Effect of Superficial Application of Yttrium Oxides with Various Activities on High Temperature Oxidation of Chromium

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In high-temperature oxidation of heat resisting alloys, it is known that scale adherence is affected by impurities of sulfur (the sulfur effect). To make clear the origin of the sulfur effect, isothermal oxidations of chromium coated with Y_2O_3 different in activity were carried out in air at 1285 K. The scales formed on chromium with low activities of Y_2O_3 show poor adherence and those with high activities good adherence. Introducing the Gibbs energy change for segregation of sulfur, the role of the rare-earth element in the sulfur effect was thermodynamically explained by the present data and the reported results in chromia-forming alloys. The sulfur content over the solubility limit causes the poor adherence of the scale, and the rare-earth element decreases the activity of sulfur.

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I. Introduction

In high-temperature oxidation of heat resisting alloys, it is known that scale adherence is improved by surface treatment with rare-earth oxides, such as Y_2O_3 , La_2O_3 and CeO_2 , on alloys, as well as by addition of rare-earth metals or dispersion of rare-earth oxides in alloys⁽¹⁾⁽²⁾. Although several explanations on this phenomenon have been proposed⁽³⁾⁻⁽⁵⁾, it is still open to the question.

Since a decade ago some investigators pointed out that sulfur, which exists in alloys as an impurity, has the detrimental effects on the oxidation resistance of alloys⁽⁶⁾⁽⁷⁾. Recently, one explanation which is the so-called "sulfur effect" has been proposed⁽⁸⁾⁻⁽¹⁰⁾. This explains that sulfur segregates at the scale/alloy interface and weakens the adherence of the scale. The role of rare-earth metals or rare-earth oxides is to trap the sulfur and decrease the segregation of sulfur at the interface, resulting in the improvement of the adherence. In the case of surface application of Y_2O_3 to chromium, Y_2O_3 should trap sulfur at the Cr_2O_3/Cr interface. However, there has not been any thermodynamic study which confirms the possibility for trapping of sulfur by Y_2O_3 .

If the effect of Y_2O_3 is caused by thermodynamic reasons, the difference of the Y_2O_3 activity ($a_{Y_2O_3}$) brings about different behavior in oxidation. In the present study, isothermal oxidation of Cr coated with Y_2O_3 of various activities was carried out to clarify the effect of $a_{Y_2O_3}$ on the high temperature oxidation, especially on the scale adherence.

II. Thermodynamic Background on "Sulfur Effect"

Figure 1 shows the phase stability diagram of the Cr-S-O system at 1300 K, which was calculated using thermodynamic data (see Table 1⁽¹¹⁾⁻⁽¹³⁾). The reaction in which Y_2O_3 traps sulfur is given by

Figure 1 shows a line of the phase boundary between Y_2O_3 and Y_2O_2S , as calculated assuming that $a_{Y_2O_3}$ and $a_{Y_2O_2S}$ are unity. The above line indicates that Y_2O_2S is thermodynamically stable. The possibility of reaction (1)

Fig. 1 The phase stability diagram of the Cr-S-O system at 1300 K.

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Table 1 Standard Gibbs free energy of formation, except Y_2O_3 , to calculate the phase stability diagram. The data on Y_2O_3 is the Gibbs energy change of reaction.

Compound	T/K	$\Delta_f G^\circ / J \cdot mol^{-1}$
$Cr_2O_3^{(11)}$	1150–1540	$-1.115 \times 10^6 + 2.501 \times 10^2 T \pm 1500$
$CrS^{(12)}$	1000–1600	$-2.130 \times 10^5 + 6.222 \times 10 T$
$Cr_6S_7^{(12)}$	1000–1500	$-2.335 \times 10^5 + 7.520 \times 10 T$
$Y_2O_3S^{*(13)}$	1190–1500	$6.533 \times 10^4 + 3.387 \times 10 T$

* The reaction is $Y_2O_3 + \frac{1}{2}S_2 = Y_2O_3S + \frac{1}{2}O_2$

can be judged by the oxygen and sulfur activities at the interface.

In the case of superficial application of Y_2O_3 , it can be thought that the oxygen activity at the interface is determined by the following reaction:

The present authors reported the oxygen activity at the equilibrium over Cr – Y_2O_3 – $YCrO_3$ and the Gibbs energy change of reaction (2) by using solid electrochemical cells⁽¹⁴⁾.

$$\log a_{O_2} = 10.6 - 4.39 \times 10^4 \frac{1}{T} \pm 0.1 \quad (1385 \sim 1470 \text{ K}) \quad (3)$$

$$\Delta G_{(2)}^\circ / J \cdot mol^{-1} = -6.30 \times 10^5 + 1.52 \times 10^2 T \pm 2 \times 10^3 \quad (4)$$

At 1300 K, the oxygen activity is 6.8×10^{-24} as shown in Fig. 1. Y_2O_3 ($a_{Y_2O_3} = 1$) can decrease the sulfur activity, a_{S_2} , down to 4.2×10^{-15} (Point A). To our knowledge, there has been only one report on the activity-concentration relationship of sulfur in solid chromium. Oudar and Barbouth reported the relation between the activity and content of sulfur in Cr ⁽¹⁵⁾. Using their result, $a_{S_2} = 4.2 \times 10^{-15}$ (Point A) corresponded to the sulfur content of 3.2×10^{-3} ppm. That is to say, Y_2O_3 decreases the sulfur content down to 3.2×10^{-3} ppm. The above discussion agrees with the Y_2O_3 effects on oxidation of Cr reported by several investigators, because reagent grade Cr is generally expected to contain some ten ppm sulfur.

Figure 2 illustrates the activity change of Y_2O_3 in the Y_2O_3 – Cr_2O_3 system at 1300 K, which is calculated from the Gibbs energy change of the following reaction⁽¹⁶⁾:

$$\Delta G_{(5)} = \Delta G_{(5)}^\circ + RT \ln \frac{a_{YCrO_3}}{a_{Y_2O_3}^{1/2} a_{Cr_2O_3}^{1/2}} \quad (6)$$

When Y_2O_3 and $YCrO_3$ coexist, $a_{Y_2O_3}$ is almost equal to 1 because of negligible solubility of Cr_2O_3 in Y_2O_3 . On the other hand, in the case of coexistence of $YCrO_3$ and Cr_2O_3 in equilibrium ($\Delta G_{(5)} = 0$, $a_{Cr_2O_3} = 1$ and $a_{YCrO_3} = 1$), $a_{Y_2O_3}$ is expressed as

$$a_{Y_2O_3} = \exp\left(\frac{2\Delta G_{(5)}^\circ}{RT}\right) \quad (7)$$

Using the standard Gibbs energy of formation of

Fig. 2 Phase diagram of the Y_2O_3 – Cr_2O_3 system⁽³¹⁾ and the activity change of Y_2O_3 at 1300 K.

$Cr_2O_3^{(11)}$ and eq. (4), one can calculate the Gibbs energy change of reaction (5) as

$$\Delta G_{(5)}^\circ / J \cdot mol = -7.25 \times 10^4 + 2.69 \times 10 T \pm 2.1 \times 10^3 \quad (8)$$

Substituting eq. (8) into eq. (7), the activity of Y_2O_3 is estimated as $a_{Y_2O_3} = 9.6 \times 10^{-4}$ ($\cong 10^{-3}$). Therefore, $a_{Y_2O_3}$ in $YCrO_3$ is markedly different between coexistence of Y_2O_3 and $YCrO_3$ and that of $YCrO_3$ and Cr_2O_3 . During the high-temperature oxidation, the Cr_2O_3 scale reacts with Y_2O_3 and finally consumes all of Y_2O_3 , resulting in the change in $a_{Y_2O_3}$ from 1 to about 10^{-3} .

In Fig. 1, it is also drawn the phase boundary of Y_2O_3 – Y_2O_3S with $a_{Y_2O_3} = 10^{-3}$. In this case, the oxygen activity at the Cr / Cr_2O_3 interface is determined by the equilibrium of Cr – Cr_2O_3 – $YCrO_3$ and is almost the same as that of Cr – Cr_2O_3 because of $a_{Cr_2O_3} = 1$. At this oxygen activity, the phase boundary of Y_2O_3 – Y_2O_3S is located at higher sulfur activity than that of Cr – CrS . This means that $YCrO_3$ cannot decrease the sulfur activity in Cr .

III. Experimental

Specimen were cut off from the Cr plate to $1 \times 10 \times 15$ mm, drilled $\phi 1.6$ mm for hanging, grinded with SiC-paper of #600, and cleaned using an ultrasonic cleaner with acetone for 1.8 ks (30 min). The chemical composition of Cr is shown in Table 2. The content of sulfur is 10 ppm.

Spray pyrolysis of nitrate was used for superficial appli-

Table 2 Concentration of impurities in a chromium sample.

Element	Content in ppm
H	3
N	44
S	10
O	150
C	60
Pb	1
Cu	2
Al	40
Si	130
P	1
Fe	210

Fig. 3 The spray method to coat the specimen.

cation of oxide on specimen. The superficial application of oxide of Cr_2O_3 - Y_2O_3 system was performed by spraying their nitrates diluted with glycerin and water (2:1 volume ratio) to the chromium plate heated at about 773 K as shown in Fig. 3. To obtain the constant thickness of oxide, the nitrate solution was precisely sprayed one surface of the plate for 30 s from the distance of 0.3 m. After that, turning over the plate, the nitrate solution was sprayed another surface similarly.

In the sprayed solution, the sum of Cr and Y ion was about $5.5 \times 10^{-6} \text{ mol/m}^3$ and ratio of Cr:Y were $x:y = 1:0, 3:2, 2:3, 1:2, 1:3, 1:4$ and $0:1$. The sprayed solution with $x > y$ thermally decomposed on Cr specimen as

giving the YCrO_3 - Cr_2O_3 mixture with a low activity of Y_2O_3 . The sprayed solution with $x < y$ decomposes as

giving the YCrO_3 - Y_2O_3 mixture with a high activity of Y_2O_3 . In the following text, Cr specimen coated with $\text{Cr:Y} = x:y$ is denoted as $x\text{Cr}y\text{Y}-z$ where z means the run number. The amount of the sprayed oxide was less than 1 mg. It is difficult to determine the accurate value of the sprayed oxide because of the error in weighing by the chemical balance.

The specimen was set in a high temperature microbalance system (Shimadzu TGA-41, Japan) with quartz chain. Mixed gas of 79% N_2 -21% O_2 was flowed at about $1.7 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$ ($10 \text{ cm}^3/\text{min}$). The specimen was heated from room temperature to 1285 K with 2.4 ks (40 min). After 100 ks (28 h), the furnace was turned off and the specimen was cooled in the furnace. Adherence of the scale was judged by spallation during cooling after oxidation. Scale structure was observed with a scanning electron microscope (SEM).

IV. Results

Figure 4(a) shows the mass gains of non-coated Cr (N-1) and Cr coated with Cr_2O_3 (1Cr-1, -2) during oxidation. These samples showed a large weight gain during oxidation. In cooling, the weights of N-1 and 1Cr-2 were greatly decreased by spalling. Figure 4(b) shows oxidation curves of Cr coated with $\text{Cr}_2\text{O}_3 + \text{YCrO}_3$. 3Cr2Y-2 shows spalling in cooling. Figure 4(c) shows oxidation curves of Cr coated with $\text{YCrO}_3 + \text{Y}_2\text{O}_3$ (2Cr3Y-1, -2, 1Cr2Y-1, -2, 1Cr3Y-1, 1Cr4Y-1). The mass gains are about 1/2 times smaller than that of Cr with low activity Y_2O_3 . There is no spalling in cooling except in 1Cr2Y-2 and 1Cr4Y-1 which shows small spallation. Figure 4(d) shows oxidation curves of Cr coated with Y_2O_3 (1Y-1, -2). Both samples indicate no spalling, good adherent of the scale and reproducibility in weight gain.

Figure 5 shows SEM images of the edge of specimens after the oxidation. Although the weight changes of the specimens coated with same oxide were dispersed, the scale morphology depended largely on the activity of Y_2O_3 and showed the good reproducibility. On Cr coated with Cr_2O_3 and $\text{Cr}_2\text{O}_3 + \text{YCrO}_3$ (low $a_{\text{Y}_2\text{O}_3}$), the scales are wavy and thick. There are large voids between the scales and substrates, which generally means poor adherence. On the other hand the scales, which are formed on the $\text{YCrO}_3 + \text{Y}_2\text{O}_3$ and Y_2O_3 coated Cr ($a_{\text{Y}_2\text{O}_3} = 1$), are flat and adherent with Cr.

V. Discussion

1. Oxidation of chromium

Y_2O_3 in the sprayed oxide is consumed by reaction (5). Assuming the infinite reaction plane and the diffusion controlled reaction in YCrO_3 , the relation between an initial thickness of Y_2O_3 , y_{initial} , and a final thickness of the formed YCrO_3 , x_{final} is represented by

$$x_{\text{final}} = \left(\frac{2V_{\text{YCrO}_3}}{V_{\text{Y}_2\text{O}_3}} \right) y_{\text{initial}} \quad (11)$$

Fig. 4 Weight gain per unit area vs. time of oxidation of Cr and Cr_2O_3 -coated Cr: (a) coated with low activity of Y_2O_3 ; (b) coated with high activity of Y_2O_3 ; (c) coated with Y_2O_3 (d). At 1285 K in 79% N_2 -21% O_2 at 1.0×10^5 Pa.

where V_{YCrO_3} and $V_{\text{Y}_2\text{O}_3}$ are the molar volume of YCrO_3 and Y_2O_3 , respectively. Using the parabolic rate constant of reaction (5)⁽¹⁶⁾, k_p , the time for eliminating Y_2O_3 , t_{life} , is expressed as

$$t_{\text{life}} = \frac{1}{2k_p} \left(\frac{2V_{\text{YCrO}_3}}{V_{\text{Y}_2\text{O}_3}} y_{\text{initial}} \right)^2 \quad (12)$$

To be existed as Y_2O_3 after 100 ks, it is necessary for the thickness of the sprayed Y_2O_3 to be more than 0.1 μm .

Although it is reasonable to consider that the superficial application of oxide is not a dense film because of the sprayed method, we can make rough estimation. In the present study, the amount of the sprayed Y_2O_3 was less than 1 mg. Assuming the dense film, the weight of Y_2O_3 corresponds to 0.6 μm as the thickness of Y_2O_3 film, which is comparable to the rough estimated value in consumed Y_2O_3 for 100 ks. This is considered as one of the reasons for the dispersion of the oxidation behavior. However, on the whole, the oxidation behavior was

strongly affected by the activity of superficially applied Y_2O_3 .

The weight loss on cooling means scale spalling. The amount of scale spalling was strongly affected by the activity of superficially applied Y_2O_3 . Present results show that the samples coated with $a_{\text{Y}_2\text{O}_3} = 1$ (samples coated with Y_2O_3) or ≈ 1 (samples coated with Y_2O_3 - YCrO_3 mixtures) are improved scale adherence and that with $a_{\text{Y}_2\text{O}_3} = 10^{-3}$ (samples coated with YCrO_3 - Cr_2O_3 mixtures) is scarcely improved on the basis of that with $a_{\text{Y}_2\text{O}_3} = 0$ (samples coated with Cr_2O_3 or nothing). These results are consistent with the expectation from Fig. 1.

The Gibbs energy change for the segregation of sulfur, ΔG_s , which corresponds to the driving force of sulfur segregation, is represented by

$$\Delta G_s = -RT \ln \left(\frac{C_s}{C_s^0} \right) \quad (13)$$

where C_s is the sulfur content and C_s^0 is solubility limit of

Fig. 5 SEM micrographs of the edge of the sample after the oxidation at 1285 K for 100 ks (28 h) and ultrasonic vibration in an ultrasonic cleaner. (a) Cr_2O_3 -coated Cr (10Cr-1), (b) $\text{Cr}_2\text{O}_3 + \text{YCrO}_3$ -coated Cr (6Cr4Y-1), (c) $\text{YCrO}_3 + \text{Y}_2\text{O}_3$ -coated Cr (4Cr6Y-1), and (d) Y_2O_3 -coated Cr (10Y-1).

sulfur. The solubility limit of sulfur in Cr at 1285 K is 0.17 ppm⁽¹⁵⁾. The sulfur content of 10 ppm in the sample means that sulfur exist over the solubility limit and the driving force of segregation is $-4.4 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$. When the samples coated with $\text{Cr}_2\text{O}_3 + \text{YCrO}_3$ ($a_{\text{Y}_2\text{O}_3} = 8.2 \times 10^{-4}$ at 1285 K), the equilibrium a_{S_2} over Y_2O_3 and Y_2S is 3.3×10^{-7} at the equilibrium oxygen activity over the Cr- Cr_2O_3 interface, which is higher than the a_{S_2} over the Cr and CrS coexistence ($a_{\text{S}_2} = 1.5 \times 10^{-11}$).

When $a_{\text{Y}_2\text{O}_3}$ is unity at the scale/metal interface, Y_2O_3 would trap the sulfur and decrease the sulfur content down to 1.9×10^{-3} ppm which corresponds to $\Delta G_{\text{S}} = 4.8 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$. If the effect of Y is caused by trapping of sulfur, scale adherence is improved. The present result are consistent with the above discussion. It is

considered that the scale adherence depends upon the driving force of sulfur segregation.

Lees⁽¹⁰⁾ and Melas *et al.*⁽¹⁷⁾ observed the oxidation of Cr containing 120 and 40 ppm sulfur at 1223 K. At their temperature, the solubility limit of sulfur is 0.04 ppm⁽¹⁵⁾. The sulfur contents of 120 ppm and 40 ppm corresponded to $\Delta G_{\text{S}} = -8.14 \times 10^4$ and $-7.02 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, respectively. Although both samples contained sulfur over the solubility limit, the adherence of the scale was reported to be improved on the sample with 40 ppm sulfur. This result is consistent with the concept which the increase of ΔG_{S} improves the adherence of the scale. However, the change of ΔG_{S} was small. The sample with 40 ppm sulfur was achieved by annealing sample with 120 ppm sulfur in hydrogen flow meant that the sample contained 40 ppm

sulfur as a whole. Therefore, it is considered that the sulfur content was drastically decreased at the surface of the sample with 40 ppm sulfur and the actual ΔG_S might be positive.

2. Extension of the concept to high temperature oxidation of chromia forming alloys

(1) Fe-Cr alloys

It is necessary for the relation between sulfur content and activity, and activity of Cr (a_{Cr}) in alloys to draw the phase stability diagram of the Cr-O-S system. Table 3⁽¹⁵⁾⁻⁽²⁵⁾ shows the relations between the sulfur content and activity in Fe-Cr alloys and other materials.

Figure 6 represents the reported a_{Cr} in Fe-Cr alloys. McCabe *et al.*⁽²⁶⁾ and Kubaschewski and Heymer⁽²⁷⁾ measured by using the Knudsen cell. Jeannin *et al.*⁽²⁸⁾ determined by the oxygen partial pressure from gas equilibrium between P_{H_2} and P_{H_2O} ($2Cr + 3H_2O = Cr_2O_3 + 3H_2$). Although measurements were carried out at different temperatures, the values of Kubaschewski and Heymer agreed with that of Jeannin *et al.* Therefore, temperature dependence of a_{Cr} in Fe-Cr alloys are negligible. In the present study, the values reported by Jeannin *et al.* at 1313 K were adopted as a_{Cr} in Fe-Cr alloys. The stability regions of α and γ phases at 1300 K are drawn based on the phase diagram⁽²⁹⁾.

Rhys-Jones *et al.*⁽³⁰⁾ observed high temperature oxida-

tion of Fe-20Cr alloys with 55 ppm sulfur and with 230 ppm sulfur at 1273 K. They represented acceleration of oxidation rate by addition of sulfur. Figure 7 shows phase stability diagram of Fe-20Cr alloys at 1273 K. Chromium activity was estimated as $a_{Cr}=0.33$ based on Fig. 6. The solubility limit of sulfur calculated from the relation between the content and activity of sulfur reported by Grolière and Barbouth⁽¹⁹⁾. In the sample of Rhys-Jones *et al.*, sulfur dissolved over the solubility limit in Fe-20Cr alloys whose ΔG_S was decreased from -5.7×10^3 to -2.1×10^4 J·mol⁻¹ with addition of sulfur. They pointed out that Fe-20Cr with 230 ppm sulfur had formed a highly convoluted (non-adherent) Cr_2O_3 scale at the early stage and increased oxidation rate than that with 55 ppm sulfur. Furthermore, they indicated

Table 3 Relation between sulfur solubility and activity.

Materials	T/K	log(C_S /ppm)	
		$= \log \frac{a_{H_2S}}{a_{H_2}} + A + \frac{B}{T}$	
		A	B
Cr ⁽¹⁵⁾	1273-1473	11.8	-10588
Fe-90Cr ⁽¹⁵⁾	1273-1473	2.09	4114
Fe-80Cr ⁽¹⁵⁾	1273-1473	4.48	1429
Fe-78Cr ⁽¹⁵⁾	1273-1473	6.55	-2035
Fe-75Cr ⁽¹⁵⁾	1273-1473	7.78	-3521
Fe-70Cr ⁽¹⁵⁾	1273-1473	7.758	-3341
Fe-60Cr ⁽¹⁵⁾	1273-1473	7.31	-2535
Fe-50Cr ⁽¹⁵⁾	1273-1473	6.9	-1928
Fe-45Cr ⁽¹⁵⁾	1273-1473	7.55	-2969
Fe-40Cr ⁽¹⁵⁾	1273-1473	7.044	-2100
Fe-30Cr ⁽¹⁸⁾⁽¹⁹⁾	1368-1458	0.625	6500
Fe-23Cr ⁽¹⁸⁾⁽¹⁹⁾	1368-1458	0	7280
Fe-18Cr ⁽¹⁸⁾⁽¹⁹⁾	1348-1473	3.294	2666
Fe-13Cr ⁽¹⁸⁾⁽¹⁹⁾	1258-1458	8.673	-4918
Fe-10Cr ⁽¹⁸⁾⁽¹⁹⁾	1258-1458	6.67	-2955
Fe-5Cr ⁽¹⁸⁾⁽¹⁹⁾	1258-1458	6.72	-3185
γ -Fe ⁽²⁰⁾	1223-1523	6.44	-3090
Ni ⁽²⁰⁾	1173-1473	6.28	-1840
Co ⁽²⁰⁾	1223-1523	7.3	-5000
Fe-25Ni ⁽²¹⁾		7.09	-3565
Fe-50Ni ⁽²¹⁾		6.96	-3291
Fe-75Ni ⁽²¹⁾		7	-3256
Fe-18Cr-10Ni ⁽²²⁾		6.96	-2742
Ni-15Cr-10Fe ⁽²³⁾	1173-1473	6.58	-2110
γ -Fe ⁽²⁴⁾	C_S^s /ppm (1273 K)=132		
Fe-10Cr ⁽²⁴⁾	C_S^s /ppm (1273 K)=13		
Fe-(20~50Cr) ⁽²⁵⁾	C_S^s /ppm (1573 K)≅500

Fig. 6 Activities of chromium in Fe-Cr alloys⁽²⁶⁾⁻⁽²⁸⁾. The broken line shows Raoultian ideal. The solid line is the expected value at 1300 K.

Fig. 7 Phase stability diagram of the (Fe-20Cr)-O-S system at 1273 K.

that the scale on Fe-20Cr (containing 160 ppm sulfur) with addition of Ce showed higher adherence than on Fe-20Cr containing 55 ppm sulfur.

Figure 8 shows the phase relation of Ce-Cr-O system estimated by that of the $\text{CeO}_2(\text{Ce}_2\text{O}_3)\text{-Cr}_2\text{O}_3$ system⁽³¹⁾. Chromium is in equilibrium with Ce_2O_3 and CeCrO_3 . Although one adds CeO_2 to alloy, it is considered that cerium oxide is reduced and exists as Ce_2O_3 at the alloy/scale interface. Therefore, cerium oxide may trap sulfur at the alloy/scale interface as follows:

Reaction (14) depends on the oxygen activity. The oxygen activity at the interface corresponds to the oxygen activity at the equilibrium over Cr-Ce₂O₃-CeCrO₃ as shown in Fig. 8.

Figure 7 shows the phase boundary between Ce_2O_3 and $\text{Ce}_2\text{O}_2\text{S}$ ⁽¹³⁾, which indicates the ability of sulfur trapping by Ce_2O_3 , and the equilibrium oxygen activity over Cr-Ce₂O₃-CeCrO₃ calculated from the reported value (Table 4⁽¹³⁾⁽³²⁾⁽³³⁾). Under the experimental condition employed by Rhys-Jones *et al.*, although the oxygen activity corresponds to that of Cr-Cr₂O₃, it is expected that Ce_2O_3 traps sulfur. They demonstrated that the addition of Ce improves scale adherence.

Fig. 8 Phase relation of the Ce-Cr-O system at 1300 K.

Table 4 Standard Gibbs free energy change of reaction to calculate the phase stability from literature.

Reaction	T/K	$\Delta G^\circ/\text{J} \cdot \text{mol}^{-1}$
$2\text{CeO}_2 + \frac{1}{2}\text{S}_2 = \text{Ce}_2\text{O}_2\text{S} + \text{O}_2$ ⁽¹³⁾	1180–1530	$4.2391 \times 10^5 - 1.045 \times 10^2 T \pm 2300$
$\text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2 = 2\text{CeO}_2$ ⁽³²⁾	1000–1600	$-3.8123 \times 10^5 + 1.295 \times 10^2 T$
$\text{Ce}_2\text{O}_3 + \text{Cr}_2\text{O}_3 = 2\text{CeCrO}_3$ ⁽³³⁾	1400–1800	$-8.74 \times 10^4 - 22.2T \pm 8000$

Rhys-Jones *et al.*⁽³⁰⁾ also observed about Fe-10Cr alloys. It was assumed that the activity of Cr in Fe-10Cr at 1273 K is about 0.21 based on Fig. 6. The activity change of Cr from 0.33 to 0.21 is negligibly small in Fig. 7. The solubility limit of sulfur in Fe-10Cr alloy was calculated to be 4.6 ppm from the relation between sulfur content and activity by Grolière and Barbouth⁽¹⁹⁾. An Fe-10Cr sample of Rhys-Jones *et al.* contained 24 ppm sulfur which is over the solubility limit. Therefore, it is expected that the addition of Ce causes trapping of sulfur and improves adherence of the scale. Actually, it was reported that adherence of the scale was improved.

Papaïacovou *et al.*⁽³⁴⁾ investigated high temperature oxidation of Fe-20Cr alloys coated with cerium oxide at 1173 K. Figure 9 shows phase stability diagram of Fe-20Cr alloy at 1173 K. Chromium activity was assumed as 0.33 based on Fig. 6. Figure 9 includes the phase boundary between $\text{Ce}_2\text{O}_3\text{-Ce}_2\text{O}_2\text{S}$. The substrate used by Papaïacovou *et al.* contained 550 ppm sulfur over the solubility limit. If sulfur is trapped by cerium oxide coating, the sulfur activity is decreased up to 2.2×10^{-21} and scale adherence is improved. In practice, the reported results shows improvement of scale adherence. Moreover, Papaïacovou *et al.* analyzed amount of sulfur at the alloy/scale interface by SIMS and described that there were no differences between the sulfur quantities with and without CeO_2 coating. Although the alloy was coated with CeO_2 , it was impossible to decrease the amount of sulfur segregation from the inner alloy. However, if there were CeO_2 , the scale adherence would be improved because of the inhibiting segregation of sulfur by trapping.

(2) Ni-Cr alloy

Ecer and Meier⁽³⁵⁾ observed a high temperature oxidation of the Ni-50Cr alloy with and without addition of

Fig. 9 Phase stability diagram of the (Fe-20Cr)-O-S system at 1173 K.

Ce. They judged adherence of scale from cyclic oxidation at 1373 K. The Ni–Cr system is an eutectic where the two-phase mixture region is spread over about 90–45 mol% Cr content at 1373 K⁽³⁶⁾. When the activity of Cr obeys the Raoult law, a_{Cr} in Ni–50Cr is almost equal to 0.9 because Cr dissolves Ni about 10 mol% and Ni–50Cr exists as an eutectic mixture. Since it makes only a small difference between $a_{Cr}=0.9$ and 1, one can reasonably use the phase stability diagram of the Cr–O–S system at 1373 K by using $a_{Cr}=1$ (Fig. 10). The specimen used by Ecer and Meier contained 50–60 ppm sulfur. Since the solubility of sulfur in Cr and Ni–15Cr–10Fe was reported to be 1.2 ppm and 55 ppm at 1373 K⁽²³⁾, respectively, it is considered that the specimen of Ecer and Meier had sulfur

over the solubility limit. Therefore, it is expected that the addition of Ce causes trapping of sulfur. Ecer and Meier reported improvements in scale adherence.

(3) Austenitic stainless steel

Barbouth *et al.*⁽²²⁾ determined solubility limit of sulfur, the relationship between the sulphur activity and content, and the activity of Cr in Fe–18Cr–10Ni at 1173–1473 K. By using their value of $a_{Cr}=0.25$, Fig. 11 shows a phase stability diagram of the Cr–O–S in the Fe–18Cr–10Ni system at 1373 and 1473 K.

Fujikawa *et al.*⁽⁶⁾ observed oxidation of austenitic stainless steel as a function of sulfur impurity, which was based on the composition of Fe–19Cr–13Ni–3.5Si. They pointed out that at 1473 K scale adherence was decreased by the increasing of sulfur content from 8 to 60 ppm. The sulfur contents in their samples were less than the solubility limit, since the solubility limit of sulfur is 119 ppm in Fe–18Cr–10Ni at 1473 K⁽²²⁾.

Mitra *et al.*⁽²⁾ evaluated oxidation resistance of austenitic stainless steel Fe–18Cr–9Ni (ANSI 304) containing 150 ppm of sulfur with and without superficially applied CeO_2 . They reported the decrease of the oxidation rate by superficial application of CeO_2 and improvement of scale adherence by using texture observation.

Ikeda *et al.*⁽⁸⁾ carried out high-temperature oxidation of austenitic stainless steel based on Fe–25Cr–20Ni (SUS 310S) with and without La or mischmetal (70%Ce, 30%La) at 1450 K. Assuming that there is no difference in the solubility limit of sulfur between the Fe–25Cr–20Ni alloy and the Fe–18Cr–10Ni alloy, 70 ppm sulfur in the Fe–25Cr–20Ni alloy might correspond to be almost saturated. Ikeda *et al.* showed improvements in scale adherence by the addition of rare-earth elements.

3. The sulfur effect in Cr_2O_3 forming alloys

By using the driving forces to segregate the sulfur impurity, the scale adherence can be expressed as in Fig. 12. The scale adherence dramatically changes across the solubility limit of sulfur regardless of the alloy systems of Cr, Fe–Cr, Ni–Cr and Fe–Ni–Cr. The result reported by Lees⁽¹⁰⁾ only showed a different tendency. His sample with low sulfur content was prepared by annealing in hydrogen flow. The sulfur content on the surface was probably low enough to provide the good scale adherence although the bulk concentration was still higher than the solubility limit.

In conclusion, the rare earth elements decrease the segregation of sulfur at the alloy/scale interface and brings about improvements in scale adherence. And the driving force to segregate sulfur can be used as an index to estimate the scale adherence. The sulfur effect was proved by Ikeda *et al.*⁽³⁷⁾ with TEM and EDX analyses which indicated sulfur concentrating around the dispersed Y_2O_3 particle. Although their samples were Al_2O_3 scale systems, a similar state would be observed in Cr_2O_3 scale systems.

Fig. 10 Phase stability diagram of the Cr–O–S system at 1373 K.

Fig. 11 Phase stability diagram of the (Fe–18Cr–10Ni)–O–S system at 1373 K and 1473 K.

Fig. 12 Relation between driving force to segregate sulfur and scale adherence.

VI. Conclusion

In the high-temperature oxidation of Cr_2O_3 -forming alloys, it is thermodynamically demonstrated that the segregation of sulfur is decreased by rare-earth oxides. In this case, the scale adherences is improved. It has been found that it is important to decrease the sulfur content below the solubility limit, and the driving force of sulfur segregation $\Delta G (= -RT \ln(C_s/C_s^0))$ is a good measure for the "sulfur effect".

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