



Hot corrosion behavior of porous nickel-based alloys containing molybdenum in the presence of NaCl at 750 °C



Lingyun Chen^{a,b}, Hao Lan^b, Chuanbing Huang^b, Bin Yang^{a,c,*}, Lingzhong Du^b, Weigang Zhang^{b,*}

^a State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, PR China

^b Laboratory of Particle Science and Engineering, State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

^c Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, PR China

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ABSTRACT

The hot corrosion of porous Ni-23Cr-xMo (0%, 4.5%, 9.0%, 13.5%, mass fraction) alloys tested at 750 °C under cyclic procedure was investigated in order to elucidate the effect of Mo addition on hot corrosion in the presence of NaCl. The hot corrosion experiments were performed at 750 °C in air with 4 mg cm⁻² NaCl deposit. The performance of the alloys was evaluated by the results of weight change kinetics. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were used to characterize the corrosion products. The results indicate that NaCl accelerated the oxidation of the alloys by chloridized elements Mo and Cr. Among the porous Ni-23Cr-xMo alloys, Ni-23Cr-9Mo alloy exhibited the best hot corrosion resistance due to the formation of NiO-NiCr₂O₄-Cr₂O₃ oxide scales. Furthermore, these oxide scales were confirmed more effective to protect the alloys after adding of Mo.

1. Introduction

Naval aircrafts are always exposed to the marine environment where salty fog and high humidity are concentrated during their parking time, which could account for > 90% the service life [1,2]. Generally, NaCl enters the turbines as an aerosol and deposits on the blades and coatings. Solid NaCl at higher temperatures accelerate the hot corrosion of the turbines [3–6].

Corrosion damage is the second most frequent observed damage in aircraft structures except for fatigue cracks, especially for some parts which are easily corroded, such as the porous abrasible coatings [7,8]. The abrasible coatings are mostly composed of metal phase, self-lubricating nonmetal phase and a defined level of porosity. However, the abrasible coatings are easily destroyed due to the pores provide penetrating paths for corrosion medium and formed galvanic cells [9,10].

Ni-based alloys are mainly used in aircraft engines as structural or coating materials due to their excellent high temperature strength and corrosion resistance [11,12]. Ni-based alloy coating is a kind of middle-temperature sealing coating, which has been widely applied in the aircraft turbine compressor casing [1]. Both Cr and Mo are important alloying elements in Ni-based alloys to improve mechanical properties by solid solution hardening. They seem to exert a synergistic effect together, especially on localized corrosion. Many researchers reported that Ni-based alloy coating containing Cr exhibits good against high temperature corrosion because of the selective oxidation of Cr to form stable and protective Cr₂O₃ [13–15]. The elements Mo is also an important element to resistant corrosion environment [16]. However, Mo enters the fused salt and forms a corrosive liquid phase of Na₂SO₄-MoO₃ in the

* Corresponding authors.

E-mail addresses: byang@ustb.edu.cn (B. Yang), wgzhang@home.ipe.ac.cn (W. Zhang).

Table 1
Chemical composition of various alloys (wt%).

Alloy	Ni	Cr	Mo
A1	Bal.	23	0
A2			4.5
A3			9
A4			13.5

presence of Na_2SO_4 , which can lead to alloy-induced acidic fluxing of Ni [17]. Moreover, Mo is also found to have a negative effect on the oxidation at elevated temperature [18]. However, the fundamental understanding to explain this behavior is still lacking, which is a significant issue to be solve in the present research.

Compared with dense mass materials, coatings with a porous multi-phase structure are easy to be corroded. In this paper, the corrosion on a simulate coating structure of porous Ni-23Cr-xMo (0%, 4.5%, 9.0%, 13.5%, mass fraction) alloys caused by NaCl at 750 °C was studied to evaluate the effect of Mo. The reason why we test at 750 °C was based on the service temperatures (~760 °C [19]) of the alloys and NaCl melting point.

2. Experimental

2.1. Preparation of the porous materials

The Ni-based porous alloys for the present study were prepared by mixing ultrafine Ni (> 99.9% pure, 5–8 μm), Cr (> 99.9% pure, 1–2 μm), Mo (> 99.9% pure, 1–2 μm) and NH_4HCO_3 powders. The NH_4HCO_3 was added as the pore former. The chemical compositions of these alloys are reported in Table 1. The contents of Mo in A1, A2, A3 and A4 alloys were 0%, 4.5%, 9.0% and 13.5% respectively, which were used the experience of haynes625 and hastelloyC-22 for reference [16]. The evenly mixed powders were pressed into plates with a size of $35.0 \times 25.0 \times 3.0 \text{ mm}^3$ under pressure of 200 MPa for 1 min. Then the plates were sintered at 1000 °C for 8 h under flowing H_2 . The porosity was $10 \pm 2\%$ which was estimated by measuring the cross-sectional images of them with software Image Pro Plus 6.0. The samples for corrosion experiments were cut into $20.0 \times 10.0 \times 2.0 \text{ mm}^3$ blocks.

2.2. NaCl-induced hot corrosion tests

Cyclic hot corrosion tests were performed in static air after NaCl was deposited on the surfaces of the samples at 750 °C. The purpose of cyclic tests was to create severe conditions for hot corrosion under repeatedly changed temperature, which simulates the service environment of the alloys [20]. At least three samples were tested to confirm the data reproducibility.

First, all the samples were mechanically grinded on SiC papers up to 1000 grit, and were ultrasonically cleaned in ethanol and acetone. And then the samples were placed in alumina crucibles and dried at 110 °C for 1 h. After that, they were weighed and sprayed with aqueous saturated NaCl solution to ensure at least $4 \text{ mg}\cdot\text{cm}^{-2}$ NaCl on the surfaces. Second, the samples were treated in a muffle furnace kept at 750 °C for 10 h and cooled to room temperature. Then they were washed in boiling water for dissolving the residual salts. Finally, the cleaned samples were dried and weighed by a physical balance with a sensitivity of 10^{-4} g to determine the mass change after each cycle. Before the samples were brought back into the furnace, the same amount of fresh NaCl (i.e. $4 \text{ mg}\cdot\text{cm}^{-2}$) was sprayed on the surface of the samples in order to a new cycle of the corrosion test was begun. The cycle was repeated for 15 times (i.e. 150 h).

The microstructure and morphology of the corrosion products were characterized by scanning electronic microscopy (SEM, JSM-7001F) and energy dispersive X-ray spectroscopy (EDS, INCA X-MAX). Phase identifications of the corrosion products were carried out by X-ray diffractometer (XRD, PANalytical B.V., X'Pert Pro MPD) using Cu $K\alpha$ radiation. Thermodynamics calculations were performed with the HSC Chemistry 6.0 software in order to reveal corrosion mechanisms. The kinetics of corrosion was determined from the weight change measurements. And the weight change rate of the samples (Δw) was calculated according to the following formula:

$$\text{Weight change rate } \Delta w = \frac{\text{weight change}}{\text{sample surface area}} \quad (1)$$

3. Results and discussions

3.1. Weight change kinetics

The corrosion kinetics of the alloys have been studied by mass gain measurements. The weight change kinetics of the alloys after 15 cycles are shown in Fig. 1. In the case of NaCl corrosion, the weight losses of A1, A2 and A3 alloys as a function of corrosion time were quite obvious. In contrast, the A4 alloy did not lose its weight even after 150 h. One can see that slight mass gains of the A3 and A4 alloys were observed at the early stage. The overall weight gain of the A4 alloy was $0.56 \text{ mg}\cdot\text{cm}^{-2}$. After 3 cycles, weight gain of

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