co</th>
<th>W</th>
<th>Mo</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>Nb</th>
<th>Ta</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1–0.2</td>
<td>15.7–16.3</td>
<td>8–9</td>
<td>2.4–2.8</td>
<td>1.5–2</td>
<td>3.2–3.7</td>
<td>3.0–3.5</td>
<td>=&lt;0.5</td>
<td>0.6–1.1</td>
<td>1.5–2.0</td>
<td>0.05–0.15</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Fig. 1. Corrosion kinetics of cast alloys and sputtered coatings for 100 hours in molten sulfate at 900 °C.

Fig. 2. Macro-morphology of cast K38, cast K38Y, sputtered K38-0Y coating and K38-0.5Y coating after 100 h immersion in molten sulfate at 900 °C.
(Fig. 6b), which implies a thin protective scale formed on the coating. For the coating K38-0.5Y, only Al₂O₃ was identified in diffraction pattern.

Figs. 7 and 8 show the X-ray maps of the coating K38-0Y and K38-0.5Y, respectively. As can be seen in Fig. 7, the external scale mainly consisted of the oxide of alumina, a Cr-rich zone with slight depletion
of Ti formed beneath the scale. The internal oxidation and sulfidation were evidently inhibited beneath the external scale, notwithstanding a little amount of S and Ti were locally segregated in the scale. Fig. 8 shows that a thinner Al-rich scale formed on the coating K38-0.5Y compared to the coating without Y addition. No segregation of S and depletion of Ti were observed within the detection limits, which

![X-ray maps of cast K38 alloy with 0.5 wt.% Y addition after 100 h immersion in molten sulfate at 900 °C.](image)

![Surface morphologies of K38-0Y (a) and K38-0.5Y (b) coatings after 100 h immersion in molten sulfate at 900 °C.](image)
implies that the protective alumina scale formed rapidly on the surface of coating K38-0.5Y to prevent the oxidation and sulfidation of Ti.

4. Discussion

In the case of cast K38 alloy, the formation of oxides decreases the oxygen activity at the oxide-salt interface, which leads to the increasing of sulfur activity, Eq. (1).

\[
\text{SO}_4^{2-} = \text{O}^{2-} + \frac{3}{2}\text{O}_2 + \frac{1}{2}\text{S}_2
\]  

Where the \( \text{O}^{2-} \) dissolves in salt, and \( \text{O}_2 \) and \( \text{S}_2 \) are used to form oxide and sulfide. Since the oxide scale is not protective, the sulfur penetrates into the alloy to form sulfides beneath the oxide. The removal of oxygen and sulfur from the sulfate is to increasing the oxide-ion activity, results in the dissolution of oxide scale by the formation of \( \text{MO}_2^{2-} \) according to Eq. (2).

\[
\text{MO} + \text{O}^{2-} \leftrightarrow \text{MO}_2^{2-}
\]  

Since the increased oxide-ion activity is restrict to the scale-salt interface, therefore, \( \text{MO}_2^{2-} \) decomposes into oxide particles as they diffused outwardly from the scale [11]. This might be the formation mechanism of the fibriform product.

It is well known that the active elements can act as "gettering" of sulfur. For cast K38Y alloy, the reaction of yttrium with sulfur decreased the activity of sulfur in corrosion front, thus reduced the sulfidation of Al and Cr and enhanced the selective oxidation of them. Therefore, the cast K38Y alloy had better corrosion resistance and exhibited lower weight gain than K38 alloy.

It has been reported that nanocrystallization can promote the rapid formation of protective oxide scale due to the fast outward
diffusion of Al through nano-grain boundaries [1,2]. Our previous work also showed a less-protective mixed oxide scale formed on the cast K38 alloy after oxidation at 900 °C but the protective scale on the nanocrystalline coating, even though the chemical composition of the coating is the same with the cast alloy. Therefore, it can be assumed that a protective alumina scale rapidly formed on the coated sample, which impeded the penetration of sulfur. The accumulation of sulfur decreases the oxide-ion activity at the scale-salt interface, thus reduced the dissolution of surface scale. As can be seen from the observation, no porous corrosion product was observed on the surface of coated sample with the yttrium addition. Compared to the coating without yttrium addition, the thinner scale formed on the coating with 0.5 wt.% Y, no evident segregation of sulfur and development of Ti-depletion zone were observed within the detection limits. The previous work [9] showed that the over-doping of Y (0.5 wt.%) had detrimental effect on the oxidation resistance of sputtered K38 coating. That is because the formation of Y₃O₃ in high oxygen pressure perhaps led to the stress concentration [12] and rapid O transport through the Y-rich oxide particles [13]. However, Y was prone to react with S in molten sulfide due to the high sulfur activity and low oxygen activity. Thus, it is speculated that the reaction of Y with S decreased the sulfur activity in the corrosion front, inhibited the sulfidation of Al, and therefore, promoted the nucleation and growth of alumina at early stage. The rapid formation of protective alumina scale prevented the penetration of sulfur and consequently the dissolution of oxide scale during the corrosion test.

5. Conclusions

The high-temperature corrosion behavior of sputtered K38 nanocrystalline coatings with and without yttrium addition was investigated in molten sulfate at 900 °C in air. The corrosion test was also carried out on the cast alloys as a comparison. The results showed that the basic fluxing induced by sulfidation occurred on the cast alloy. However, nanocrystallization evidently promoted the formation of protective oxide scale, which greatly impeded the penetration of
sulfur from molten salt into the metal. The further addition of yttrium is obviously beneficial to the corrosion resistance of nanostructured coating.

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References