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ARTICLE

Influence of Si on Microstructures and High-Temperature Properties of *M*CrAlY Type Coating

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Abstract: The CoCrAlSiY alloy coating with Si mass concentrations of 0%, 2% and 5% was prepared. The effect of Si element on the structure and properties of the alloy powder and coating was analyzed. In addition, the function of Si element on the high temperature performance of the coating was also discussed. The results show that the Si element is mainly distributed in the β phase, whose volume content and distribution have a great influence on the high temperature performance of the coatings. Furthermore, the Si element promotes the change from internal oxidation to external oxidation of the alloy and the formation of the protective oxide film. However, the much higher Si content results in a higher PBR (Pilling-Bed worth ratio) value of the oxide film, and increases the oxide film stress, which is not beneficial to the improvement of the coating thermal shock resistance at high temperatures.

Key words: *M*CrAlY; Si; high temperature; internal oxidation; thermal shock resistance

*M*CrAlY coatings (*M*=Ni, Co or their combination) are high temperature oxidation and corrosion resistant coatings, which are widely used in the aircraft engines and gas turbine. *M*CrAlY coatings are industrially-used bond coating material applied between the superalloy substrate and the thermal barrier topcoat (TBC)[1,2]. A thin thermally grown oxide (TGO), typically Cr_2O_3 or Al_2O_3, forms on the alloy surface that protects the underlying alloy from oxidation [3-5].Thermal aging and subsequent TGO thickening may cause the spallation of the top coat, resulting in TBC failure[6]. Studies indicate the growth rate of TGO can be suppressed by improving the alloy composition [7,8]. In order to improve the high temperature oxidation resistance and hot corrosion resistance of *M*CrAlY coating, a lot of experimental studies have been undertaken, such as adding modifying elements (Re, Zr, Hf, Ta, Si, etc.) to *M*CrAlY coating system [9-11]. *M*CrAlY coating with added Si element is an important kind of high temperature anti-oxidation protective coating, which is applied to protect it from hot corrosion of equipment in the marine environment[12-14]. However, the work related to selective oxidation and hot corrosion resistance (above 800 °C) of *M*CrAlY coating with Si element is rather limited. Therefore, the CoCrAlSiY coatings with different Si concentrations were designed in this work. The distribution of Si element in the alloy coating and its effect on high temperature performance of the coating will be discussed. In addition, the function of Si in the CoCrAlY alloy system will be investigated.

1 Experiment

Three kinds of CoCrAlY alloy powders with Si mass concentrations of 2% and 5% were designed and prepared by VIGA-16 vacuum atomization furnace in the study. Their chemical composition is listed in Table 1. The CoCrAlSiY coating, in a thickness about 0.2 mm, was prepared on a GH907 substrate in a diameter of 22 mm by using GTV-K2 high velocity oxygen fuel apparatus. A constant oxidation test at 1050 °C was performed in a muffle furnace . An automatic cycle thermal shock test machine was applied to investigate the coating thermal shock resistance at 1050 °C. After keeping for 10 min in the high temperature test facility, the samples were taken out and

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Table 1 Chemical composition of the alloy powders (wt%)

No.	Si	Al	Y	Cr	Co	O
1	0	6	0.5	24	Bal.	3.112×10^{-6}
2	2	6	0.5	24	Bal.	2.718×10^{-6}
3	5	6	0.5	24	Bal.	2.430×10^{-6}

quenched in (20±5) °C water for 1 min. For each thermal shock cycling step, the sample appearance was photographed. In addition, scanning electron microscopy (SEM) was used to gain knowledge of the micro structure and surface oxide film of the alloy powder and coatings. The distribution of different elements in the powders was analyzed by EDS.

2 Results and Discussion

2.1 Effect of Si on Microstructure of alloy powder

In order to investigate the effect of Si on the properties of CoCrAlY alloy system, the phase constitution and microstructure of the CoCrAlY alloy powder with different Si contents were analyzed. The previous work [15] showed that all three kinds of powders consist of the same phases, which are Co_3Al as the matrix and CoAl β phase on it. Scanning electron micrographs from the cross-sections of the three types of alloy powders are shown in Fig.1. It can be seen that the element distribution in the different powders is uniform. The results of backscattered electron image (BEI) show that β phase of CoCrAlY powder without Si is not obvious (Fig1a), while the powders with Si addition of 2% and 5% clearly have two-phase microstructures, in which the matrix phase is light and the β phase is dark, as shown in Fig.2. In addition, the volume content of β phase is gradually enhanced with increasing Si content (Fig.1b, 1c).

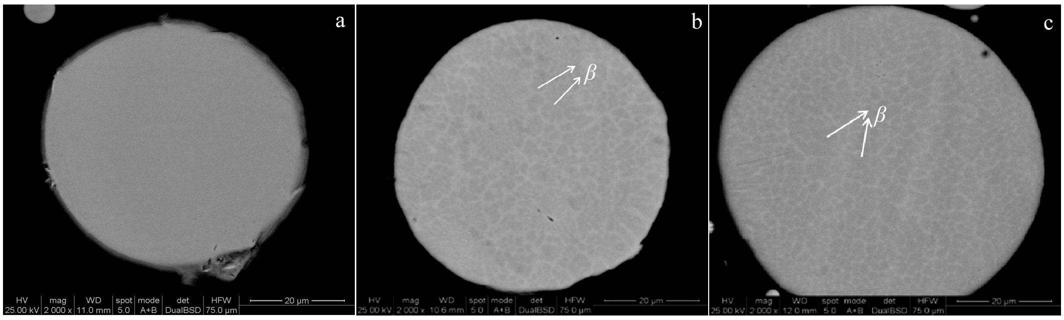

Fig.1 SEM images of the cross section for alloy powders with different Si contents: (a) 0%, (b) 2%, and (c) 5%

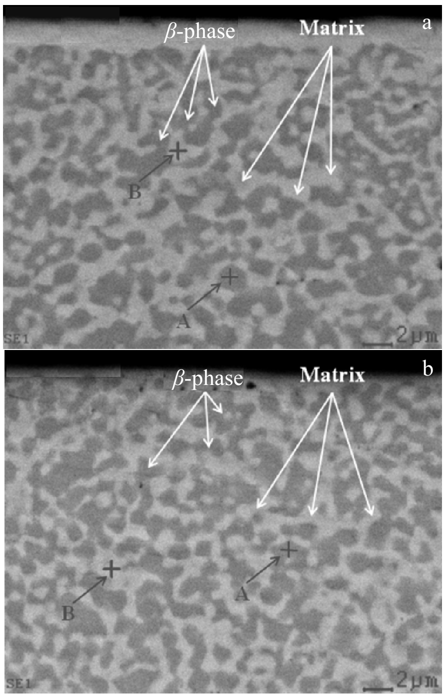

Fig.2 Microstructure of CoCrAlSiY coating: (a) 2% Si, and (b) 5% Si

The oxidation and corrosion resistance of *M*CrAlY coatings is related mostly to the dense oxide film formed by Al_2O_3 and Cr_2O_3 on the coating surface. These oxide films can act as an oxygen barrier layer or a shielding layer to prevent further oxidation and corrosion of the substrate. The phase constitution of *M*CrAlY coatings mainly includes matrix phase and β-NiAl or CoAl intermetallic compound. By the formation of Al_2O_3 film, and thermally grown oxide (TGO), Al content of the β phase decreases at high temperature, and then changes to a γ' strengthening phase. Oxidation resistance of the bond layer decreases, as the β phase vanishes. Therefore, the volume content of β phase and its distribution is an important criterion for evaluating the oxidation resistance of *M*CrAlY coating[16,17]. The EDS analytical results on the coatings with Si addition of 2% and 5% are shown in Table 2.

For all of the tested coatings, the concentrations of both Al and Si in the β phase are obviously higher than those in the matrix phase. Furthermore, the Si content in the β phase increases from 3% to 6% when Si addition increases from 2% to 5%. It can be seen that the added Si element is mostly portioned to the β phase. The high temperature oxidation resistance of CoCrAlY coating is mainly affected by the volume

Table 2 EDS analysis of coating (wt%)

Si content	Element	Co	Cr	Al	Si
2%	β phase	27.87	59.55	10.52	03.06
	Matrix	32.79	56.81	07.95	01.46
5%	β phase	54.97	27.13	12.57	06.33
	Matrix	53.37	30.42	10.43	04.37

fraction and distribution of the β phase. The results of this paper show that Si can improve the oxidation resistance of the coating by increasing the content of the β phase.

2.2 Effect of Si on oxidation resistance of coating

Three types of CoCrAlY coatings with different Si additions were oxidized at 1000 and 1050 °C for 300 h. The coating oxidation kinetics show that the addition of Si element could significantly improve the oxidation resistance of the coating and weaken its mass gain[18]. The scanning electron micrographs of coatings with different Si contents after 300 h oxidation at 1050 °C are given in Fig.3. With increasing Si addition, the residual β phase content in the coating increases obviously, and the internal oxidation point in the coating becomes smaller.

The oxidation process of *M*CrAlY coating is complex. Each element in the alloy shows the different affinity with oxygen, and thus oxide formation free energy of each element is different. Under different conditions, it is possible to form two or more kinds of metal oxides. In the *M*CrAlY alloy system, when the alloy contains an appropriate amount of Cr, Al or Si element, Cr_2O_3, Al_2O_3, SiO_2 or composite oxide film can be formed by the oxidation, which may be a process for the added elements of Cr, Al or Si[19]. The selective oxidation occurs in the external oxidation process of materials system, which requires a certain concentration of solute metal. According to the Wagner theory, Al and Si elements can be considered as the solute metal in the CoCrAlSiY system, and their concentration is influenced by $N_O^{(S)}$ (oxygen partial pressure), D_O (oxygen diffusion coefficient) and D_B (diffusion coefficient of B element).

$$N_B^{(0)} > \left[\frac{\pi g^*}{2b} \cdot N_O^{(S)} \frac{D_O V_m}{D_B V_{OX}}\right]^{1/2} \quad (1)$$

Where D_O is oxygen diffusion coefficient, $N_O^{(S)}$ is oxygen concentration on the surface of alloy, D_B is the smaller solute diffusion coefficient, $N_B^{(0)}$ is critical concentration of solute, g^* is critical volume fraction of oxide, b is valence state of metal, V_m is molar volume of metal, V_{ox} is molar volume of oxide film.

From the formula, it can be seen that the higher oxygen diffusion coefficient (D_O) results in a higher oxygen concentration on the surface of alloy ($N_O^{(S)}$) or a higher oxygen partial pressure. While the smaller solute diffusion coefficient (D_B) leads to the higher solute concentration in the alloy under the condition of external oxidation. According to the analysis mentioned above, increasing Si content will improve the anti-oxidant element content, and the solute elements in the alloy system are easy to reach the critical concentration. Thus, the change from internal oxidation to external oxidation of the alloy occurs. The XRD analysis in the previous work shows that adding Si element could promote the formation of protective oxide film Al_2O_3. Therefore, the internal oxidation phenomenon of CoCrAlY coating with Si element is weakened, and the coating oxidation resistance is improved.

2.3 Effect of Si on thermal shock resistance of coating

The thermal shock resistance represents the bonding strength between the oxide film and the alloy under the condition of rapid temperature change and shows the interface state between the oxide film and matrix under the condition of the thermal stress. It is an important high temperature property of the coating. The different coatings before and after 50 times thermal shock recycle at 1050 ºC show that the cracks on the three coating surface are obviously different after 50 times recycles. Their thermal shock resistance decreases with the increase of Si concentration. For the coating with a Si mass concentration of 2%, the cracks occur at the coating edge. While, for the coating with a Si mass concentration of 5%, the cracks in the shape of “spider web”, appear at the coating

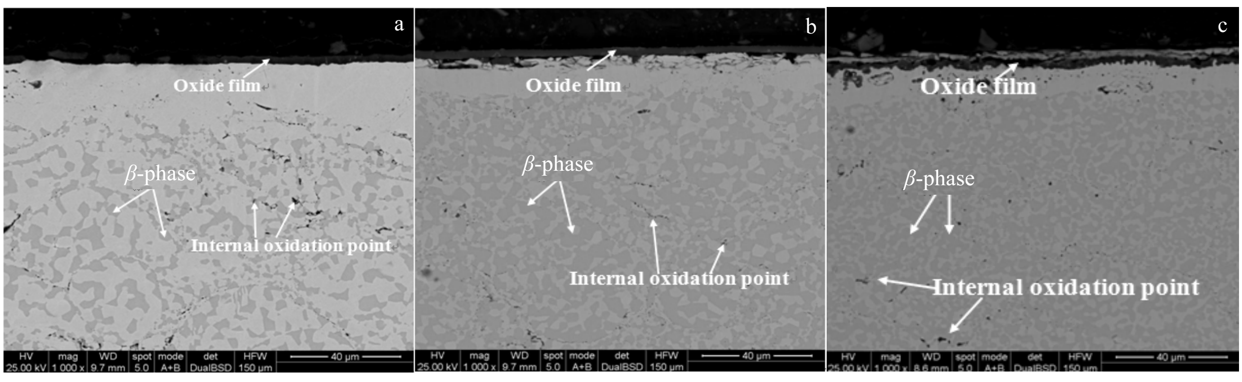

Fig.3 SEM images of CoCrAlY coatings after 300 h oxidation at 1050 °C: (a) 0% Si, (b) 2% Si, and (c) 5% Si

center and edge, and the coating has lost the protective ability for the matrix.

In order to discuss the effect of Si on the coating thermal shock resistance, the thermal expansion coefficients (α) of the three coatings were tested and the results are shown in Fig.4. It can be seen that the thermal expansion coefficient of the coating improves with the increase of Si content.

Pilling-Bed worth Ratio (PBR), the volumetric ratio between the oxide and metal consumed, was calculated. PBR indicates the integrity of the oxide film. When PBR is less than 1, the metal oxide film is small and could not cover the entire metal surface, so the oxide film has no protective ability. However, when PBR is greater than 3, the tensile stress in the oxide film is so strong that the oxide film cracks easily; thus, the oxide film also has no protective ability [20, 21].

For the CoCrAlSiY coating, Lei's work[22] shows that the PBR value is about 1.94, assuming that the oxidation product of Co30Cr6Al alloy is only Al_2O_3. However, the oxidation products of the alloy coatings with Si-addition mainly consist of Al_2O_3 and SiO_2. According to the PBR calculation method of the composite oxides, the PBR values of the CoCrAlSiY alloy oxide film with Si mass concentrations of 2% and 5% are 2.51 and 3.05, respectively. Therefore, the PBR value of oxide film is enhanced with the increase of Si content. However, according to the growth strain (bulk strain, $\varepsilon_r=[1-(PBR)^{1/3}]$) caused by the oxide film PBR, the higher PBR value of oxide film results in a larger tensile stress of the oxide film when the temperature drops, so the alloy oxide film with the high thermal expansion coefficient is much easier to crack. The scanning electron micrograph of the alloy powder with a Si mass concentration of 5% after 300 h oxidation at 1050 °C is demonstrated in Fig.5. It can be seen that the serious oxide film cracks occur on the alloy surface. The oxide film and the alloy are completely separated. Thus, the oxide film also has no protective ability. This is the main reason for the decreasing coating thermal shock resistance, due to an increase in Si content from 2% to 5%.

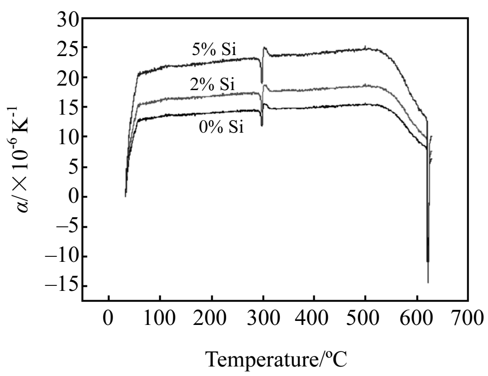

Fig.4 Curves of thermal expansion coefficient of coatings

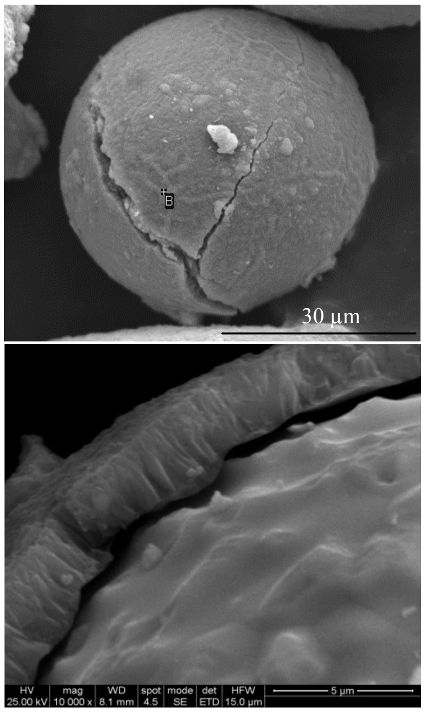

Fig.5 SEM images of alloy powder with 5% Si after 300 h oxidation at 1050 °C

3 Conclusions

1) For the CoCrAlY alloys containing Si element, the Si content in the β phase is higher than that in the matrix phase. With the increase of Si addition, the β phase ratio in the powder and coating increases. In fact, the high temperature performance of the coatings depends on the volume content and distribution of β phase, which is related to Si content in the alloys.

2) Under the oxidation condition of 300 h at 1050 °C, the higher addition of Si-element will induce an increased volume content of the residual β phase, and the internal oxidation point in the coating becomes smaller. Si increases the concentration of antioxidant elements in CoCrAlY, accelerates the process of internal oxidation to external oxidation, and promotes the formation of protective oxide film.

3) The increased Si-addition results in a decreased coating thermal shock resistance. In addition, the PBR value of oxide film is enhanced with the increase of Si content. Therefore, the tensile stress of the oxide film gradually increases due to a quenching process, so the oxide film is much easier to crack.

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Si 对 *M*CrAlY 涂层微观结构及性能的影响

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摘　要：制备了 Si 含量分别为 0%，2%及 5%的 CoCrAlSiY 合金涂层，研究了 Si 元素的添加对合金粉末及涂层的组织、结构及性能的影响，初步探讨了 Si 元素对涂层高温性能的作用机理。研究结果表明：Si 元素主要分布在涂层的 β 相中，通过影响 β 相的含量和分布对涂层的高温性能产生影响，Si 推进了合金由内氧化向外氧化发生的过程，促进了保护性氧化膜的形成，但 Si 含量过高，会引起氧化膜的 PBR 值增加，氧化膜的应力变大，不利于涂层高温抗热震性能的提高。

关键词：*M*CrAlY；Si；高温；内氧化；抗热震性能

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