Effect of Si Addition on Oxidation Behavior of Nb Containing Ferritic Stainless Steel

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The effect of Si on the oxidation resistance of high purity Nb containing 19% Cr ferritic stainless steels has been investigated by means of isothermal heating at temperatures up to 1 273 K in air and, the structures of the scale and scale/metal interface were investigated with FE-SEM and FE-TEM. The results are as follows:

Si improved the oxidation resistance, as reported in previous studies. The Si addition of about 0.1% improved the limit temperature of the oxidation resistance more than 100 K. The presence of an amorphous SiO₂ layer was found in the interface between the Cr₂O₃ scale and the metal. This layer might act as an oxidation resistance barrier. In the Si-free steel, a NbO₂ layer formed under the Cr₂O₃ scale, and the Fe₂Nb-free region formed beneath the surface. On the other hand, when Si was added, the formation of NbO₂ layer was suppressed. In case of 1%Si, no NbO₂ layer formed and the Fe₂Nb-free region was eliminated. In addition, Fe particles were present in the Cr₂O₃ scale in the Si-added steel.

KEY WORDS: ferritic stainless steel; Niobium; Silicon; oxidation; air; scale; SEM; TEM; NbO₂.

1. Introduction

Stainless steels that contain a large amount of Cr exhibit a superior corrosion resistance at high temperatures as well as at room temperature. This is due to the formation of the protective oxide layer containing Cr. Moreover, they have superior mechanical properties at high temperatures. Therefore, ferritic stainless steels are used as the heat-resistant materials as well as the corrosion-resistant materials.¹⁾ In particular, Nb containing ferritic stainless steels show the superior heat resistance due to the effect of the Nb addition on increasing the high temperature strength. Moreover, ferritic stainless steels are relatively low cost, because they do not contain an expensive Ni. Therefore, ferritic stainless steels are used as materials for combustion components.²⁾ Recently, they are extensively used as materials for automotive exhaust systems including exhaust manifolds because of their excellent cost performance.^{3,4)} In this application, superior oxidation resistance is simultaneously required together with the excellent high temperature strength and thermal fatigue resistance. Thus, they usually contain Si and Mn as elements that improve oxidation resistance.

The effect of Si on oxidation resistance was studied by many previous researchers.^{5–11)} Si has been recognized as the element improving oxidation resistance. The two kinds

of mechanism were proposed for improving oxidation resistance. One is that Si decreases the defects in the Cr₂O₃ scale, leading to the pure and fine Cr₂O₃ scale, as proposed by Francis⁵⁾ and Radavich *et al.*⁶⁾ The other is that Si forms a thin SiO₂ layer at the scale/metal interface and prevents the outward diffusion of metal ion and the inward diffusion of oxygen, as proposed by Caplan and Cohen,⁷⁾ and Nakayama and Oshida.⁸⁾ Shoji *et al.*⁹⁾ tried to elucidate these two ideas using austenite stainless steels with the high Si addition. Despite the fact that they detected a thin SiO₂ layer in the interface, they could not draw any clear reason for their improvement. For ferritic stainless steels, Wood *et al.*¹⁰⁾ studied the Si effect on high temperature oxidation using Fe-26–29%Cr-0–5%Si and Fe-14%Cr-4%Si (hereafter, % means mass%). They reported that Si addition suppressed the mass gain during oxidation. A SiO₂ layer formed under the Cr₂O₃ scale was confirmed to be responsible for the suppression of the mass gain by oxidation. On the other hand, they reported that Si addition promoted the scale spallation. In addition, Fujikawa *et al.*¹¹⁾ investigated the effect of Si on oxidation behavior in air using the Nb containing ferritic stainless steels with 0–2%Si and 11–19%Cr. They proposed that the Si addition improved the oxidation resistance, which was brought about by the suppression of the γ phase formation. The effect of Si itself was supposed not to be large, but as large as that of Cr. In other words, the oxidation resistance depends on whether or not γ phase forms. This is postulated to stem from the fact that the diffusion in γ

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phase is slower than that in α phase. When γ phase forms under the scale, the supply of Cr to the scale is insufficient. Moreover, the thermal expansion coefficient of the γ phase is larger than that of the α phase. Thus, the scale becomes easy to crack due to the difference in thermal expansion between the metal and scale. Furthermore, the formation of a protective scale is suppressed, resulting in a decrease in the oxidation resistance.

Si has been recognized as the element improving oxidation resistance, however, there still remain many questions about the behavior of Si during oxidation. Therefore, the mechanism of improving the oxidation resistance by Si has not been comprehensively understood. Because stainless steel consists of high contents of various alloy elements and they act in a complicated manner, the behavior of each element during oxidation is hard to be clearly understood. In the case of practical stainless steel, more elements are often added which makes it difficult to separate the effect of each element on oxidation resistance.

Thus, in the present study, oxidation behavior of high-purity Nb containing 19%Cr ferritic stainless steels without and with Si was investigated to clearly discuss the effect of the Si addition. In particular, the structures of the scale and the scale/metal interface were focused to be investigated. In the steels used, the contents of Mn and other impurities (P, S) were reduced as much as possible. In addition, the contents of Cr in the steels were 19% to avoid the influence of γ phase on the oxidation behavior.

2. Experimental Procedure

2.1. Sample Preparation

The high-purity 18.5%Cr-0.5%Nb ferritic stainless steels with about 50 ppm of N and 100 ppm of C, containing 0–1%Si, were used. These steels were melted in a vacuum induction furnace and cast to obtain 50 kg ingots.

The chemical compositions of steels used are shown in **Table 1**. To remove the effect of the structural factor on the oxidation behavior, the used steels were intended to have 19%Cr, which were expected to be stable α phase without the formation of γ phase. Each ingot was hot-rolled and cold-rolled followed by annealing at 1 323 K for 60 s. Finally, steel sheets of 2 mm in thickness were prepared. The oxidation test specimens were prepared by machining these steel sheets. The specimen was 2 mm in thickness, 20 mm in width and 20 mm in length. The surfaces of the specimens were wet-polished after grinding with emery paper up to #400. The specimens were further cleansed by acetone.

2.2. Oxidation Test in Air

The oxidation tests were performed in air at temperatures

between 1 073 and 1 273 K for 720 ks using a tubular furnace. The oxidation test specimens, which were made to stand diagonally against a sample holder made of quartz, were inserted in a furnace. In addition, to correctly measure the mass gain owing to oxidation, spallation of scale was taken into consideration during cooling. In other words, the specimens were drawn out from a furnace and were transferred to each vessel with a lid and cooled down to room temperature. All the scales containing the spalled one were succeeded in being collected. Two pieces of the specimens were tested on each condition.

2.3. Evaluation Test of Scale

After oxidation test, the appearance of oxidized specimens was investigated by various methods and the mass gains of them were measured by a balance. In this study, the spalled scale was collected, therefore, the measured value of mass gain included the spalled one. Since the measurement limit of the balance is 0.01 μg , the measurement limit of the mass gain becomes 0.1 g/m^2 .

Furthermore, X-ray diffraction measurement of these specimens was carried out using $\text{CuK}\alpha$ radiation to identify the phase of their surface region. In addition, some of the oxidized specimens were subjected to field emission scanning electron microscopy (FE-SEM) to investigate the structure of the scale and the scale/metal interface. Specimens for FE-SEM were prepared by a cross sectioning polisher (CP). The element analysis and the element mapping were also performed using electron energy dispersive X-ray spectroscopy (EDS). Furthermore, detailed analyses of the structures of the scale and the scale/metal interface were performed using field emission transmission electron microscopy (FE-TEM). TEM specimens were prepared by means of a focused ion beam (FIB) method. TEM specimens were prepared by a conventional FIB manufacturing method after W deposition on the surface of oxidized specimens to protect the scale. These specimens were observed by FE-TEM. Each observed phase was analyzed by μ -diffraction as well as μ -EDS methods.

3. Results

3.1. Oxidation Test

The effect of Si on the mass gain of oxidized samples is shown in **Fig. 1**, while the appearance of oxidized samples is demonstrated in **Fig. 2**. The mass gain increased with increasing temperature. The oxidation resistance of the steels oxidized at 1 073 K, which was the lowest temperature in this study, was excellent irrespective of the Si content. However, the mass gain seems to slightly decrease with increasing the Si content. The mass gain of the 0.1%Si steel was the lowest at 1 073 K oxidation. However, the difference between this value and that of steel without Si is less than 0.4 g/m^2 . Considering that the measurement limit of the mass gain is 0.1 g/m^2 , this difference is supposed to be within the error range. Therefore, the mass gain at 1 073 K is judged to be almost the same irrespective of the Si content.

For the Si-free steel (Steel A), the mass gains increased sharply from 1 273 K. Nodule-like oxides were observed in samples oxidized at 1 223 and 1 273 K (**Fig. 2**). The so-

Table 1. Chemical compositions of alloys used (mass%).

Steel	C	Si	Mn	P	S	Cr	Al	Nb	Ti	N
A	0.005	<0.02	<0.01	<0.01	<0.0003	18.5	0.05	0.50	<0.01	0.009
B	0.005	0.1	<0.01	<0.01	<0.0003	18.4	0.05	0.49	<0.01	0.010
C	0.005	0.5	<0.01	<0.01	<0.0003	18.4	0.05	0.49	<0.01	0.010
D	0.007	1.0	<0.01	<0.01	<0.0003	18.4	0.05	0.49	<0.01	0.010

called abnormal oxidation was indicated in these samples. In contrast, the 0.1%Si steel (Steel B) shows lower mass gain than that of Steel A, in particular at temperatures higher than 1 223 K. Steel C and D, containing more than 0.5% Si represent the similar behavior as that of Steel B. But the mass gains of these steels are apparently lower than that of steel B at temperatures higher than 1 173 K. The appearance observation of the oxidized specimens of steel B, C and D did not show abnormal oxidation at all.

Though the Si addition has been reported to promote scale spallation,¹²⁾ it was not observed in all the specimens in the present study.

3.2. X-ray Diffraction Measurement

The results of X-ray diffraction of specimens oxidized at 1 173 K are shown in Fig. 3 as a function of the Si content. For Steel A without Si, three phases were identified such as α -Fe(Cr) as the metal, and Cr_2O_3 and NbO_2 as the oxides. The result of Steel B with 0.1%Si was almost the same as

that of Steel A. In contrast, for Steel C and D with more than 0.5%Si, NbO_2 was not detected, while α -Fe(Cr) and Cr_2O_3 were detected. The phases identified by X-ray diffraction for specimens oxidized at various temperatures are summarized in Table 2. The results of the specimens of Steel A, oxidized at 1 223 and 1 273 K, which showed abnormal oxidation, were obtained from the limited area where normal oxidation took place.

In all specimens, α -Fe(Cr) as the metal and Cr_2O_3 as the scale were detected. However, NbO_2 were detected in Steel A without Si, oxidized at all temperatures tested, and in Steel B with 0.1%Si oxidized at temperatures between 1 173

Fig. 1. Temperature dependence of mass gain of samples with different Si contents oxidized at 1 073–1 273 K for 720 ks in air.

Fig. 2. Appearance of samples with different Si contents oxidized at 1 073–1 273 K for 720 ks in air.

Fig. 4. FE-SEM observation results for samples with different Si contents oxidized at 1 173 K for 720 k in air.

and 1 273 K. Meanwhile, NbO_2 were no longer detected in Steel C and D with more than 0.5%Si oxidized at all temperatures tested. Therefore, it may be concluded that the Si addition suppresses the formation of NbO_2 .

3.3. FE-SEM Observation

To observe the microstructure of the scale and the scale/metal interface in detail, the specimens with the different amounts of Si oxidized at 1 173 K within normal oxidation condition were selected for FE-SEM observation. **Figure 4** shows the results of the backscattering electron images (BSE) and the maps of the characteristic X-ray of O, Si, Al, Nb and Si obtained by EDS. It is clear that O and Cr accumulated in the outermost layer, irrespective of the amount of Si. Thus, this layer is assumed to be the Cr_2O_3 scale. In addition, Cr_2O_3 scales became thinner with increasing Si content. In all specimens, needle-like accumulations of Al were detected in the region under the scale. They are likely to correspond to Al_2O_3 as internal oxides because of the simultaneous accumulation of O. In the Si-free steel (Steel A), the accumulation layer of Nb was found under the Cr_2O_3 scale. However, in the 0.1%Si steel (Steel B), the accumulation of Nb became slightly small. Considering that the Nb accumulation located at the lowest region of the O accumu-

lation layer (Fig. 4) together with the identification of NbO_2 by X-ray diffraction (Fig. 3), the Nb accumulation layer in Fig. 4 is considered a NbO_2 layer. On the other hand, in Steel C and D with more than 0.5%Si, no Nb accumulation layer was found and grain-like Nb accumulation was found instead. This result corresponds to the results of X-ray diffraction in the sense that no NbO_2 was detected. From the Si maps, it was revealed that the accumulation of Si under the Cr_2O_3 scale increased with increasing Si content. Thus, Si is considered to accumulate under a scale with increasing Si content.

For the purpose of investigating the microstructure of the scale and the scale/metal interface in detail, the specimens of the Si-free steel (Steel A) and the 1%Si steel (Steel D), oxidized at 1 173 K, were observed in cross-section by FE-SEM. **Figure 5** shows that the Cr_2O_3 layer became thinner

Table 2. Identification of phases by X-ray diffraction in samples oxidized at 1 073–1 273 K for 720 ks in air.

Temperature (K)	Si (%)			
	<0.02	0.1	0.5	1.0
1 073	α -Fe	α -Fe	α -Fe	α -Fe
	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
	NbO_2			
1 123	α -Fe	α -Fe	α -Fe	α -Fe
	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
	NbO_2			
1 173	α -Fe	α -Fe	α -Fe	α -Fe
	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
	NbO_2	NbO_2		
1 223	(*) α -Fe	α -Fe	α -Fe	α -Fe
	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
	NbO_2	NbO_2		
1 273	(*) α -Fe	α -Fe	α -Fe	α -Fe
	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
	NbO_2	NbO_2		

(*) X-ray results taken from the area of normal oxidation

Fig. 3. X-ray diffraction profiles of samples with different Si contents oxidized at 1 173 K for 720 ks in air.

Steel A (Si:<0.02%)

Steel D (Si:1%)

Fig. 5. FE-SEM micrographs showing cross-sectional views of samples without Si and with 1%Si, oxidized at 1 173 K for 720 ks in air.

in the 1%Si steel than in the Si-free steel. The NbO_2 layer was present under the Cr_2O_3 layer in the Si-free steel, but not in the 1%Si steel. Instead of the NbO_2 layer, granular precipitates were present both under the scale and in the metal. These precipitates are considered Fe_2Nb (Laves phase) by evaluating the Nb/Fe peak ratio of EDS analyses.

Figure 6 shows the cross-sectional views of both steels with low magnification. In the Si-free steel (Steel A), white precipitates were observed inside the metal, but not in the surface region of the metal. In contrast, in the 1%Si steel (Steel D), white precipitates were observed from the surface to the inside of the metal. These precipitates are considered Fe_2Nb (Laves phase) based on the results of Fig. 5. In other words, in the Si-free steel (Steel A), Fe_2Nb (Laves phase) forms only inside of the metal and not in the surface region of the metal. Thus, the Fe_2Nb -free zone is present in the surface region. By contrast, in the 1%Si steel (Steel D), Fe_2Nb is present from the top surface to inside of the steel. This phenomenon is postulated to be caused by the Si addition.

3.4. FE-TEM Observation

The Si-free steel (Steel A) and the 1%Si steel (Steel D), oxidized at 1 173 K, were subjected to the cross-sectional observation by FE-TEM. These are the same specimens observed by FE-SEM (Figs. 4–6). **Figure 7** represents the low-magnification micrographs showing the entire region manufactured by FIB. The samples were manufactured slightly in excess by FIB, which indicates that some part of the outer layer of the scale was shaved and eliminated. The outermost layer position is estimated by the dotted line from the residual state of W deposited to protect the surface. Making a comparison between the Si-free steel (Steel A) and the 1%Si steel (Steel D), the scale of Steel D is thinner than that of Steel A. Therefore, it is concluded that the Si addition suppresses oxidation. In addition, the scale of Steel A is more undulated than that of Steel D.

Figure 8 shows the results of TEM observation of the Si-free steel (Steel A). It was confirmed that the outermost layer was Cr_2O_3 , which corresponded to the results by X-ray diffraction and FE-SEM. The analyses by μ -diffraction and μ -EDS revealed again that the outermost layer is Cr_2O_3 with less impurities with the 3–5 μm in thickness (Fig. 8(a)). The Cu peak of μ -EDS is considered to originate from the Cu-mesh to fix the TEM samples during the observation.

Though it has been already clarified that the NbO_2 layer formed under the Cr_2O_3 layer by X-ray diffraction and FE-SEM, Fig. 8(b) reveals that this layer contains Nb and O by μ -EDS of FE-TEM. Moreover, μ -diffraction reveals that this layer has the rutile-like structure as indicated by X-ray diffraction. Therefore, this layer was identified as NbO_2 . Moreover, many voids were observed in the Cr_2O_3 and/or in the interface between Cr_2O_3 and NbO_2 . Figure 8(c) shows that the crystal grain near the void is Cr_2O_3 containing a lot of Fe, *i.e.*, $(\text{Fe,Cr})_2\text{O}_3$. Furthermore, Al oxides were observed under scale as the internal oxides. Al oxide was present until at the position of 10 μm in depth. The oxides near the surface were relatively small and those at a deeper position were relatively large. Figure 8(e) proved that these were θ - Al_2O_3 by μ -diffraction. Though the electron diffraction pattern shown in Fig. 8(d) was not clear enough to analyze, this is also suggested to be θ - Al_2O_3 from the morphology and the results of μ -EDS.

TEM observation results of the 1%Si steel (Steel D) are shown in **Fig. 9**. The outermost layer is Cr_2O_3 as the same as Steel A. However, the layer is thinner than that of Steel D and approximately 2 μm in thickness. Figure 9(a) shows that this layer is Cr_2O_3 with less impurities by μ -EDS. No NbO_2 layer formed under the Cr_2O_3 layer. Instead, granular particles, which are confirmed to be Fe_2Nb by μ -EDS in Fig. 9(b), are present. Also, the amorphous SiO_2 layer

Fig. 7. Low magnification micrographs of FE-SEM showing cross-sectional views of sub-surfaces of alloys without Si and with 1%Si, oxidized at 1 173 K for 720 ks in air.

Fig. 6. Low magnification micrographs of FE-SEM showing cross-sectional views of samples without Si and with 1%Si, oxidized at 1 173 K for 720 ks in air.

Fig. 8. FE-TEM micrographs showing identification of phases by μ -diffraction and μ -EDS in a sample without Si, oxidized at 1 173 K for 720 ks in air.

Fig. 9. FE-TEM micrographs showing identification of phases by μ -diffraction and μ -EDS in a sample with 1%Si, oxidized at 1 173 K for 720 ks in air.

(a) Steel A (Si:<0.02%) (b) Steel D (Si:1%)

Fig. 10. FE-TEM micrographs showing results of identification of phases in surfaces of alloys without Si (a) and with 1%Si (b), oxidized at 1 173 K for 720 ks in air.

with less than 100 nm in thickness was found under Cr_2O_3 . Figure 9(c) reveals that this layer is identified amorphous SiO_2 because the μ -diffraction of this layer indicated a halo pattern. The diffraction spots shown in the figure were confirmed to come from the Cr_2O_3 scale. In addition, unlike Steel A, there are few voids in the Cr_2O_3 of Steel D. Furthermore, as shown in Fig. 9(d), the presence of α -Fe(Cr) particles in the metal side of the Cr_2O_3 layer was confirmed, however, these particles were not observed in Steel A. Figure 9(e), shows Al oxides as the internal oxides similar to Steel A. They were present from just under the scale to the position of around 5 μm in depth. They were located shallower in Steel D than in Steel A. Internal oxides were identified as θ - Al_2O_3 by μ -diffraction. Consequently, the results of microstructure of the scale and the scale/metal interface of Steel A and D are summarized in Fig. 10. For Steel A, the outermost layer is Cr_2O_3 , and the NbO_2 layer is under the Cr_2O_3 , and θ - Al_2O_3 exists as the internal oxides. In contrast, for Steel D, the outermost layer is Cr_2O_3 , and the amorphous SiO_2 layer is under the Cr_2O_3 layer, and θ - Al_2O_3 forms as the internal oxides and Fe_2Nb is present through the thickness besides them.

4. Discussion

4.1. The Effect of Si Addition on the Oxidation Behavior

Figure 11 shows the change in mass gain during oxidation with the Si content. It indicates that the small amount of the Si addition of about 0.1% apparently decreases mass gain, compared with the Si-free steel. Also, the limit temperature of oxidation resistance increases to more than 100 K since Si addition prevents abnormal oxidation. The effect of Si addition on oxidation resistance increases with increasing Si content. But this effect saturates at the Si content near 0.5%.

Many previous papers⁵⁻¹¹⁾ reported that Si addition improved oxidation resistance and Si has recognized to be the element improving oxidation resistance. Wood *et al.*¹⁰⁾ and Fujikawa *et al.*¹¹⁾ reported that Si addition improved oxidation resistance using ferritic stainless steels with various Si contents. Our results are similar to the previous works in the sense that Si addition improves the oxidation resistance for high-purity Nb containing ferritic stainless steels. The following two kinds of mechanism that Si addi-

Fig. 11. Change in mass gain with Si content of samples oxidized at 1 073–1 273 K for 720 ks in air.

tion improves the oxidation resistance were proposed in the previous study. One is that Si decreases the defects in the Cr_2O_3 scale and makes the Cr_2O_3 scale much pure and fine.^{5,6)} The other is that Si makes thin amorphous SiO_2 layer at the scale/metal interface and prevents the outward diffusion of metal ion and the inward diffusion of oxygen.⁷⁻⁹⁾ In this study, based on the observation results by means of FE-SEM and FE-TEM, an amorphous SiO_2 layer was confirmed to form under Cr_2O_3 . Therefore, the later mechanism is likely to act. However, considering that there are many voids in Cr_2O_3 for the Si-free steel, no void for the 1%Si steel and the Cr_2O_3 scale becomes thinner with increasing the Si content, the former may still act. Therefore, we have not elucidated the detailed mechanism yet.

The previous work¹⁰⁾ reported that Si improves the oxidation resistance, despite that Si promotes the scale spallation. However, the scale spallation does not occur in this study. In the previous report, it is postulated that the materials used included many other elements. Therefore, an interaction between Si and other elements is supposed to promote the spallation. As far as practically used steels are concerned, Mn is the candidate as the harmful impurity elements. The interaction between Si and Mn is likely to promote the scale spallation.

4.2. Formation of NbO₂

The present study has clarified that the formation of NbO₂ during the oxidation is limited to the case where the Si content is less than 0.1%. Thus, NbO₂ forms just under Cr₂O₃ in the ferritic stainless steel with the very small amount of Si; however, only the small amount of the Si addition has a tendency to suppress the formation of NbO₂. This mechanism is discussed.

The binary phase diagram of Nb–O system is shown in **Fig. 12**. There exist three kinds of the stable oxides in this system. They are NbO, NbO₂ and Nb₂O₅. Among these oxides, only NbO₂ was found in this study. **Figure 13** shows the diagram of standard free energies of formation for the oxides mentioned in this study, which is the so-called Ellingham diagram. The standard free energy of formation for oxides was assumed to be expressed as $\Delta G^0 = A + BT$. ΔG^0 was calculated by inserting the values of A and B, which were gathered from the literature.¹³⁾ In comparison

Fig. 12. Phase diagram of Nb–O system.¹²⁾ Reprinted with permission of ASM international.

Fig. 13. Standard formation free energy (ΔG^0) for the oxidation of some metals.

to Cr_2O_3 , FeO is hard to form, and SiO_2 and Al_2O_3 are easy to form. In other words, in comparison to Cr , Fe is hard to be oxidized, and Si and Al are easy to be oxidized. As for Nb oxides, Nb_2O_5 is almost at the same level with Cr_2O_3 , and NbO_2 and NbO are below Cr_2O_3 . Therefore, it may be mentioned that Nb is slightly easier to be oxidized than Cr . In the circumstance where Nb can be oxidized sufficiently, a three-layered structure comprising Nb_2O_5 , NbO_2 and NbO from the top surface was expected. However, only NbO_2 was found in this study. The reason why no Nb_2O_5 was present is proposed as below. The formation energy of Nb_2O_5 is nearly the same as that of Cr_2O_3 . However, the mass of Nb is much less than that of Cr . Therefore, Nb_2O_5 could not form due to the preferential formation of Cr_2O_3 . Since the Nb content is small, NbO is inferred to be relatively hard to form in comparison to NbO_2 . In the previous report,¹⁶⁾ Cr can dissolve in NbO_2 and Nb can dissolve in

Cr_2O_3 . Thus, the existence of $(\text{Cr,Nb})_2\text{O}_3$ and $(\text{Cr,Nb})\text{O}_2$ is expected. Therefore, it is likely that NbO_2 is more stable due to the solution of Cr in NbO_2 , while NbO is unable to form. When steel is exposed to oxidizing atmosphere at a high temperature, the oxidation behavior of each element competes at the early stage of oxidation. In this study, the amount of Fe and Cr is much larger than that of any other elements. Therefore, the competition between these two elements mainly plays a dominant role at the early stage of oxidation. Since the amount of Cr is 19% and relatively high in this study, Cr tended to be selectively oxidized and Cr_2O_3 formed as a protective scale at the early stage of oxidation. In this process, the contents of other elements such as Nb, Si and Al are very small and their influences are assumed to be negligible. Thus, the oxidation behavior of Nb, Si and Al after the formation of a Cr_2O_3 scale becomes important and is discussed as follow. After Cr_2O_3 has formed as a layered scale, the P_{O_2} under Cr_2O_3 sharply decreases and reaches approximately the dissociation pressure of Cr_2O_3 . For example, $P_{\text{O}_2} = 3.9 \times 10^{-19}$ Pa may be reached at a temperature of 1 173 K when $a_{\text{Cr}} = 0.19$ is assumed. When P_{O_2} reaches this value, Fe and Cr cannot be oxidized and the oxidation behavior of the other minor elements such as Nb, Si and Al becomes important at a later stage of oxidation process.

In the case of the Si-free steels, Nb and Al are the elements that can be oxidized under Cr_2O_3 . Nb and Al have no complex oxides each other. Consequently, they are oxidized without interfering with each other. The content of Nb is 0.5% and that of Al is 0.05%, thus the mass of Nb is more than that of Al even in the atomic ratio. As a result, Nb is mainly oxidized. As shown in Fig. 14, NbO_2 forms under Cr_2O_3 scale, grows in the lateral direction and constructs layer structure. It is not clear whether the effect of the formation of NbO_2 on high temperature oxidation is positive or negative in the present study. This problem remains as a future study. As shown in Fig. 8, some of Cr dissolves in NbO_2 . Thus, it is suggested that the supply of Cr to the Cr_2O_3 scale is not suppressed by NbO_2 . Impurities such as Fe were hardly detected in the Cr_2O_3 scale except in the region near the voids. Thus, the formation of NbO_2 is postulated to hardly influence the growth and the quality of the Cr_2O_3 scale. Under NbO_2 , Al is the only element that can be oxidized. Thus, Al is oxidized and the Al oxides form as inner oxides. The dissociation pressure of Al_2O_3 is much lower than that of NbO_2 . Thus, Al can be oxidized in the deep region from the metal surface and the needle-like oxides form. As shown in Figs. 5 and 10(a), it is possible to explain the structure of the scale and the scale/metal interface of the Si-free steels.

Fig. 14. Schematic illustration of NbO_2 formation under the Cr_2O_3 scale.

On the other hand, in the case of the 1%Si steels, Nb, Si and Al are the elements that can be oxidized under Cr_2O_3 . The content of Nb is 0.5%, that of Si is 1% and that of Al is 0.05%. Considering the atomic ratio, Si is the most and is followed by Nb. In this case, under Cr_2O_3 , SiO_2 and NbO_2 compete to form; however, SiO_2 preferentially forms because the supply of Si atoms is much larger than that of Nb and NbO_2 does not form. The dissociation pressure of SiO_2 is much lower than that of Cr_2O_3 . Thus, the internal oxide particles can form. The diffusion of Si and O in SiO_2 is too slow. Therefore, SiO_2 is supposed to form as a layer instead of the particles. Under SiO_2 , Al is the only element that can be oxidized. Al is oxidized and the needle-like Al oxides form as a same manner as the Si-free steels. Since the dissociation pressure of the oxide on the interface between the scale and the metal is low in comparison to the Si-free steels, the internal diffusion flux of O becomes small. Consequently the region with the internal Al oxides becomes shallow. As shown in Figs. 6 and 10(b), it is possible to comprehend the microstructure of the scale and the scale/metal interface regions of the Si-free Si bearing steels.

4.3. Disappearing of Laves (Fe_2Nb) Phase

As shown in Fig. 6, in the Si-free steel, the NbO_2 layer forms under the Cr_2O_3 layer and no Laves phase (Fe_2Nb) is present under the NbO_2 layer. On the other hand, in the 1%Si steel, no NbO_2 forms and the Laves phase (Fe_2Nb) is present through the thickness. Moreover, the formation of NbO_2 is closely related to the presence of the Laves phase and the behavior changes according to the Si addition.

As Fujita and Kikuchi reported,¹⁴⁾ the Laves phase (Fe_2Nb) is unstable at 1 223 K. Thus, the Laves phase is implied to be less stable than NbO_2 at 1 173 K. Therefore, the formation of NbO_2 is favorable, and Fe_2Nb cannot form. It may be possible for Fe_2Nb to form first and then to dissociate later, resulting in the formation of NbO_2 .

As shown in Fig. 6, in the Si-free steel, the deficiency of Nb occurs in the surface region of the metal by the formation of NbO_2 . Consequently, the formation of Fe_2Nb becomes difficult, leading to the disappearing region of Fe_2Nb from the top surface to approximately 40 μm in depth. The diffusion of Nb from the metal is necessary for the growth of the NbO_2 layer. When the diffusion coefficient (D) of Nb in α -Fe was adopted in the figure of the literature¹⁵⁾ the value of $D \approx 5 \times 10^{-14}$ (m^2s^{-1}) at 1 173 K is estimated. The diffusion distance, x for 720 ks at 1 173 K, is calculated to be $x = 190$ μm . Therefore, the fact that the disappearing region of Fe_2Nb with approximately 40 μm in depth is roughly understood. In the 1%Si steel, no NbO_2 layer forms, which suggests no deficiency of Nb and leads to form Fe_2Nb in the surface region as well as inside of the metal.

4.4. Metal Particles Precipitated in the Scale

Figure 9 shows granular particles observed in the Cr_2O_3 scale in the Si-added steel, which are presumably metal particles by their contrast. They are predicted to be the metal Fe particles. Here, this formation mechanism is discussed.

The Fe atoms in the scale were originally oxidized and dissolved in the scale as Fe ions at the early stage of oxidation. It is supposed that Fe ions were reduced and Fe precipitates due to the decrease in P_{O_2} in the Cr_2O_3 scale with

the progress of the oxidation. Concerning the precipitation of the metal Fe in Cr_2O_3 scale owing to reduction, the following mechanism is proposed. There are many voids in the scale. The P_{O_2} around the voids is slightly high by the presence of oxygen in voids. Therefore, Fe ions diffusing to a void become the Fe oxides at the interface between the void and the scale. Since a void is extremely small in the Si-added steel, a void is likely to be filled up with the Fe oxide by volume expansion. When a void is filled with the Fe oxide, P_{O_2} in the Fe oxide decreases and the Fe oxide is reduced, resulting in the precipitation of the metal Fe particle.

4.5. Oxidation Behavior of Al in Steels Oxidized in Air

In this study, the observed Al oxide is only $\theta\text{-Al}_2\text{O}_3$ and not $\alpha\text{-Al}_2\text{O}_3$. Thermodynamically stable Al oxide is considered $\alpha\text{-Al}_2\text{O}_3$, but many metastable oxides named θ -, δ -, γ -, κ -, χ -, and $\eta\text{-Al}_2\text{O}_3$ exist. Among these oxides, $\theta\text{-Al}_2\text{O}_3$ is regarded as the second most stable one after $\alpha\text{-Al}_2\text{O}_3$ at a high temperature.¹⁶⁾ As Andoh *et al.* reported,¹⁷⁾ $\alpha\text{-Al}_2\text{O}_3$ becomes stable with increasing temperature and time of heat treatment. The metastable phases, which form during the low-temperature and short-time heat treatment, gradually change to the α phase during heat treatment. In addition, the reason why the metastable oxide phases form is considered to be the influence of impurities.

However, in the present study the Al-oxides form by internal oxidation, which suggests that the other elements such as Fe, Cr are not oxidized. Therefore, the influence of impurities on Al oxide formation is considered small. Therefore, the reason why the metastable phase, $\theta\text{-Al}_2\text{O}_3$, forms is postulated that the content of Al is very small and the temperature of the oxidation is relatively low. However, the detail of this phenomenon is still unknown and further future study is needed.

5. Conclusions

The effect of Si addition on the oxidation behavior in air focusing on the structure change of the scale and the scale/metal interface have been investigated using the high-purity Nb containing 19%Cr ferritic stainless steels by reducing

the contents of Mn and other impurities (P, S) as much as possible. The results obtained are as follows:

- (1) Si addition improves the oxidation resistance. Si addition as much as about 0.1% improves the critical temperature of the oxidation resistance more than 100 K.
- (2) An amorphous SiO_2 layer between the Cr_2O_3 scale and the metal in the Si bearing steel acts as an oxidation barrier and improves the oxidation resistance.
- (3) In the Si-free steel, a NbO_2 layer forms under the Cr_2O_3 scale, and the Fe_2Nb -free region forms beneath the surface.
- (4) When Si is added, the formation of the NbO_2 layer is suppressed. In case of 1%Si, no NbO_2 layer forms and Fe_2Nb is present through the thickness of the steel.

Thus, the addition of Si in the Nb containing ferritic stainless steel is concluded to improve the oxidation resistance due to the Si effect of the suppression of oxidation of Nb as well as Cr.

REFERENCES

- 1) Y. Hosoi: Sutenresukou no Kagaku to Saishinn-gijutu, Japan Stainless Steel Association, Tokyo, (2011), 127.
- 2) K. Saito, M. Kobayashi, S. Akiyama and K. Ogawa: *Nippon Stainless Tech. Rep.*, **18** (1983), 83.
- 3) Y. Tarutani, K. Higuchi, T. Matsuda, M. Miyahara and N. Hiraide: *Sumitomo Met.*, **47** (1995), 76.
- 4) N. Fujita, K. Ohmura, M. Kikuchi, T. Suzuki, S. Funaki and I. Hiroshige: *Scr. Mater.*, **35** (1996), 705.
- 5) J. M. Francis: *J. Iron Steel Inst.*, **204** (1966), 910.
- 6) J. F. Radavich: *Corrosion*, **15** (1959), 613t.
- 7) D. Caplan and M. Cohen: *J. Met.*, **4** (1952), 1057.
- 8) T. Nakayama and Y. Oshida: *J. Jpn. Inst. Met.*, **35** (1971), 358.
- 9) Y. Shoji, S. Akiyama, S. Kisaichi, K. Nagatoshi and H. Hoshi: *Tetsu-to-Hagané*, **63** (1977), 700.
- 10) G. C. Wood, J. A. Richardson, M. G. Hobby and J. Boustead: *Corros. Sci.*, **9** (1969), 659.
- 11) H. Fujikawa, J. Murayama and N. Fujino: *Tetsu-to-Hagané*, **69** (1983), 678.
- 12) Binary Alloy Phase Diagrams, 2nd ed., Vol. 3, ed. by T. B. Massalski *et al.*, ASM International, Materials Park, OH, (1990), 2749.
- 13) Handbook of Iron and Steel, 3rd ed., Vol. 1, ed. by ISIJ, Maruzen, Tokyo, (1981), 14.
- 14) N. Fujita and M. Kikuchi: *Tetsu-to-Hagané*, **89** (2003), 510.
- 15) Handbook of Stainless Steel, 3rd ed., ed. by M. Hasegawa *et al.*, Nikkann-Kogyo-Shinbunn, Tokyo, (1995), 157.
- 16) W. H. Gilzen: Alumina as a Ceramic Material, American Ceramic Society, Inc., Columbus, OH, (1970), 17.
- 17) A. Andoh, S. Taniguchi and T. Shibata: *Mater. Sci. Forum*, **369-372** (2001), 303.