

GH3625合金在SO₂酸性环境下的高温腐蚀行为

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摘要: 研究了GH3625合金在900 °C的SO₂酸性环境下的腐蚀行为。通过扫描电子显微镜 (SEM), 能量色散谱 (EDS) 和X射线衍射 (XRD) 研究了腐蚀后试样的表面形态和腐蚀产物。通过SEM, EDS和电子探针微量分析仪 (EPMA) 检查横截面形态, 以观察样品内部的腐蚀。结果表明: GH3625合金在酸性气氛下的腐蚀速率随SO₂浓度的增加而轻微增加。合金表面形成了一层主要是Cr₂O₃的致密氧化膜, 该氧化层可以有效阻止SO₂扩散到合金基体内部。另外, 基体内部的铬能够以CrS的形式与硫元素结合, 减缓腐蚀。GH3625合金在高温SO₂环境中具有优异的耐腐蚀性。

关键词: 腐蚀行为; SO₂浓度; 高温; GH3625合金

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GH3625 alloy is used to a great extent in the manufacturing of key parts such as gas turbine engines, nuclear power equipment, aerospace engines, and marine applications due to its good oxidation and corrosion resistance properties, as well as good thermal stability and creep strength^[1-4]. Various corrosion problems cause great economic losses and security risks. Stress corrosion^[5-7] and hot corrosion in molten salts at high temperature^[8-11] have been studied extensively, but the investigation of acidic atmosphere corrosion has been rarely studied, especially in pure SO₂^[12-15].

Yang et al^[16] investigated corrosion behavior of a new Ni-Cr-Fe base alloy GH984G at 700 °C in a synthetic flue gas environment. A dense protective Cr₂O₃-rich scale forms on the sample surface, leading to good corrosion resistance. Gillot et al^[17] studied the corrosion behavior of chromium and manganese in pure SO₂ (890~1350 K, 0.01~0.5 atm). The duplex sulfide/oxide layer formed during the initial exposure can be explained by the direct reaction of SO₂ with the metal rather than oxygen and sulfur.

In this work, the main objective is to determine the effects of SO₂ concentration on the corrosion mechanism of GH3625. The corrosion tests were performed at 900 °C for 48 h in three gas mixtures (vol%): 2% SO₂/98% Ar, 3% SO₂/97% Ar and 100% SO₂. The results were compared with atmospheric oxidation. Corrosion behavior was studied through mass gain, surface characteristics, and cross-sectional morphology.

1 Experiment

1.1 Material preparation

The main chemical composition (wt%) of the GH3625 alloy used in this study is as follows: 60.63% Ni, 21.77% Cr, 8.79% Mo, 3.75% Nb, 3.68% Fe, 0.4% Ti, 0.21% Al, 0.2% Mn, 0.19% Co, 0.12% Si, 0.042% C. The 10 mm×10 mm×10 mm specimens were obtained from the original alloy bar by wire electrical discharging machining (EDM). The specimen surfaces were polished with emery papers of 240#, 600#, 800#, 1000#, and 1500# grit sizes, followed by cloth polishing with a buffing compound with a grain size of 0.1 μm. The samples were then cleaned with acetone, ethanol, and distilled water and immediately dried with compressed air. Corundum crucibles used in the test were cleaned and heated at 200 °C to a stable weight. The sample-filled corundum crucibles were weighed by a digital

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weighing balance (DahoMeter FA1004) with 0.0001 mg accuracy.

1.2 Hot corrosion test

Corrosion tests were carried out for 48 h in a chemical vapor deposition furnace (PECVD-12II-3Z/G) at 900 °C with three gas mixtures (vol%): 2% SO₂-98% Ar, 3% SO₂-97% Ar, and 100% SO₂ (impurities: O₂<4 μL/L, H₂O<5 μL/L). The contrast specimen was tested at 900 °C in air. First, the samples were placed in the tubular furnace. Next, the furnace was degassed to negative pressure with a vacuum pump. Finally, the furnace was filled with the gas mixture. Heating was conducted under vacuum, and cooling was conducted under pure argon flow.

As shown in Fig.1, the two gases were charged into the mixing tank at different flow rates, and then the gas mixture was charged into the reaction furnace.

The sample-filled corundum crucibles were cooled to room temperature and weighed. The corrosion rate was determined by the relationship between the mass gain per unit area and the corrosion time in each gas mixture. The surface morphologies of the corroded specimens were investigated with scanning electron microscopy (SEM). The corrosion products were identified BY energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) with a Cu Kα X-ray source. The specimens were then carefully ground and mechanically polished for cross-sectional observation with SEM and EDS.

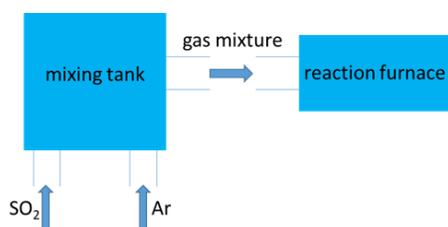


Fig.1 Schematic diagram of gas mixing principle

2 Results and Discussion

2.1 Corrosion rate analyses

Fig. 2 shows the area specific mass gain ΔM of the GH3625 alloy after 48 h corrosion at 900 °C with different gas mixtures. The samples have a slight weight gain and no serious corrosion when the SO₂ concentration is less than 2%. Even in 100% SO₂ atmosphere, the mass gain is only about 4.5 mg/cm². The increase in mass gain indicates that SO₂ accelerates the corrosion of the material. The corrosion rate V_c ($V_c = \Delta M/t$) is calculated by the data in Fig.2, as

shown in Table 1. The rate of corrosion increases slightly from 0.2861 g·m⁻²·h⁻¹ in air to 0.3750 g·m⁻²·h⁻¹ in 100% SO₂.

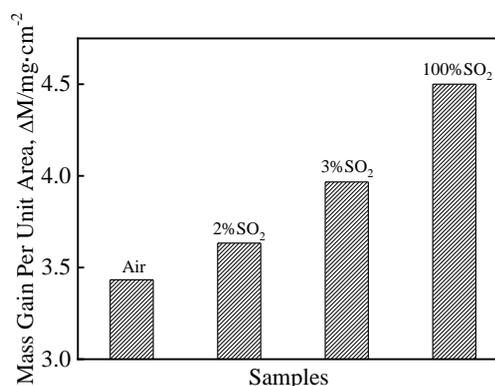


Fig.2 Mass gain of GH3625 alloy corroded in gas mixtures at 900 °C for 48 h

Table 1 Corrosion rate V_c of GH3625 alloy in each gas mixture

Gas mixture	V_c /g·m ⁻² ·h ⁻¹
Air	0.2861
2%SO ₂ + 98%Ar	0.3028
3%SO ₂ + 97%Ar	0.3306
100%SO ₂	0.3750

2.2 Surface morphology and phase constitution

2.2.1 XRD analysis

Fig.3 shows the XRD patterns of the GH3625 alloy before and after the corrosion test under experimental conditions. Fig.3a shows the XRD patterns of the unprocessed GH3625 alloy, in which the diffraction peaks indicate the presence of only Ni-Cr-Co-Mo. Fig.3b shows the XRD pattern of the GH3625 alloy after the corrosion tests in different atmospheres at 900 °C for 48 h. The oxidation products of GH3625 alloy in air are primarily Cr₂O₃, NiCr₂O₄, and NiO. The highest diffraction peak is Ni-Cr-Co-Mo, and the diffraction peaks of the oxidation products are low, indicating that the oxidation scale is thin. The result also shows that the corrosion products of the GH3625 alloy in gas mixtures with different SO₂ concentrations are similar, mainly Cr₂O₃, NiO, Ni₂S₃, CrS, and a small amount of Nb₂O₅. Neither Al₂O₃ nor TiO₂ were detected from XRD analysis, perhaps owing to their low concentration. The diffraction peaks of Ni-Cr-Co-Mo are still obvious, and the diffraction peaks of the corrosion products are low, showing that the corrosion scale is thin. With increasing the concentration of SO₂, the diffraction peak intensity of Cr₂O₃ increases, indi-

cating that the degree of corrosion increases.

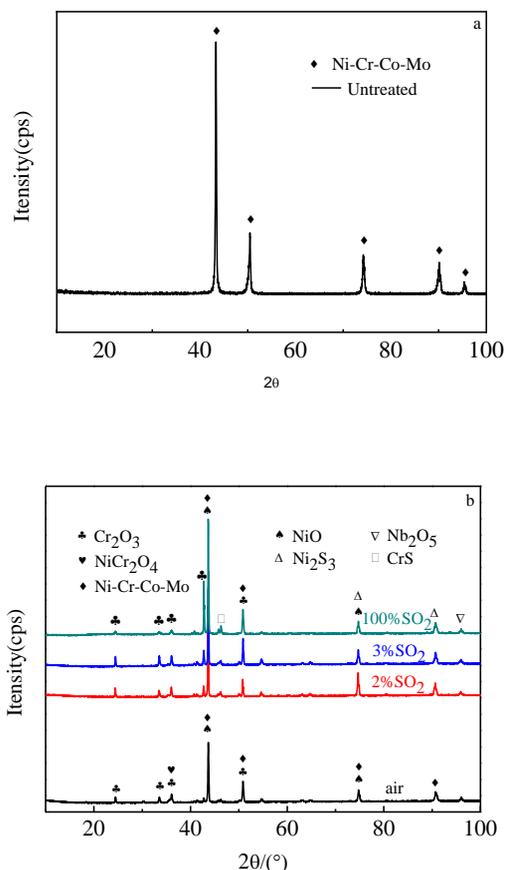


Fig.3 XRD patterns of the GH3625 alloy, (a) unprocessed; (b) corrosion in air, 2%SO₂, 3%SO₂ and 100%SO₂

2.2.2 Surface corrosion scale characteristics

Fig.4 shows SEM images of the GH3625 alloy after corrosion in different atmospheres at 900 °C for 48 h. As shown in Figs.4a~4d, the alloy shows different features after the corrosion test. Fig. 5 shows the EDS analysis of chemical compositions of the surface corrosion of the GH3625 alloy, which shows significant changes at different locations of the corrosion scale.

The SEM plain-view image in Fig.4a demonstrates the massive and granular oxide unevenly and densely distributed on the surface of the oxide scale. On the surface, the corrosion scale (Fig.4a, point 1) is rich in Cr, Ni, and O, as shown in Fig.5a. XRD analysis confirms that the granule-like oxides are Cr₂O₃ and NiO. At the same time, a larger cellular oxide formed by agglomeration of the granular oxide is observed on the surface of the oxide scale (as shown in point 2 in Fig.4a). EDS analysis shows a significant increase in Ni concentration and a significant decrease in Cr concentration. XRD analysis shows that the cellular oxide

is mainly composed of NiO, NiCr₂O₄, and a small amount of Cr₂O₃. It can be concluded that the surface oxidation scale of the alloy is primarily Cr₂O₃, NiO, and NiCr₂O₄.

As shown in EDS analysis and Fig.4b~4d, under each experimental condition with SO₂, a dense scale forms on the surface of the alloy. XRD analysis shows that the oxidation scale of the GH3625 alloy in different SO₂ environments is still generally Cr₂O₃ and NiO (as shown in points 3, 4, 6, 8, 10, and 11). However, as shown in Fig.5b, sulfur can be detected in the corrosion products on the surface of the alloy. XRD results demonstrate that sulfur likely exists as Ni₂S₃ and CrS in the corrosion products (as shown in points 5, 7, 9, and 11).

2.3 Cross-sectional morphology

The corresponding elemental mapping of the GH3625 alloy after oxidation in air is shown in Fig. 6, where a thin layer of ~1 μm forms on the surface of the alloy. The scanning results of the cross-sectional mapping (as shown in Fig.6b~6h) show that the main components in the scale are elemental Cr and O, which can form Cr₂O₃, and there is a depletion of elemental Mo and Nb. Cr₂O₃ can effectively organize the diffusion of oxygen into the interior of the alloy matrix, as can be seen from the low distribution of oxygen in the matrix (Fig.6d).

Fig.6 Cross-sectional SEM image (a) and EDS mapping (b~f) of the GH3625 alloy after oxidation at 900 °C for 48 h

Corrosion severity was also investigated through cross-sectional morphology analysis. Fig.7 shows the cross-sectional morphology images of the GH3625 alloy after corrosion testing. The images show that a thin scale (approximately 0.8 to 2.5 μm) forms on the surface of the alloy with some eroding holes.

Fig.8 shows the line distribution characteristics of the alloy elements of the GH3625 alloy after corrosion, along a direction perpendicular to the interface between the substrate and the scale. As shown in Fig.8, the elements of the surface oxide layer are generally Cr and O. In the vicinity of the contact between the oxide layer and the alloy substrate, the concentration of elemental S and Ni increases. From these data, it can be seen that the thin layer is Cr₂O₃, and that elemental sulfur can penetrate into the alloy matrix through the oxidation layer.

Fig.9 shows the cross-sectional EPMA mapping of the GH3625 alloy after corrosion in 2% SO₂. Table 2 shows the EDS results of chemical compositions of the corrosion

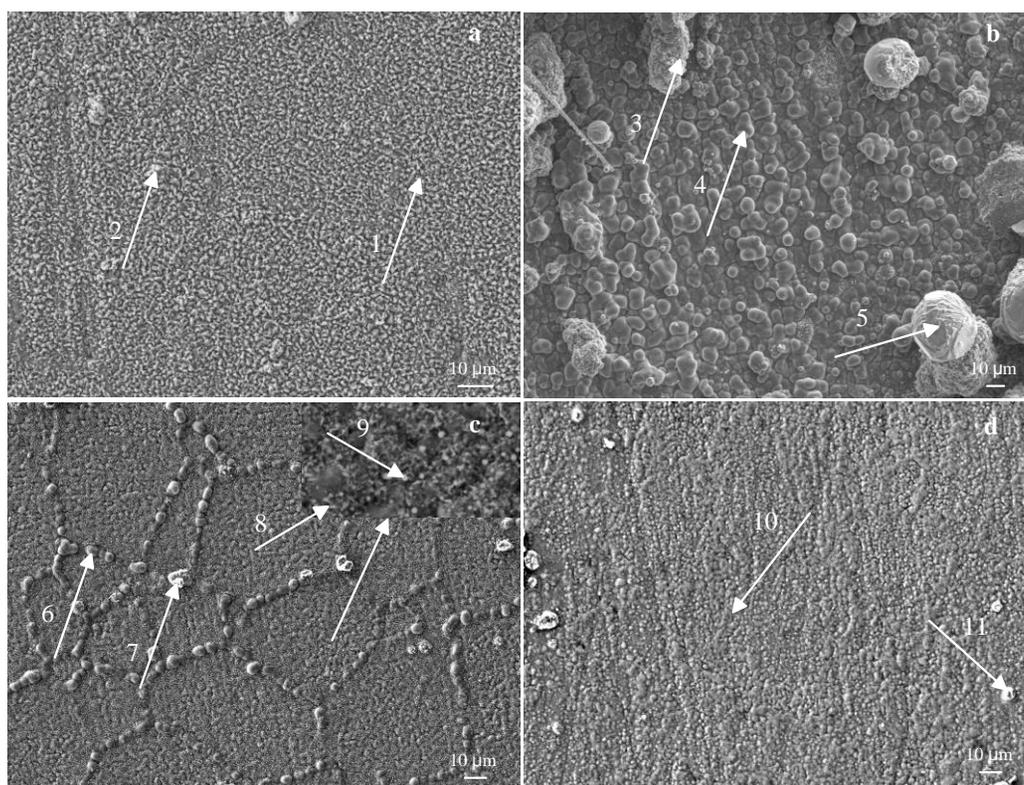


Fig.4 SEM images of GH3625 alloy after corrosion in different atmospheres at 900 °C for 48 h: (a) air, (b) 2% SO₂+98% Ar, (c) 3% SO₂+97% Ar, and (d) 100% SO₂

products of the GH3625 alloy. It is shown that the outer layer is rich in Cr and O and contains a small amount of Ni, Mo and Nb, as shown in Fig.9b~9f and point 1 in Table 2). Combined with XRD data, it is confirmed that it is a layer of Cr₂O₃ with Mo and Nb oxides. The segregation of Mo and Nb is found at the interface between the oxide layer and the alloy matrix. At the same time, Ni and S increase and S extends into the interior of the alloy matrix with approximately the same distribution (as shown in Figs.9e and 9g). In the internal corrosion area, it is found that the two substances are mainly gray and white (as shown in points 2 and 3 in Fig. 9a). Combined with EDS analysis results shown in Table 2, compounds in these distribution areas are primarily CrS with a small amount of eutectic Ni-Ni₃S₂, which is consistent with the XRD results in Fig. 3. Although the formation of the Cr₂O₃ layer can protect the substrate from corrosion, sulfur still penetrates the oxide layer and enters the interior of the substrate (as shown in Fig.9g), which exacerbates alloy corrosion. At point 4 in Fig.9a, it is found through EDS and EPMA results that the element composition here is basically the same as that of the matrix element, and no S element or O element is detected, indicating that the corrosion is basically stopped.

2.4 Corrosion mechanism

Alloy oxidation depends on the concentration of a certain element and its Gibbs free energy^[18-20]. Based on the analysis of Fig.6~9, the GH3625 alloy first forms an outer oxide layer of Cr₂O₃ under experimental conditions that contains NiO, a small amount of NiCr₂O₄ and TiO₂. From thermodynamic analysis, the Gibbs free energy of Cr₂O₃ is low and the Cr concentration is high, so a layer of continuous and dense Cr₂O₃ film is preferentially formed. Ni has low oxidizing driving force and is oxidized to form NiO, which may react with the Cr₂O₃ solid phase to form NiCr₂O₄. Ti has a strong affinity for oxygen, and the outward migration rate is relatively high^[21], but the concentration is too low to detect with XRD.

When SO₂ and O₂ are present in the simulated flue gas environment, they appear as corrosion of a metal-sulfur-oxygen system, and the formation of oxides is usually accompanied by the formation of sulfides^[17]. When the SO₂ concentration is higher than 1%, SO₂ will directly react with metal^[22]. Since the concentration of SO₂ in this experimental environment is higher than 1%, the reaction can be performed according to Eq.(1) and Eq.(2). This is consistent with the XRD results in Fig.2b.

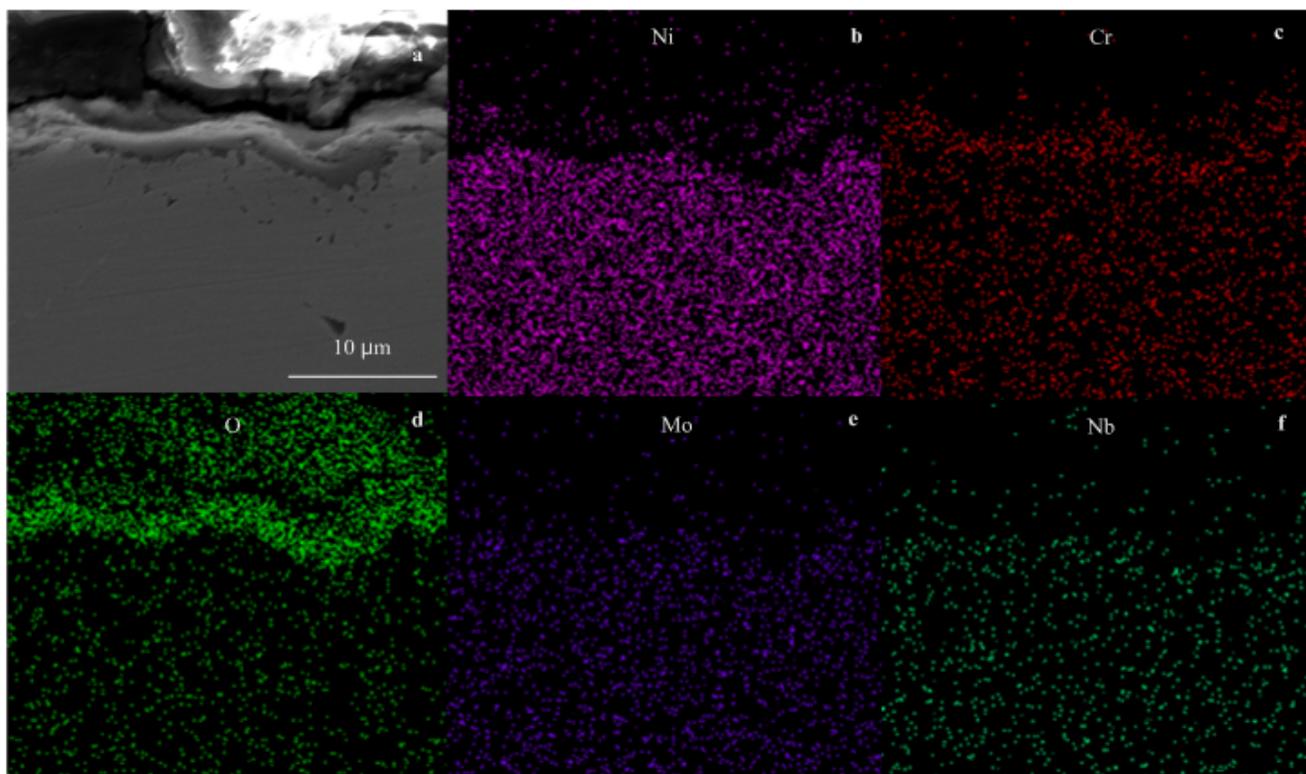
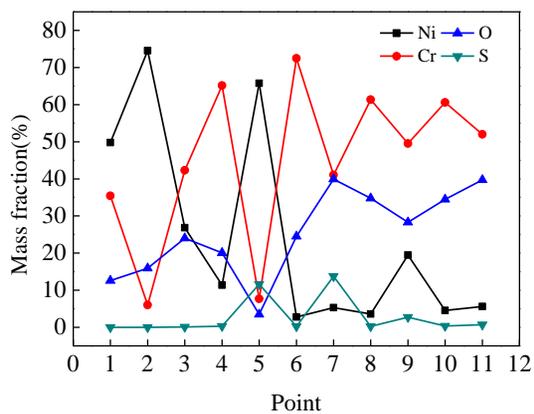


Fig.5 Chemical composition of points marked in Fig.4 of GH3625 alloy after corrosion test

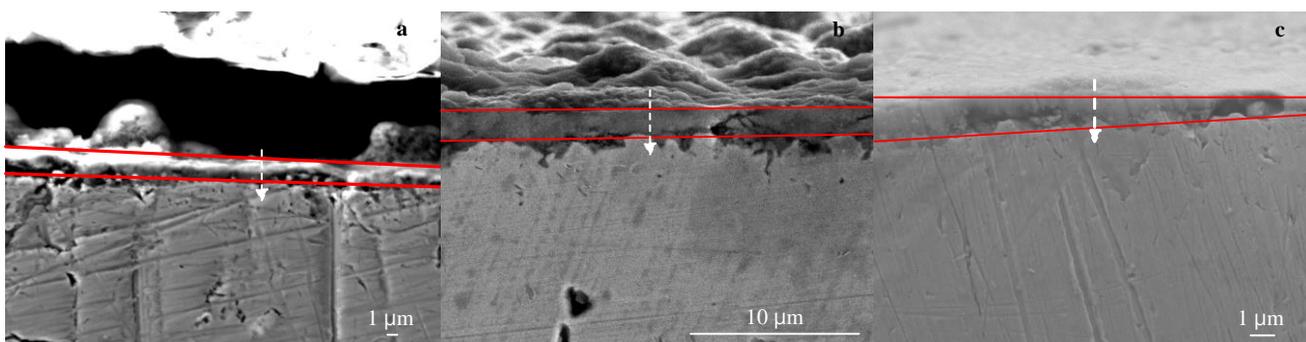


Fig.7 Cross-sectional morphologies of the GH3625 alloy after corrosion testing at 900 °C for 48 h in different environments: (a) 2% SO₂, (b) 3% SO₂, and (c) 100% SO₂

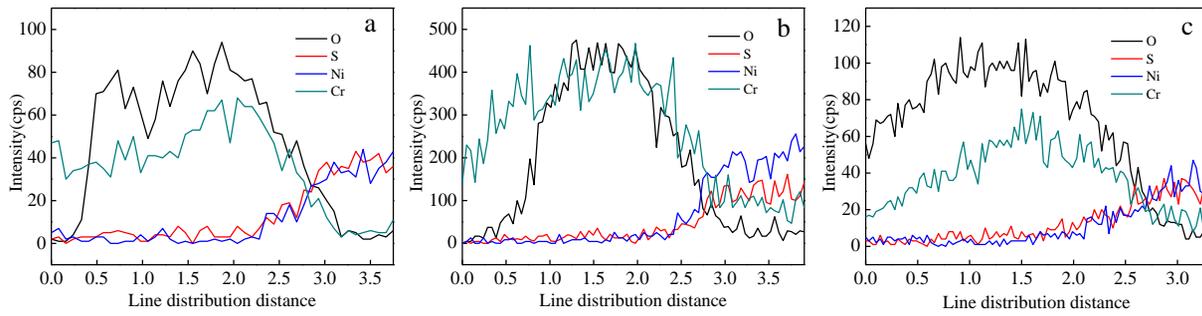


Fig.8 Line scan results of the GH3625 alloy after corrosion testing in different atmospheres at 900 °C for 48 h. (a) 2% SO₂; (b) 3% SO₂; and (c) 100% SO₂

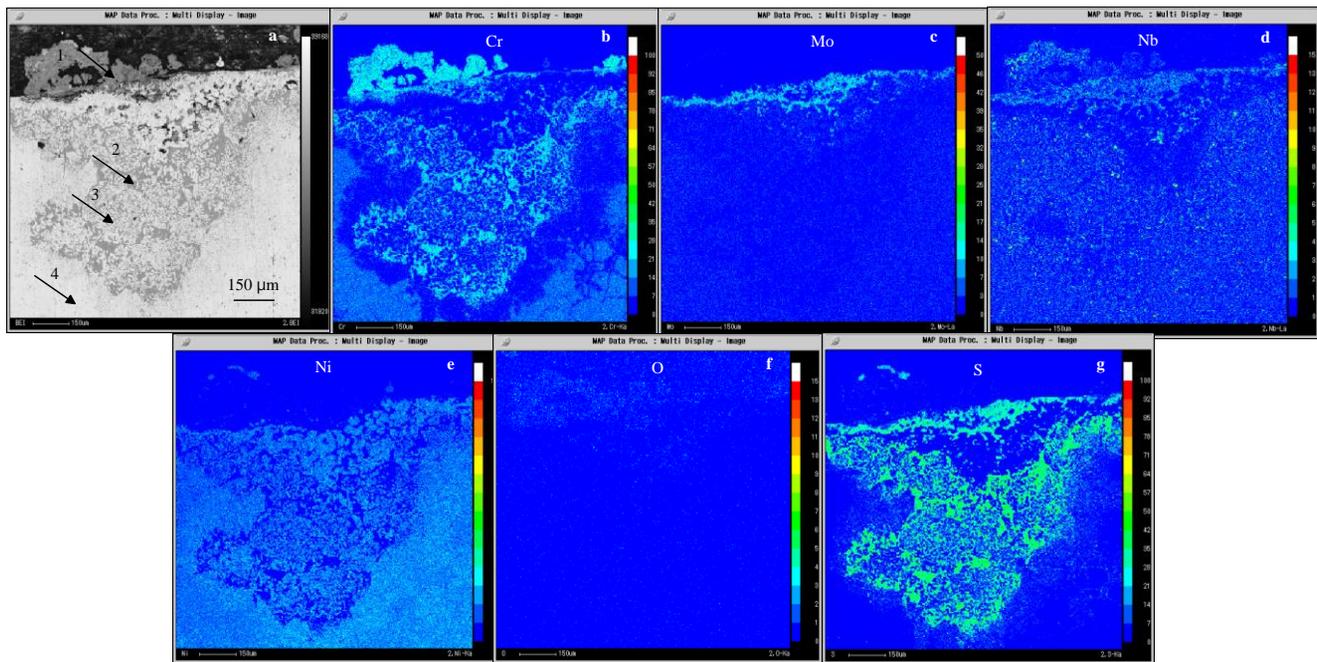
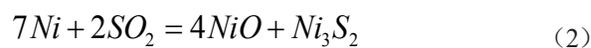
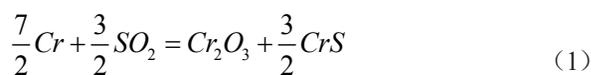


Fig.9 SEM image in backscattered electron mode (a) and cross-sectional EPMA mapping of the GH3625 alloy after corrosion in 2% SO₂ atmosphere at 900 °C for 48 h (b~g)

Table 2 Chemical composition of points marked in Fig. 9a of GH3625 alloy after corrosion test

Point	Ni	Cr	O	S	Mo	Nb
1	3.4	59.2	29.4	2	0.3	5.7
2	4.8	42.7	0.2	47.6	1.5	3.2
3	10.1	42.0	0	42.2	1.9	3.8
4	69.4	20.6	0	0	7.6	2.4



In the initial stage of corrosion, the surface of the alloy forms a dense Cr₂O₃ oxide scale, so it has better physical resistance to SO₂ penetration and resists the SO₂ corrosion in the alloy matrix^[23]. As the experiment progresses, a large

concentration of Cr is consumed, forming a Cr-depleted region in the matrix near the oxide film. The Cr concentration is too low to continuously form a dense Cr₂O₃ oxide layer which causes the oxide layer to be weak or defective in the nearby area. Therefore, SO₂ can penetrate into the interior of the matrix through the physical defects in the surface corrosion layer and further form sulfides. Meanwhile, the corrosion rate of metal sulfide is one to two orders of magnitude higher than that of simple oxidation^[17]. The main reason is that the defects in the metal sulfide are several orders of magnitude higher than the corresponding oxides. Therefore, as the SO₂ concentration increases, the corrosion intensifies.

According to Gibbs free energy, the thermodynamic driving force of chromium vulcanization is the strongest, and

the stability of sulfides is strong, so chromium can preferentially fix sulfur in the form of sulfides (primarily CrS). The element S is fixed, thereby reducing the appearance of eutectic Ni-Ni₃S₂^[24] with a melting point of 645 °C^[25]. At 900 °C, the Ni-Ni₃S₂ eutectic will be in a molten state, destroying the oxide film and accelerating the alloy corrosion. Therefore, reducing its presence can effectively protect the oxide layer and retard alloy corrosion.

3 Conclusions

1) The degree of corrosion of the GH3625 increases with increasing the SO₂ concentrations.

2) Due to the high concentration of Cr in the GH3625 alloy, a dense Cr₂O₃ oxide layer forms on the surface of the alloy, shielding against penetration by oxygen and sulfur, in different concentrations of SO₂ at 900 °C for 48 h. At the same time, chromium can fix sulfur in the form of sulfide, thereby slowing the corrosion rate of the alloy. Therefore, the GH3625 alloy exhibits excellent corrosion resistance in SO₂ environment.

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High Temperature Corrosion Behavior of GH3625 Alloy Under Acidic Atmosphere SO₂

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Abstract: The corrosion behavior of GH3625 alloy under acidic atmosphere SO₂ at 900 °C was investigated. The surface morphologies of the corroded specimens and the corrosion products were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The cross-sectional morphology was examined by SEM, EDS, and electron probe micro-analyzer (EPMA) to analyze the internal corrosion. The results demonstrate that the corrosion rate of the GH3625 alloy only slightly increases with increasing the SO₂

concentration in the acidic environment. A dense oxide film (primarily Cr_2O_3) forms on the alloy surface which can effectively prevent SO_2 from diffusing into the interior of the alloy matrix. Additionally, chromium inside the matrix can combine with sulfur (primarily CrS) to retard corrosion. GH3625 alloy exhibits excellent corrosion resistance in an SO_2 environment.

Key words: corrosion behavior; SO_2 concentration; high temperature; GH3625 alloy

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