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Research on the oxidation kinetics curve of 1Cr11Ni2W2MoV steel hot-dipped Al

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Abstract: In this paper, 1Cr11Ni2W2MoV steel that is aerial engine blade materials was hot dipped Al-6%Si-4%RE in order to improve its application temperature. According to GB/T13303-91 standard, samples with coating and without coating were oxidated at 700°C from 5 h to 600 h. Two oxidation kinetics curves were drawn in terms of data of tests. The results showed that oxidation resistance of 1Cr11Ni2W2MoV steel hot-dipped Al-6%Si-4%RE is better than one without coating. From SEM and EMPA, the surface of coating formed dense and uninterrupted α -Al₂O₃, which is the bars of oxidation resistance. In addition, according to one crossing point of the two curves, it was suggested that hot dipped aluminum steel should be annealed before used.

Key words: oxidation kinetics curve; hot-dipped Al-6%Si-4%RE; 1Cr11Ni2W2MoV steel

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1 Introduction

With application requirments of aerial engine blade materials increasing, especially using temperature, the neck problem of heat resistance on alloys need to be solved recently. Hot-dipped Al technology could introduce abundant element instead of rare metal, and decreased the price of coating. It is applied in many fields including chemical industry, oil industry and transportation^[1]. In this experiment, 1Cr11Ni2W2MoV steel was hot dipped Al-6%Si-4%RE In terms of testing results, the two curves were analyzed in detail, and the suggestion was advanced.

2 Experimental procedures

1Cr11Ni2W2MoV steel is the substrate. Its nominal composition is listed in the Table 1. The size of samples was machined 20 mm×10 mm×2mm and Ra=0.8. Dipping metal component is made up of Al-6%Si-4%RE. Hot-Dipped process is pretreatment (including in dipping hot water, degreasing, cleanout, getting rid of rust, cleanout, assisting planning and drying)→hot-dipped→passivation dealing. Hot-dipped temperature is controlled at 720-740°C, and hot-dipped time is limited (6±0.16) min.

According to GB/T13303-91 standard, the high temperature oxidation corrosion test was carried out between coating and without coating in the SM-28 type electrothermal furnace. The weight and size of samples were measured before oxygenation. Oxidation temperature was confirmed 700°C, and thermal retarda-

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tion time was 5 h, 10 h, 30 h, 50 h, 100 h, 150 h, 200 h, 300 h, 400 h, 500 h, 600 h. 1Cr11Ni2W2MoV steel with coating and without coating took eleven teams individually, and there were two samples in each team. Each team was measured by electronic balance (FA1004 shape) that its precision is 10^{-4} g after sampling cooling to room temperature and observed by magnifying glass. The Olympus-PM3 shape metalloscope, FEI Sirion shape scan electronic measure (SEM) and EMPA indicated the surface, the microstructure and the content of samples which had been etched (etching reagent: nancic acid 50 mL, HNO₃ 10 mL, HF 2 mL).

Table 1 Compositions of 1Cr11Ni2W2MoV steel

Element	C	Mn	Mo	S	Cr	Ni	W	V
Content/% (mass fraction)	0.10-0.16	≤0.60	0.35-0.50	10.5-12.0	10.5-12.0	1.40-1.80	1.50-2.00	0.18-0.30

3 Results and discussion

In terms of the data of eleven measuring point, the two oxidation kinetics curves about specimens with hot-dipped (HD) and without HD were drawn by least-squares procedure and origin software (see Fig. 1). The results showed that the tendency of oxidation liveweight gain of the two curves was similar during 600 hours. They are parabolic curves. However, oxidation liveweight gain of specimens with HD is lower apparently than without HD, so oxidation resistance of 1Cr11Ni2W2MoV steel with coating is better than one without coating. From Table 2, namely oxidation velocity was computed according to oxidation gaining in weight ratio between 400 hours and 500 hours, oxidation liveweight gain of samples with HD lessened about half as much as without HD. With oxidation time increasing, the surface of coating transit to θ -Al₂O₃ layer whose surface is like needle structure in the Fig. 3 from discontinuous oxidation film in initial stage, Fig. 2 shown. Doychak found θ -Al₂O₃ belong to the fault structure. Fault interface supplied the channel which Al³⁺ was able to diffuse quickly through. But Schumann consider that θ -Al₂O₃ belong to the compound twin structure whose interface could become the way of Al³⁺ diffusion. Though their viewpoint is different, the same point is that θ -Al₂O₃ is provided with face defect which is able to supply the direct short way of Al³⁺ diffusion. This is the reason that the surface of coating could transform corundum structure, namely α -Al₂O₃ layer^[2] (see Fig. 4). The brushy structure on the surface is α -Al₂O₃. Its Crystal lattic constant is $a=0.79$ nm, melting point is 2047°C. Its dense is excellent, and its chemical prosperity is stable. Existence of α -Al₂O₃ layer is the reason that oxidation resistance of HD coating is outstanding. As can be proved by $0.0024 \text{ g/m}^2 \cdot \text{h}$ (oxidation velocity between 500 h and 600 h) $< 0.005 \text{ g/m}^2 \cdot \text{h}$ (average oxidation velocity).

It should be noticed that a crossing point occurred in the two kinetics curves of the same coordinate when oxidation time was about 13 hours, as shown in Fig. 5. 1Cr11Ni2W2MoV steel without HD contains higher Cr element whose capacity of combination O is more excellent than Fe element, and diffusion coefficient of Cr³⁺ is twice and triplication order higher than O^[2,3]. So oxidation film grows in the matrix/interface^[4]. The thin oxidation film Cr₂O₃ grows on the surface of 1Cr11Ni2W2MoV steel without HD at initial

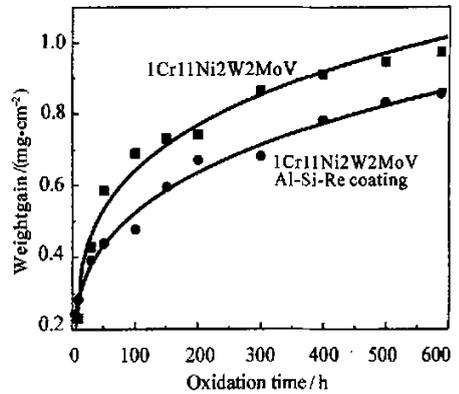


Fig. 1 The oxidation kinetics with coating and without coating at 700°C for 600 h

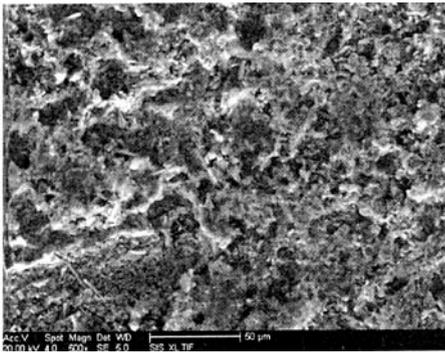


Fig. 2 The oxidation surface with coating at 700 °C for 10 h

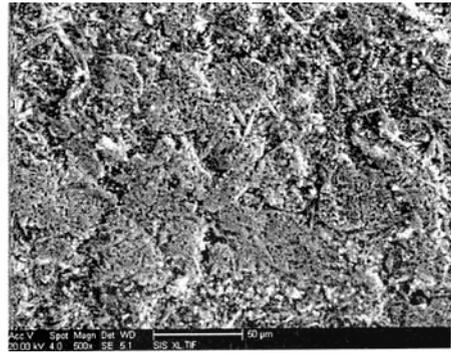


Fig. 3 The oxidation surface with coating at 700 °C for 150 h

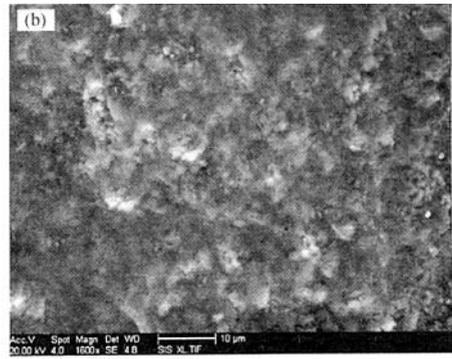
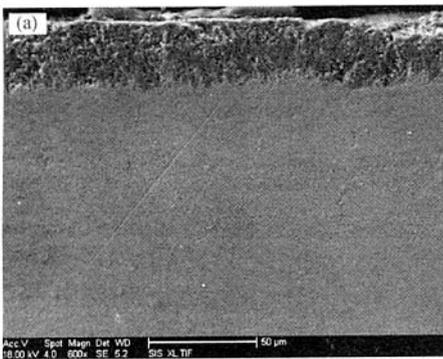


Fig. 4 The coating oxygenized at 700 °C for 600 h

(a) — the pattern of the section; (b) — the pattern of the surface

oxidation stage, which could protect substrate not to be oxidized temporarily. But in this stage, the affluent Al layer of coating burned rapidly and did not formed compact and continuous Al_2O_3 oxidation film. Liveweigh gain of samples without HD is lower than with HD. With oxidation time increasing, the surface of samples with HD formed continuous oxidation layers gradually. Its non-stoichiometric degree and spare space of the Al_2O_3 oxidation film is very little, and the diffusion velocity of O^{2-} is 10^{-3} slower than in the Cr_2O_3 oxidation film^[6]. While the diffusion velocity of metal ion in the Al_2O_3 oxidation film is 2×10^{-3} or 3×10^{-3} slower than in the Cr_2O_3 oxidation film. This is the reason that the Al_2O_3 oxidation film is more stable than the Cr_2O_3 oxidation film, and its oxidation resistance is better than the Cr_2O_3 oxidation film. So the oxidation resistance of 1Cr11Ni2W2MoV steel hot-dipped Al-Si-RE is more excellent than without coating.

In terms of this crossing point, it is suggested that hot-dipped devices Al should be annealed in the definitive time and temperature range before used. It is shown that the surface of coating would shrinkage

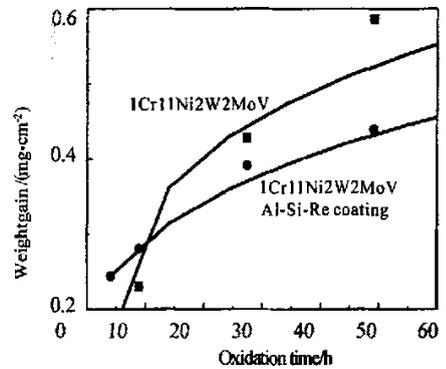


Fig. 5 The oxidation kinetics crossing point with coating and without coating for 600 h at 700 °C

8%—13%, which produce 15 GPa stress, when θ phase become α phase. This stress beyond tension strength of Al_2O_3 layer, and can create spalling and dehiscence of large area. Then annealing time should be higher than 800°C which is the existence temperature of θ phase. However, some researchers reported HD samples would produce the crack after annealed at 950°C for 4—6 hours. So the annealing time and temperature of the steel hot-dipped Al need to research hard.

Table 2 Oxidation resistance property with coating and without coating for 600 h at 700°C

	Gain in weigh /($\text{mg} \cdot \text{cm}^{-2}$)	Average oxidation velocity/ ($\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)	Oxidation velocity (non-coating /coating)
With HD	0.9462	0.76×10^3	1.52 times
Without HD	0.8329	0.50×10^3	

4 Conclusion

(1) Both the oxidation kinetics curves of 1Cr11Ni2W2MoV steel with coating and without coating tend to the para-curve. But high temperature oxidation resistance of HD samples is excellent than non coating.

(2) During the long oxidation time, the surface of 1Cr11Ni2W2MoV steel hot-dipped Al-Si-RE would form compact and continuous α - Al_2O_3 oxidation film, and it is the bars of high temperature corrosion oxidation resistance.

(3) In terms of the crossing point of the two high temperature oxidation kinetics curves, the suggestion that hot-dipped Al devices should be annealed before using, and annealing temperature should beyond 800°C.

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