

Effect of Si on Hot Corrosion Resistance of CoCrAlY Coating

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Abstract: The CoCrAlSiY coating was prepared by HVOF (high velocity oxygen fuel) method. The hot corrosion resistance of the CoCrAlSiY coating with different Si concentrations (0wt%, 2wt% and 5wt%) at 900 °C was discussed by hot salt coating method with a mixed salt of 75wt% Na₂SO₄+25wt% NaCl. The results show that the average corrosion penetration depth of the coating increases with the rising of temperature, while the increasing of Si concentration decreases the average corrosion penetration depth of the coating. Furthermore, CrSi, a high melting point metal silicide, is generated inside the CoCrAlSiY corrosion coating. Thus it is beneficial for improving the corrosion resistance of the coating.

Key words: MCrAlSiY; coating; oxidation; hot corrosion resistance

MCrAlY coating ($M = \text{Ni, Co}$ or their combination) has been widely recognized in the world due to its excellent features such as high temperature oxidation resistance and hot corrosion resistance. Furthermore, MCrAlY coating can also be used as a bond coating for ceramic thermal barrier coating. Therefore, MCrAlY coating has a very important practical application value^[1,2]. In order to improve the high temperature oxidation resistance and hot corrosion resistance of MCrAlY coating, a lot of experimental studies have been undertaken, such as adding modifying elements (Re, Zr, Hf, Ta, Si, etc.) to MCrAlY coating system. MCrAlY coating with added Si element is an important kind of high temperature anti-oxidation protective coating, which is applied to hot corrosion protection of equipment in the marine environment^[3-5]. Clemens^[6] discussed the effect of Si on the oxidation behavior of NiCrAlY alloy. They found that adding 1%~2% of Si could obviously improve the anti-spalling of the alloy oxide film, which enhanced its oxidation resistance. However, the work related to hot corrosion resistance of MCrAlY coating with Si element is limited. Therefore, the CoCrAlSiY coatings with different Si concentrations were designed and their high temperature

hot corrosion resistance were discussed to provide guidance for practical application in present work.

1 Experiment

In order to investigate the influence of Si concentration on the hot corrosion resistance of CoCrAlY coatings and analyze its mechanism, three kinds of CoCrAlY alloy powder with different Si concentrations (0wt%, 2wt% and 5wt%) were designed and prepared by vacuum melting inert gas atomization method in this study. Their chemical composition is summarized in Table 1 and their XRD patterns are shown in Fig.1. It can be seen that the mineralogical composition of all of the three alloy powders are CoAl and Co₃Al. This phenomenon indicates that the mineralogical composition of three alloy powders is not influenced by adding Si element in this study.

The CoCrAlSiY coating, whose thickness was about 0.2 mm, was prepared in the surface of GH907 substrate with a diameter of 22 mm by HVOF method. In order to investigate the effect of Si concentration on the coating performance under the condition of high temperature and salt corrosion, the high temperature oxidation resistance of

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Table 1 Chemical compositions of CoCrAl alloy powders (wt%)

No.	Si	Al	Y	Cr	Co	O
1	0	6	0.5	24	Bal.	0.03112
2	2	6	0.5	24	Bal.	0.02718
3	5	6	0.5	24	Bal.	0.02430

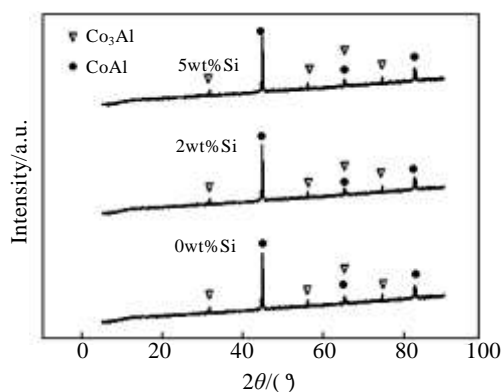


Fig.1 XRD patterns of alloy powders with different Si contents

the coating was firstly discussed by constant temperature oxidation tests. The change of coating oxide film and internal oxidation could be observed after oxidation test. It could provide the basic information for the hot salt corrosion of coating. In the hot corrosion test, a mixed salt of 75 wt% Na_2SO_4 +25 wt% NaCl was used as a corrosive medium, and its usage amount was 2 mg/cm^2 . It should be noted that samples were removed and painted with the mixed salt every 25 h. The hot corrosion test at 800 and 900 °C with a duration of 150 h was performed by QM-ISPZ-CL type muffle furnace. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were used to gain knowledge of the micro structure and surface corrosion products of the coating. In order to weaken the influence of mineralogical composition in the alloy substrate on that in the oxide film, mineralogical composition in the oxide film was analyzed by small-angle XRD analysis with the incident angle of 1° .

2 Results and Discussion

2.1 Coating mineralogical analysis after hot corrosion

The small-angle XRD patterns of coating with different Si concentrations after hot corrosion at 900 °C are described in Fig.2. The mineralogical composition of CoCrAlY coating without Si element is mainly CoCr_2O_4 and $\text{Na}_7\text{Al}_6\text{Cr}_8\text{O}_{24}\text{S}_3$. While Al_2O_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$ and CrSi are present in the coating with a Si concentration of 2wt% and 5wt%. It is due to the fact that the corrosion products of coating is related to its oxidation products at the high

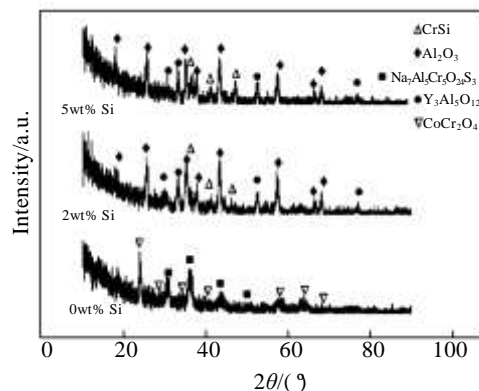


Fig.2 Small-angle XRD patterns of coatings after 150 h hot corrosion at 900 °C

temperature. The small-angle XRD patterns of alloy powders with different Si concentrations after 300 h oxidation at 1000 °C are shown in Fig.3. It can be seen that the mineralogical composition of alloy powder without Si element is mainly CoCr_2O_4 , which has a spinel type crystal structure and is produced by the high temperature reaction between CoO and Cr_2O_3 , while that of alloy powder with a Si concentration of 2wt% is Al_2O_3 , which has a good performance of anti-oxidation protection. In addition to Al_2O_3 , SiO_2 is also present in the alloy powder with a Si concentration of 5wt%. It is worth noticing that both Al_2O_3 and SiO_2 can form a dense oxide film, which would effectively protect alloy coating in the hot corrosion process^[7,8].

2.2 Coating micro analysis after hot corrosion

SEM microstructures of coating after 150 h hot corrosion at 800 °C and 900 °C are shown in Fig.4 and Fig.5. A serious hot corrosion of the CoCrAlY coating without Si element could be found after 150 h hot corrosion at 800 °C.

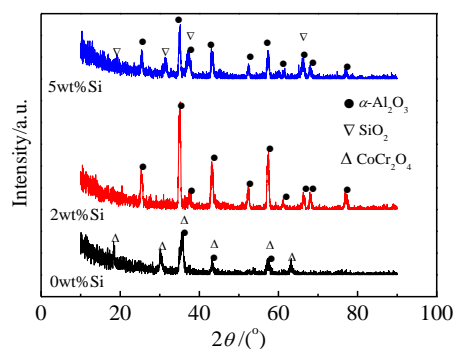


Fig.3 Small-angle XRD patterns of alloy powders after 300 h oxidation at 1000 °C

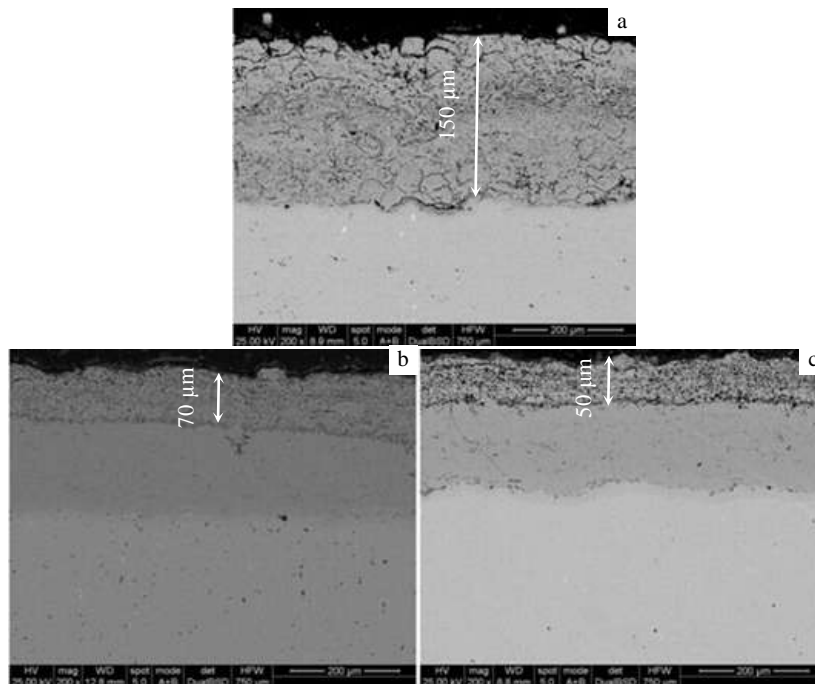


Fig.4 SEM micrographs of coatings after 150 h hot corrosion at 800 °C: (a) 0wt%Si, (b) 2wt%Si, and (c) 5wt%Si

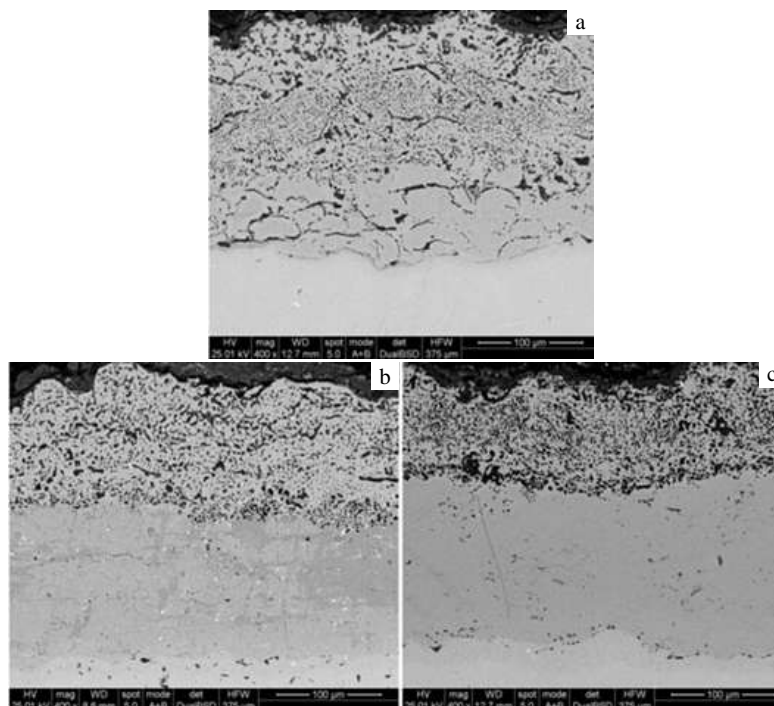


Fig.5 SEM micrographs of coatings after 150 h hot corrosion at 900 °C: (a) 0wt%Si, (b) 2wt%Si, and (c) 5wt%Si

And its average corrosion penetration depth is 150 μm. While the average corrosion penetration depth of CoCrAlY coating with Si concentration of 2wt% and 5wt% decreases to 70 and 50 μm, respectively. On the one hand, the average

coating corrosion penetration depth increases with the rising of temperature. As the hot corrosion temperature increases from 800 °C to 900 °C, the average corrosion penetration depth of coating with Si concentration

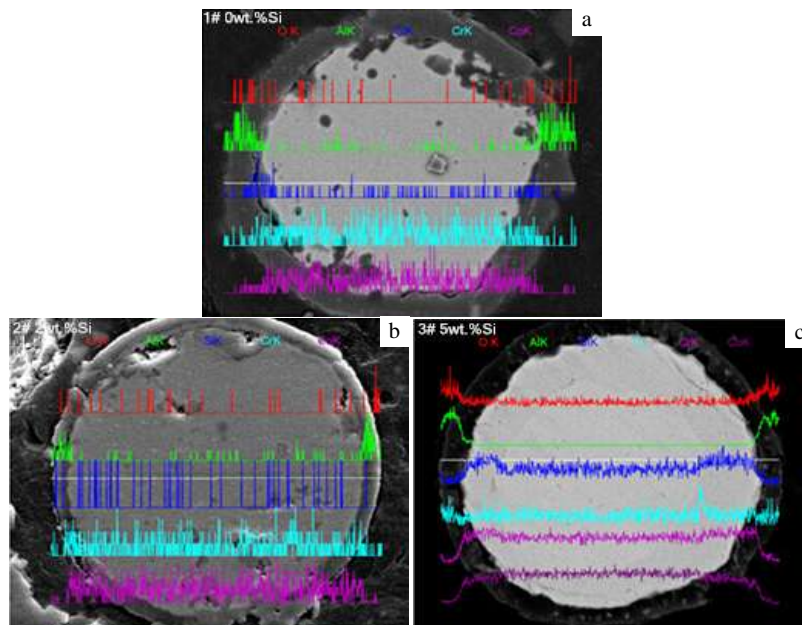


Fig.6 Elemental line scan of alloy powders after 300 h oxidation at 1000 °C: (a) 0wt%Si, (b) 2wt%Si, and (c) 5wt%Si

of 0wt%, 2wt% and 5wt% rises by 53.3%, 92.9% and 100.0%, respectively. On the other hand, the average coating corrosion penetration depth has a negative relationship with Si concentration. It can be seen that the average corrosion penetration depth of coating at 800 and 900 °C decreases by 66.7% and 56.5%, respectively, when the Si concentration gradually increases from 0% to 5%.

The elemental line scan of alloy powders after 300 h oxidation at 1000 °C is shown in Fig. 6. As mentioned above, CoCr_2O_4 , the main mineralogical composition of coating without Si element, could not form a continuous anti-oxidation protective film. Therefore, the oxidation film of alloy powder without Si element is the thickest, and its structure is relatively loose. In addition, the spinel and unoxidized alloys are not tightly bonded with each other. Based on the above reasons, the diffusion of oxygen ions and other substance could not be blocked effectively, so that the internal oxidation point exists inside the alloy powder^[9-11]. However, the oxidation film of alloy powder with a Si concentration of 2wt% is relatively dense.

Furthermore, the internal oxidation point disappears inside the alloy powder with Si concentration of 5wt%, with a tight connection between oxidation film and alloy powder. The elemental line scan results also show that a Si-rich layer is formed in the inner side of the oxide film; in other words, the Si concentration inside the alloy powder is relatively high. It is important to stabilize and repair the oxidation film formed by Al_2O_3 and SiO_2 ^[12,13]. As a consequence, the diffusion of oxygen ions and other saline material could be blocked effectively, which improves the high temperature oxidation resistance and hot corrosion

resistance of alloy coating.

The oxidation film formed in the surface of alloy provides it with the anti-oxidation ability. The continuous oxidation film, formed by Al_2O_3 , Cr_2O_3 and SiO_2 , can effectively prevent the diffusion of corrosive medium, such as O^{2-} and S^{2-} , and avoid high temperature oxidation and hot corrosion of alloy powder. For CoCrAlY coating, adding Si element restricts the oxidation of Cr element and promotes the formation of Al_2O_3 during the hot corrosion. In addition, the dense oxidation film also inhibits the dissolution of Si element in the interface of oxide/salt (O/S) and the diffusion of Cl⁻ and S^{2-} into the alloy interior, which limits the coating hot corrosion^[14-16]. Furthermore, as shown in Fig.5, it is worth noticing that the metal silicide can be found inside the hot corrosion coating with a Si concentration of 5wt%. The melting point of metal silicide is usually higher than 2000 °C, and thus CrSi is a stable compound with a high melting point and sparingly soluble in molten salt. In addition, its lower solubility in molten salt than the metal oxide, restricts the generation of sulfide, which decreases the reaction rate of internal oxidation during hot corrosion. Therefore, it is beneficial for improving molten salt corrosion resistance of coating.

3 Conclusions

1) Under the condition of high temperature oxidation at 1000 °C, the mineralogical composition of CoCrAlY alloy powder with a Si concentration of 0wt% and 2wt% is CoCr_2O_4 and Al_2O_3 , respectively. In addition to Al_2O_3 , SiO_2 is also present in the alloy powder with Si concentration of 5%.

2) The increasing Si content decreases the average corrosion penetration depth of coating. On the other hand, the average corrosion penetration depth of coating increases with the rising temperature from 800 °C to 900 °C.

3) Adding Si element not only promotes the formation of Al₂O₃ protective film, but also leads to the formation of Si-rich layer in the inner side of the oxide film. They contribute to stabilizing the thickness of the oxide film and delaying the consumption of Al, which is a key anti-oxidant element. CrSi, a high melting point and unreactive metal silicide, is generated inside the CoCrAlSiY coating, which decreases the reaction rate of internal oxidation during hot corrosion. Therefore, it is beneficial for improving molten salt corrosion resistance of the coating.

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Si 对 CoCrAlY 涂层抗热腐蚀性能的影响

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摘要: 采用 HVOF 技术制备了 CoCrAlSiY 涂层, 用质量分数 75%Na₂SO₄+25%NaCl 热盐涂敷的方法, 对比了不同质量分数 Si 含量 (0%、2% 及 5%) CoCrAlSiY 涂层在 900 °C 下的抗热腐蚀性能。结果表明: 随着反应温度升高, 涂层的平均腐蚀穿透深度呈增加趋势; 随着 Si 含量上升, 涂层的平均腐蚀穿透深度逐渐下降。腐蚀后 CoCrAlSiY 涂层内生成了高熔点的金属硅化物 CrSi, 有助于提高涂层的抗腐蚀性能。

关键词: MCrAlSiY; 涂层; 氧化; 抗热腐蚀

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