

INFLUENCES OF SMALL AMOUNTS OF Y AND Ce ON HIGH TEMPERATURE CORROSION PROPERTIES OF M38 ALLOY ^①

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ABSTRACT

High temperature corrosion properties of M38 alloy with and without 0.04 wt-% Y and 0.05 wt-% Ce additions were studied in equilibrated $\text{SO}_2 + \text{O}_2$ gas mixtures at 850°C and 900°C. It was found that adding Y or Ce decreased the corrosion rate of M38 and changed considerably the surface morphologies and composition of corrosion products on M38. The effectiveness of Y and Ce were also discussed.

Key words: Y Ce M38 alloy $\text{SO}_2 + \text{O}_2$ mixtures high temperature corrosion

1 INTRODUCTION

Small amount of rare earth elements, added into the high temperature alloys, not only could enhance the high temperature strength and the hot plasticity of the alloys, but also could improve their resistances to oxidation, sulfidation and hot corrosion^[1-14]. However, investigation has scarcely been carried out on the effectiveness of rare earth. Although the addition of rare earth may be beneficial to the corrosion resistance of the alloy, the amount of rare earth is limited. The rare earth can only be added as trace elements when the mechanical property of alloy is considered. In this paper, small amounts of Y and Ce were added

into M38 to study its corrosion behaviours and the effects of Y and Ce.

2 EXPERIMENTAL

The adding of rare earth to M38 casting alloy was conducted under the protection of Ar, when being remelted in the induction furnace. The chemical composition of M38, and the experimental procedures were the same as those in ref.[15]. The numbers and the contents of Y and Ce were as follows: 1) M38; 2) M38+0.04 wt-% Y; 3) M38+0.05 wt-% Ce.

3 RESULTS

3.1 Corrosion Kinetics

Fig.1 shows the weight gain versus time

curves of all alloys corroded for 50 h in gas mixtures of two different SO_2/O_2 ratios at 850 °C and 900 °C. The corrosion kinetics of all the three alloys followed parabolic law, which indicated that the diffusion process was the predominant controlling step in the growth of corrosion product scale. Under all experimental conditions, the corrosion rates of No. 2 and 3 alloys were lower than that of No. 1. In addition the effect of Y was larger than that of Ce. When at a constant temperature, the change of SO_2/O_2 ratio almost had no influence on the weight gains and their tendency of all alloys, but the corrosion rate increased significantly with temperature.

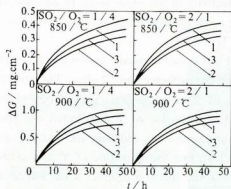


Fig.1 Weight gain vs time curves of corrosion kinetics

3. 2 Scale Morphologies and Compositions of Corrosion Products

The surfaces, cross-sections and composition of corrosion products formed on the alloys at all cases were observed and analyzed by SEM, EPMA, EDAX and XRD. Fig. 2 indicates clearly that the adding of Y or Ce changed the surface morphology of corrosion products on M38 alloy remarkably. The corrosion product scale of No. 3 alloy was more compact than that of No. 1. Larger corrosion product nodular formed on No. 2 alloy and

varied in size. A careful observation of the corrosion products on No. 2 alloy revealed that the nodular distributed gradationally. This can also be demonstrated by the EPMA photos of the elemental distributions on No. 2 alloy (see Fig. 3). The analysis by EDAX and EPMA state that the surface corrosion products on alloys No. 1 and No. 3 were mainly composed of Cr and Ti and uniformly distributed Cr_2O_3 and TiO_2 were the predominant phases composing the corrosion products. The amount of sulfides was relatively small. The surface elemental distributions of the corrosion product of alloy No. 2 were rather uneven. The distributions of Al, Co, Ni were perfectly in agreement and corresponded to the regions beneath large nodular. The sulfur content in these regions was very high. The nodular contained Cr and Ti, thereby they were the oxide mixtures of Cr and Ti. The larger the nodular, the higher the concentration of Cr in it. Fig. 3 also shows that some nodular enriched in Y on the surface of No. 2 alloy. They were oxide of Y, since they were rich in S and O and poor in other elements.

Fig.4 shows the cross-section morphology and EPMA photos of elemental distribution of the corrosion products on alloy No. 2, which were composed mainly of oxides of Cr and Ti. It was prominent that a deep internal corroded zone appeared in all alloys, in which the needle-like sulfide of $\text{Al-Al}_2\text{S}_3$ protruded into the alloy substrate. This zone was rich in Al, but poor in Cr and especially in Ti. The three alloys had almost the same corrosion product cross-sections and elemental distributions.

4 DISCUSSION

It can be concluded from the above results that small amounts of Y or Ce decreased

the corrosion rate of M38, but the effect of Y was larger than that of Ce. Neither Y nor Ce, however, changed the reaction kinetics of M38. The outward diffusions of Cr and Ti to form oxides were the controlling step of reaction, thus resulting that the corrosion kinetics of the three alloys obeyed the parabolic law. Because the oxygen partial pressure in the experimental gaseous mixtures was much higher than that of sulfur, the oxidation of the alloy was the main corrosion process. The thermodynamic equilibrium in some local areas, especially in the region near the boundary between corrosion product scale and the substrate of alloy, could result in the increasing of sulfur pressure while the oxygen pressure decreased, subsequently led to the combination of the active element Al with S to form Al_2S_3 needles in the internal corrosion zone. Al aggregated in the internal corrosion zone and combined with S, thus decreased the sulfur partial pressure in this zone and prohibited the inward diffusion of S to a certain extent, as a result provided protective screen for alloys.

The additions of Y or Ce to M38 did not change the structure and the phase species of corrosion products too. The main reason to decrease the corrosion rate of M38 was that Y or Ce had changed the corrosion product morphology and made the oxide scale formed on

M38 more compact. However, the effect of Y differed a little bit from that of Ce. It can be demonstrated from the analysis by EDAX and EPMA that the 0.04 wt-% Y made the scale composed of the mixed oxides of Al, Co and Ni and formed on the surface of M38 in the initial period of reaction being more compact and protective. This scale was beneficial to the prohibition of the outward diffusions of Cr and Ti. The growing of Cr and Ti oxides at unequal rates resulted in a nonuniform elemental distribution on the surface of alloy No.2. Ce made the mixed oxides scale of Cr_2O_3 and TiO_2 formed on M38 alloy more uniform and compact, which improved the protectivity of the oxide scale. In addition the rare earth promoted the selective oxidationsof Cr, Ti and Al.

Fig.2 shows that some thiooxide of Y formed on the surface of No. 2 alloy. The observation by various methods indicated that this kind of thiooxide of Y distributed extremely nonuniformly, in addition its amount was small. In fact the thiooxide of Y also existed right in the corrosion product scale. But to determine their positions was rather difficult, because the content of Y was very small. Ce could also be able to form thiooxide^[3], however the thiooxide of Ce was not found in the present work. This may be related to the distri-

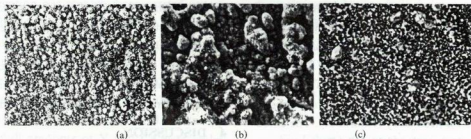


Fig.2 Surface morphologies of corrosion products, 900 °C, 50 h, $SO_2 / O_2 = 2 / 1 (\times 650)$

(a)—M38; (b)—M38+Y (c)—M38+Ce

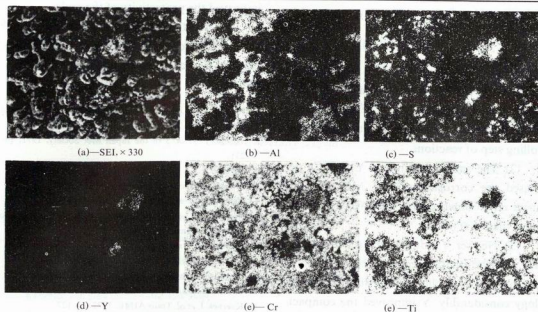


Fig.3 Surface elemental distributions of corrosion product on M38+Y alloy

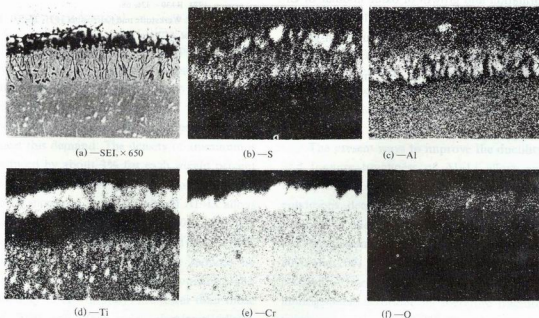
900 °C, 50 h, $\text{SO}_2 / \text{O}_2 = 2 / 1$ 

Fig.4 Cross-section and elemental distributions of corrosion product on M38+Y

900 °C, 50 h, $\text{SO}_2 / \text{O}_2 = 2 / 1$

butions of Y and Ce in the alloys, and needs further investigation.

5 CONCLUSION

(1) The corrosion kinetics of the three alloys followed parabolic law. The outward diffusion process of Cr and Ti was the main controlling step of reaction;

(2) The small amounts of Y and Ce decreased the corrosion rate of M38 alloy in mixed environments, and the effect of Y was better than that of Ce;

(3) Neither Y nor Ce changed the structure and the phase species of corrosion product on M38, but changed the surface morphology considerably. Y improved the compactness and protectivity of the mixed oxide scale formed in the initial period of reaction. The formation and growth of oxide nodular of Cr and Ti in some local areas resulted in the surface corrosion products distributing in gradation. Ce made Cr_2O_3 and TiO_2 mixed oxide scale on M38 being more compact, thereby

improved the protectivity of the scale;

(4) A bit thiooxide of Y formed on the surface of alloy containing Y, while no thiooxide of Ce was found on alloy bearing Ce.

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