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**The Effects of Cr, Nb and Ti Additions on
the Oxidation Behavior of Al₂O₃-Forming
Ferritic Stainless Steels**

**A Dissertation Submitted to Hokkaido University for
the Degree of Doctor of Philosophy**

Cong Li

Division of Materials Science and Engineering

Graduate School of Engineering

HOKKAIDO UNIVERSITY

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Chapter 1.

Introduction

1.1 Stainless steel

Stainless steels (SS) are one of the most significant classes of engineering materials developed in the 20th century due to their excellent corrosion resistance, mechanical versatility and adaptability to different aggressive working environments. Stainless steels are iron-based alloys containing at least 10.5 wt% Cr, which enables the formation of a thin, continuous Cr_2O_3 scale on the material surface in the working environments [1]. The Cr_2O_3 scale is critical for the excellent oxidation and corrosion resistance for stainless steels, compared with conventional carbon and low-alloy steels, which usually require protective coatings in aggressive environments [2-11]. Therefore, stainless steels are widely used in the world. Fig. 1 shows the stainless steel market in Japan from 2018-2030 [12]. The domestic stainless steel production and development history of Japan is shown in Fig. 2 [13].

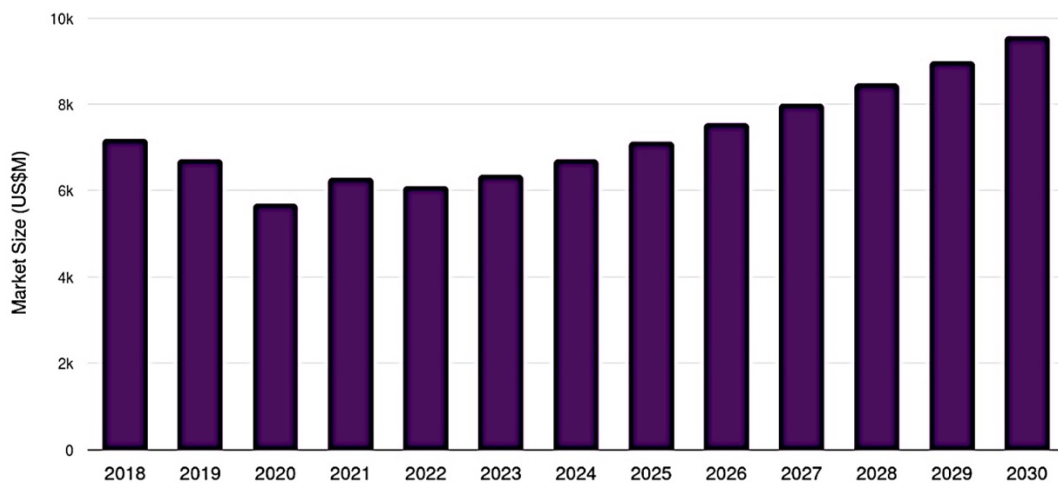


Fig. 1 Japan stainless steel market from 2018-2030

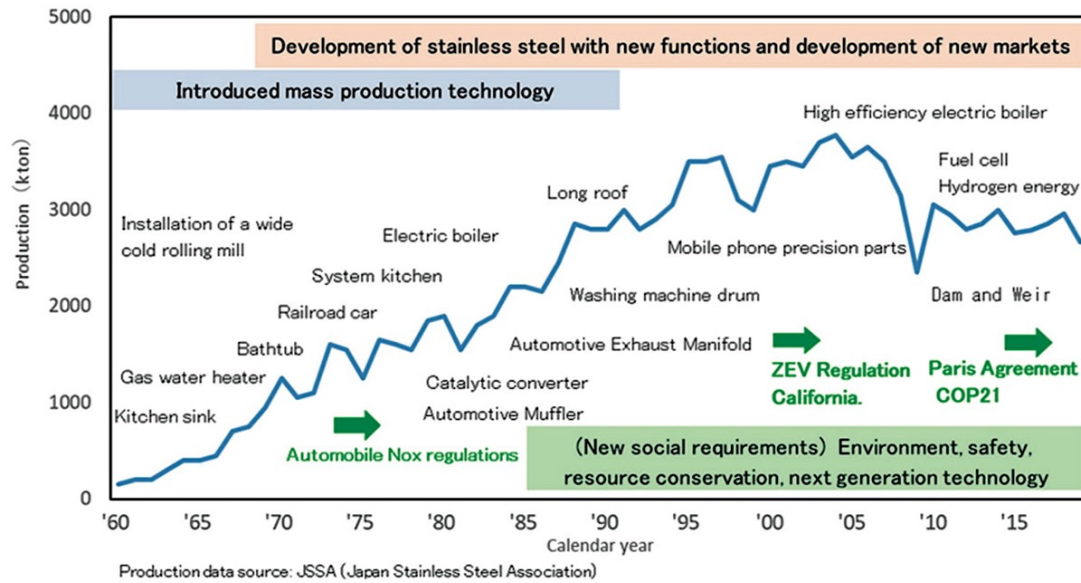


Fig. 2 Domestic stainless steel production and development history of Japan

The Cr_2O_3 scale formed on stainless steels acts as a barrier against environments, which significantly reduces metal consumption rates. The additions such as Mo, N, Mn could enhance the mechanical, oxidation and corrosion resistance in the aggressive environments, particularly the environments with chlorides [14-17]. Due to these advantages, stainless steels are often applied to various components from low to high temperatures, such as heat exchangers, seawater systems, desalination plants, chemical reactors, pipelines and medical implants.

The family of stainless steels covers a wide range of compositions and microstructures for specific working environments and fabrication requirements. The conventional classification of stainless steels is based on the crystal structures of the steels at room temperature, and these are ferritic, austenitic, martensitic, duplex and precipitation-hardening stainless steels [18-20]. Those stainless steels are produced by different phase-stabilizing elements such as Ni, C, N, Mo, Si, Mn, Ti and Nb [21-25]. Austenitic

stainless steels, such as 300 series (e.g., 304, 316) have a face-centered-cubic (FCC) crystal structure, which is stabilized by Ni or other elements, show the advantages like high ductility, excellent formability and superior corrosion resistance [26-27]. Both Ferritic and martensitic stainless steels have a body-centered-cubic (BCC) crystal structure, which often shows better thermal, magnetic and specific structural properties, although generally they have better toughness or corrosion resistance than austenitic steels [28-29]. Duplex stainless steels, which have mixture of austenitic and ferritic phases, show excellent strength and chloride-induced-stress-corrosion-cracking resistance [30-31]. Precipitation-hardening stainless steels also show excellent strength by the precipitation such as carbide or nitride [32-33]. While each family has its unique advantages and limitations, ferritic stainless steels (FSS) and austenitic stainless steels (ASS) dominate the global production and commercial markets [34-37]. Fig. 3 shows the proportion of different types of stainless steel production [3].

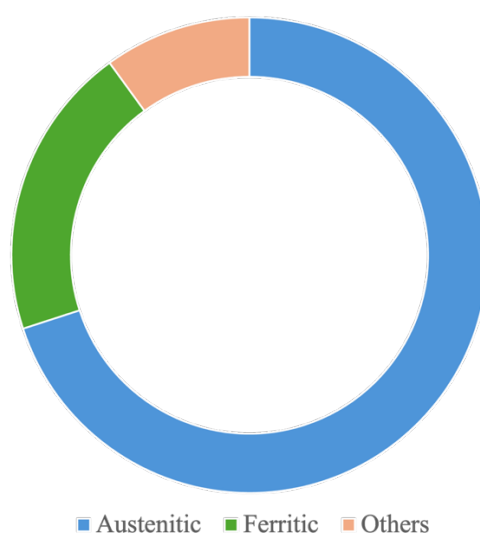


Fig. 3 The proportion of production of different types of stainless steels production

In summary, stainless steel occupies a central position in modern materials engineering due to its excellent combination of corrosion and oxidation resistance, mechanical versatility and economic viability. Ferritic stainless steel (FSS) and austenitic stainless steels (ASS) dominate global production and commercial markets.

1.2 Ferritic stainless steels

Ferritic stainless steels (FSS) constitute an important class of Fe-Cr alloys characterized primarily by their body-centered cubic (BCC) crystal structure. FSS maintain BCC crystal structure by the addition of Cr, which ranges from 10.5 to 30wt% [3]. The Cr content in FSS also enhances corrosion and oxidation resistance through the formation of a protective Cr_2O_3 scale, making FSS suitable for the applications in corrosive and other aggressive working environments [38-43].

FSS are generally divided into three groups, low-Cr (10.5-14wt%), medium-Cr (14-18wt%) and high-Cr (>18wt%) grades. The low-Cr FSS tend to exhibit moderate corrosion resistance and are commonly applied in automotive exhaust systems and heat exchangers. Medium-Cr FSS offer improved oxidation and corrosion resistance and are used for building components and cookware. High-Cr FSS, sometimes with Mo additions, have enhanced corrosion resistance and are used in more aggressive environments such as chemical processing and seawater-exposed equipment [3].

As FSS do not undergo martensitic transformation upon cooling, good dimensional stability during thermal cycling can be maintained. However, the BCC structure often results in lower ductility and toughness compared with austenitic stainless steels,

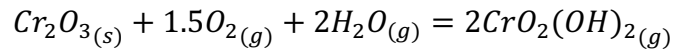
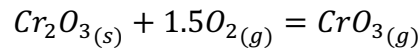
particularly at low temperatures, where FSS may exhibit ductile-to-brittle transition behavior. Advances in steelmaking, particularly vacuum melting and precise control of interstitial impurities such as C and N, have significantly improved mechanical properties such as strength. FSS are often stabilized through the addition of Ti to reduce the formation of chromium carbides and nitrides, thereby enhancing strength [44, 45]. In recent years, global interest in FSS has increased significantly due to economic and sustainability considerations. The volatility of Ni prices has encouraged manufacturers to seek Ni-free or low-Ni alternatives with comparable corrosion performance. FSS serve as material solutions for low-cost, resource-efficient applications due to their high recyclability and low environmental impact during production.

Heat-resistant ferritic stainless steels are a class of alloys designed to maintain mechanical integrity, surface stability, and oxidation and corrosion resistance at high temperatures. Cr_2O_3 forming and Al_2O_3 forming alloys are often used as the heat resistance steels in high temperature environments. Their performance arises from the combined effects of Cr, Ni, Si, Al, and rare earth (RE) additions, which promote the formation of slow-growing, adherent, and stable oxide scales to protect the alloy substrate and maintain mechanical stability. These protective scales inhibit further oxidation and corrosion, thereby increasing the service life of alloys in aggressive high-temperature environments. Heat-resistance ferritic stainless steels are widely used in petrochemical processing, power generation, heat exchangers, and industrial furnaces, where materials must maintain mechanical properties under cyclic heating, mechanical stresses and corrosive atmospheres [46-48].

1.2.1 Cr₂O₃ forming ferritic stainless steels

When Cr-containing alloys are exposed to high temperature environments, a continuous, Cr₂O₃ layer, which reduces further oxidation by acting as a diffusion barrier to both oxygen inward diffusion and alloy elements outward diffusion. This selective oxidation of Cr is thermodynamically favored due to the high stability of Cr₂O₃ and its low growth rate, enabling stainless steels to maintain structural integrity and surface protection even under high temperature conditions.

However, a Cr₂O₃ scale may evaporate at temperatures above roughly 800°C by forming various species such as CrO₃ and CrO₂(OH)₂ in water-containing atmospheres. This evaporation leads to accelerated oxidation and a loss of protective behavior as shown in the following reactions [49]:



The evaporation of CrO₂(OH)₂ is also a problem for the working environment of Cr₂O₃-forming alloys [50, 51]. Fig. 4 shows the equilibrium vapor pressures of chromium-oxygen-hydrogen gas species at 800°C with a water vapor pressure of 3 kPa [51].

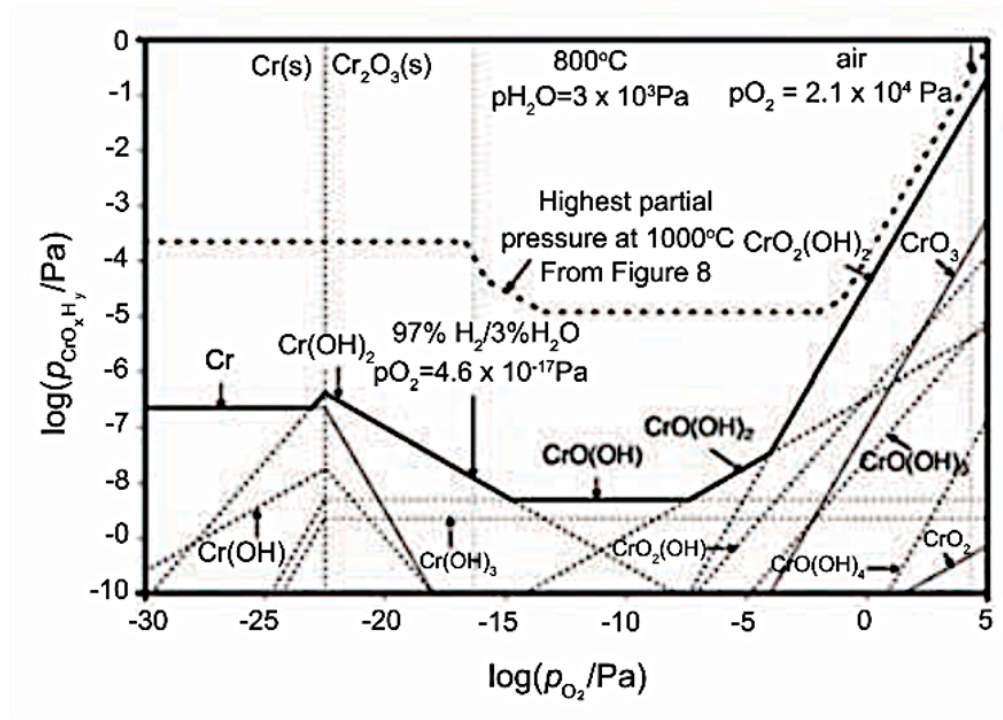


Fig. 4 Equilibrium vapor pressures of chromium-oxygen-hydrogen gas species at 800°C with a water vapor pressure of 3kPa

1.2.2 Al₂O₃ forming ferritic stainless steels

The development of advanced oxidation-resistant alloys has driven significant interest in Al₂O₃-forming ferritic stainless steels as alternatives to conventional Cr₂O₃-forming FSS for high-temperature applications. Traditional stainless steels rely on the formation of a continuous Cr₂O₃ scale, which provides effective protection in oxidizing environments up to approximately 800°C. However, at temperatures exceeding this range, the stability of Cr₂O₃ becomes compromised due to accelerated volatilization of CrO₂(OH)₂ in the presence of water vapor and the increased tendency for scale

spallation under thermal cycling [50, 51]. This limitation has motivated the design of alloys capable of forming a more thermodynamically stable Al_2O_3 scale, particularly the $\alpha\text{-Al}_2\text{O}_3$ which exhibits superior chemical and mechanical properties at high temperatures.

Compared with Cr_2O_3 , Al_2O_3 scales possess lower oxygen permeability, slower growth kinetics, and enhanced resistance to volatilization, enabling long-term oxidation resistance beyond 1100 °C. Furthermore, the adherence of Al_2O_3 under cyclic thermal loading is typically superior due to its lower growth stresses and more favorable thermal expansion mismatch with Fe-based substrates [90]. Achieving continuous and protective Al_2O_3 formation in ferritic stainless steels requires careful control of alloy chemistry, including sufficient Al content, which should be larger than 2 wt% and strategic additions of RE such as Y, Hf, Nb or Ti [52-56].

1.3 Austenitic Stainless Steels

Austenitic stainless steels (ASS) are the most widely used class of stainless steels, because of their face-centered-cubic (FCC) crystal structure, which is stabilized by the addition of austenite-stabilizing alloying elements such as Ni, Mn, and N. The FCC structure is characterized by a combination of good mechanical, chemical, and physical properties that are difficult to achieve with other steel families. The FCC phase attributes to their exceptional corrosion resistance, outstanding formability, superior toughness, and non-magnetic nature [3].

ASS can be divided into two major alloy families: the Cr–Ni 300-series and the Cr–Mn–N 200-series. The 300-series, especially grades such as 304 and 316, are often applied in industrial fields. Grade 304, containing approximately 18 wt% Cr and 8 wt% Ni, is used as the baseline composition due to its excellent general corrosion resistance and ease of fabrication. Grade 316 enhances the corrosion resistance by incorporating Mo, which significantly increases resistance to pitting and crevice corrosion in chemical environments [57-60]. The 200-series, developed originally as a response to Ni shortages, substitutes Mn and N for a portion of Ni. These alloys are increasingly used in applications where cost reduction is needed, although they typically exhibit slightly lower corrosion resistance than 300-series alloys.

The corrosion resistance of ASS is enhanced by the Cr content, typically above 16 wt%. Cr enables the formation of a self-healing passive Cr_2O_3 scale which acts as a barrier against oxidation and corrosive environments. Ni plays a crucial role in stabilizing the austenitic structure and enhancing ductility and toughness, especially at low temperatures where ferritic and martensitic stainless steels often become brittle. In recent decades, N has been used as an auxiliary austenite stabilizer because of its strong solid-solution strengthening effect and its ability to improve pitting corrosion resistance [61-64]. Based on the properties mentioned above, ASS offers an optimal balance of mechanical and corrosion-resistant characteristics suitable for aggressive working environments.

1.3.1 Cr₂O₃ forming austenitic stainless steels

In high temperature environments, the oxidation resistance of ASS is also enhanced by the Cr content, for example 304, 316 and 310 which rely on this Cr₂O₃ scale to maintain surface protection. The compact Cr₂O₃ scale shows both thermodynamic stability and low oxygen permeability yield a self-healing barrier that resists oxidation and corrosion in a wide range of environments.

Like Cr₂O₃ forming ferritic stainless steel, Cr₂O₃ forming austenitic stainless steels also degrade significantly in the environments containing water vapor to form CrO₂(OH)₂ and evaporate. This volatilization results in accelerated oxide scale breakdown and decreases the service life of alloys.

1.3.2 Al₂O₃ forming austenitic stainless steels

Al₂O₃ forming ASS offers significantly higher thermodynamic stability than Cr₂O₃ and exhibits superior resistance to volatilization. Compared with Al₂O₃ forming FSS, the ASS requires more than 4-5 wt% Al to form a continuous Al₂O₃ scale. Higher Al addition destabilizes the austenitic FCC matrix and promotes the formation of brittle intermetallic phases such as NiAl [65]. To maintain the single-phase austenitic matrix, strong austenite stabilizers such as Ni, Nb and C are required to be applied with lower Al content such as 2-4 wt% [65].

1.4 High temperature oxidation

The high-temperature oxidation is an important degradation process, which affects the performance, durability, and safety of structural materials used in energy, aerospace, chemical processing, and nuclear systems. When metals and alloys are exposed to high temperature environments, typically above 500°C, chemical reactions between the alloy and gas species—most commonly oxygen or water vapor, lead to the formation of oxide scales whose characteristics largely control the long-term integrity of the alloy. The kinetics, morphology, and protective ability of these oxide scales depend on both thermodynamic stability and diffusion-controlled processes, making high-temperature oxidation a complex phenomenon controlled by coupled chemical and transport mechanisms [65].

The principles of high temperature oxidation were established by theoretical and experimental studies, which are mostly notable works by Wagner, who developed the Wagner's Theory of Oxidation [66-68]. Wagner's theory demonstrated that the growth rate of an oxide scale as a process controlled by the diffusion of ions and electrons through the oxide scale under the influence of concentration and electric fields. Therefore, the oxide scale formed on alloys in high temperature environments is important for the service life of alloys.

The protective oxide scales such as Al_2O_3 , Cr_2O_3 , or SiO_2 are often used as protective barriers for alloys exposed to high-temperature environments. These scales can provide an effective barrier against further oxidation, but can fail due to cracking, spallation, or accelerated chemical attack. The alloys designed for high temperature environments often rely on selective oxidation of Al, Cr or Si to form adherent, slow-growing scales, which act as diffusion barriers. However, mechanical stresses, thermal cycling, or impurities such as sulfur and water vapor can decrease scale adherence to cause spallation and accelerate mass loss, and eventually material failure occurs. Additionally, advances in various high temperature systems, such as heat conversion systems have pushed operating temperatures increasingly higher, enhancing the demands for materials used in high temperature environments [65].

Therefore, understanding the fundamentals of scale growth is crucial for designing materials to use in the extreme environments at high temperature.

1.4.1 Protective oxide scale

Alloys applied in high temperature environments rely on the formation of a stable and adherent oxide scale to resist rapid degradation. When exposed to high temperatures, alloys containing elements such as Al, Cr, and Si develop thermodynamically stable oxides (Al_2O_3 , Cr_2O_3 , and SiO_2) that act as diffusion barriers to both oxygen inward diffusion and metal outward diffusion because of their dense, slow-growing,

thermodynamical stability at high temperature, good adhesion to the substrate, rapid formation, and fast establishment [69-83]. The Cr_2O_3 scale forming alloys are usually applied in the temperature range from 500°C to 800°C. The Al_2O_3 scale forming alloys are usually used in the higher temperature range from 800°C to 1000°C. SiO_2 scale forming alloys are often applied in the temperatures higher than 1200°C. Among these oxide, Cr_2O_3 - and Al_2O_3 -forming alloys represent the most widely used in industries, and their effectiveness derives from the slow diffusion within their oxide scales, which show parabolic growth kinetics and thereby limit the progressive consumption of the alloy.

The oxidation behavior of alloys is influenced by many factors, including alloy composition, microstructure, impurity contents, and environmental conditions such as oxygen partial pressure and the corrosive gas atmosphere. As the exposure environments of alloys at high temperatures are difficult to change, the composition of alloys is usually an important method to control the oxide scale formation of alloys. Additions of alloying elements such as reactive elements (e.g., Y or Zr) further enhances scale adherence and suppress various defects such as spallation and voids [84-88]. These improvements determine whether the oxide scale remains protective or transitions into a non-protective oxide product. Understanding these processes is essential for the design of high-temperature materials that will work in more aggressive high temperature environments.

1.4.2 TEE for Al_2O_3 scale

Cr addition into Fe-low Al alloys decreases the critical Al content for forming continuous Al_2O_3 scale. This Cr effect is called as the third element effect (TEE).

Wagner proposed the beneficial effect of B to cause a transition from internal oxidation to external oxidation of C on A-B-C ternary system [89-90]. The minimum concentration of Al for an exclusive Al_2O_3 scale formation on ferritic Fe-Cr-Al alloys is around 2 wt% with a minimum Cr concentration of around 15 wt% as shown in Fig.

5. When the concentration of Cr is lower than 15 wt% or the concentration of Al is lower than 2 wt%, the alloy will form nonprotective internal oxidation of Al and Fe and Cr-rich oxide scale are supposed to form. When the Cr concentration is higher than 15 wt% and Al is lower than 2 wt%, the Cr_2O_3 scale is formed. When the Al concentration is higher than 2 wt%, a protective external Al_2O_3 scale will form. Si and Pt are reported to be TEEs [91, 92].

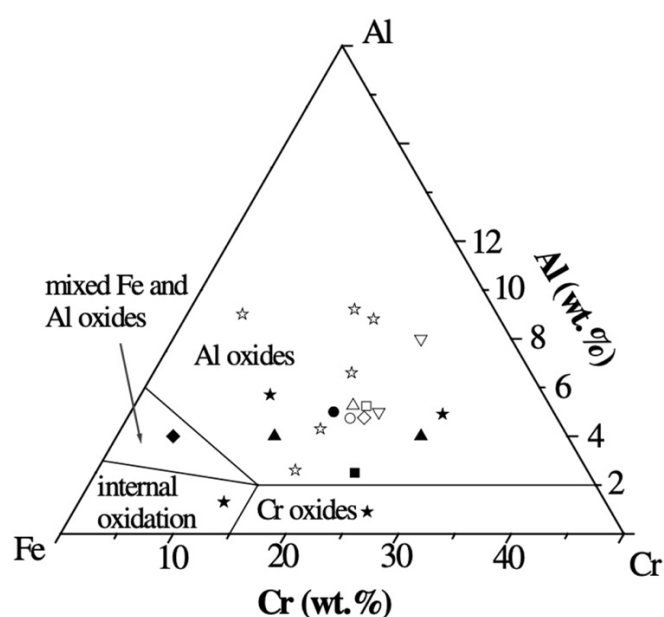


Figure 5 Oxidation properties of Fe-Cr-Al alloys at 1000°C. Solid and open symbols indicate that the oxidations were carried out in 1 atm oxygen and in air, respectively. Based on the practical significance of TEE, it has been widely utilized in the development of high temperature and corrosion resistant alloys, which can minimize the detrimental effects of Al on mechanical properties of alloys [93].

1.4.3 Effect of various elements on Al₂O₃ formation

The Al₂O₃ has outstanding properties by its low oxygen permeability, high thermodynamic stability, and slow growth rate at high temperature. Alloys forming a continuous and adherent Al₂O₃ layer exhibit superior oxidation and corrosion resistance in aggressive environments such as gas turbines, heat-treatment furnaces, and energy-conversion systems. However, the ability of an alloy to develop and maintain a stable Al₂O₃ scale mainly depends on its chemical composition, particularly the presence of reactive elements that influence nucleation, growth, morphology, and adherence of Al₂O₃ at high temperatures [85].

Elements such as Cr, Si, and Ti play significant roles in modifying oxidation behavior by altering diffusional pathways, oxide phase stability, and competitive oxide formation [74]. For example, Cr can promote Al₂O₃ scale formation, while excessive Si may lead to mixed oxides or internal oxidation [74]. In contrast, reactive elements (RE) such as Y, Hf and Zr, are well known for their profound influence on scale adhesion and microstructure through mechanisms such as grain-boundary segregation and

suppression of scale spallation [84-87]. These effects, collectively described as the reactive-element effect (REE), stabilize the Al_2O_3 scale and extend the service life of the alloy under cyclic thermal conditions.

1.5 Purpose

Recently, some studies have shown Nb can promote the protective Al_2O_3 scale formation with lower Al contents at high temperature [94-96]. However, the effect of additional elements, such as Cr, Nb and Ti on the oxidation behavior of the low Al containing FSS is not understood. In this study, the effects of Cr, Nb and Ti on the growth behavior of Al_2O_3 scale on Al_2O_3 forming FSS are investigated.

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Chapter 2.

The effect of chromium content on the oxidation behavior of alumina scale on niobium-containing ferritic stainless steel

2.1 Introduction

The addition of Cr to Fe-low-Al alloys is known to promote the formation of continuous Al_2O_3 scale [1-2]. For example, a binary Fe-Al alloy requires 10 wt% Al to form an Al_2O_3 scale at 800°C in air. However, the critical Al concentration for exclusive Al_2O_3 scale formation is decreased to around 2 wt% with the addition of 15 wt% Cr at 1000°C in air [1-2]. This beneficial effect of Cr is called the Third Element Effect (TEE). Si and Pt are also recognized as elements that promote Al_2O_3 scale formation [3-4]. Recently, Nb was found to increase the ability to form an external Al_2O_3 scale on austenitic stainless steels from 600°C to 900°C [5-7]. For example, Brady recognized that Nb addition improved the oxidation behavior of Al_2O_3 -forming austenitic steels, although the details were not discussed [7]. Hayashi et al. also reported that Nb addition to Al_2O_3 -forming austenitic steels promoted the Al_2O_3 scale formation and proposed that this beneficial Nb effect is attributed to the initial Cr_2O_3 scale formation caused by Nb addition [8]. Rapid establishment of the Cr_2O_3 scale in the early oxidation stage encourages the formation of Al_2O_3 scale [2]. In fact, Nb was confirmed to promote the formation of Cr_2O_3 scale on Ni-based alloys by the formation of CrNbO_4 which was considered to be a barrier against inward oxygen penetration [8].

The beneficial effect of Nb addition on the formation of the protective Al_2O_3 scale was also confirmed on ferritic Fe-Cr-Al alloys. Only small addition of Nb~0.5wt% was found to decrease the critical Al content to about 1 wt%. This beneficial effect of Nb on ferritic stainless steels appears to be related to the formation of Cr_2O_3 . The Cr content required to promote Al_2O_3 scale formation can be decreased to 10 wt% with Nb addition. However, the effect of Cr content on the growth behavior of the Al_2O_3 scale formed on Nb-modified Fe-Cr-Al-Nb alloys is unclear. In this chapter, we investigated the effect of Cr on the oxidation behavior of Al_2O_3 formed ferritic alloys at 850°C.

2.2 Experimental procedures

Fe-(10, 15, 20, 25) Cr-1Al-0.35Nb alloys (in wt %) were prepared by argon arc-melting with high-purity metals (99.99%). Table 1 shows the compositions of alloys used in this study. All alloy ingots were homogenized at 1200°C for 48 h under vacuum. Specimens approximately 1 mm thick were cut from homogenized ingots and polished by 3 μm diamond paste. Before the oxidation experiment, the specimens were ultrasonically cleaned in acetone.

Table 1 The chemical composition of alloys (nominal in wt%)

Alloy	Fe	Cr	Al	Si	Mn	Nb
10Cr	Bal.	10	1	0.1	0.1	0.35
15Cr	Bal.	15	1	0.1	0.1	0.35
20Cr	Bal.	20	1	0.1	0.1	0.35
25Cr	Bal.	25	1	0.1	0.1	0.35

The isothermal oxidation test was performed in a box furnace in air at 850°C for up to 1000 h. Samples were hung on an Al₂O₃ rod in an Al₂O₃ crucible and placed in the center of the box furnace. The furnace was heated from room temperature to 850°C at a rate of 10°C/min and held for the designated time. After oxidation, the samples were cooled to room temperature in the furnace. Several samples were also oxidized by thermogravimetric analysis (TGA). For the oxidation experiment in TGA, the specimen was heated at a rate of 10°C/min and cooled at a rate of 50°C/min after the oxidation experiment. After the experiment, the sample mass was measured by an electronic balance capable of weighing to a precision of 0.001 mg at room temperature. Surface and cross-sectional microstructures of the samples were observed by scanning electron microscopy (SEM). The detailed microstructure of the oxide scale was analyzed by scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectrometry (EDS). The STEM specimens were prepared by a focused ion beam system. The image analysis of the microstructure of the oxide scale was performed by using ImageJ software.

2.3 Results

2.3.1 Oxidation kinetics

Figure 1 shows the oxidation kinetics of Fe-(10, 15, 20, 25) Cr-1Al-0.35Nb alloys oxidized at 850°C in air for up to 100 h by TGA. The kinetics curves were wavy and fluctuated over a 24 h cycle because the mass gain of the sample was very small compared with the drift of the sensitive balance caused by daily changes in room

temperature. All alloys oxidized rapidly in the initial oxidation stage, followed by the slow steady-state oxidation stage, in which the oxidation went on parabolically. The mass gain of alloys increased with decreasing Cr content. The times for transition from rapid to steady-state stages were similar for all alloys; however, the oxidation mass gain of the 10Cr alloy in the transient stage of oxidation was much larger than those of the other of alloys (enlarged plot, Fig. 1(b)).

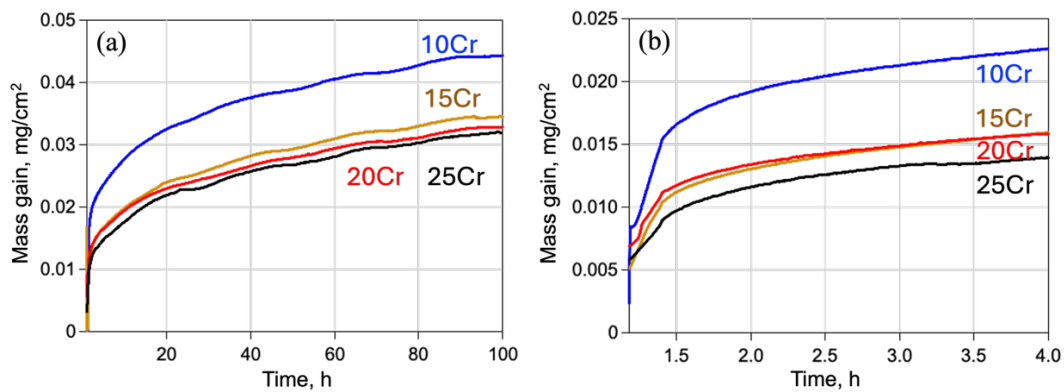


Fig. 1 Oxidation kinetics of Fe-xCr-1Al-0.35Nb alloys at 850°C in air for (a)100 h. (b) is enlarged plot of (a) up to 4 h

2.3.2 Cross-sectional microstructures of oxide scale

The cross-sectional microstructures of Fe-(10, 15, 20, 25) Cr-1Al-0.35Nb alloys oxidized at 850°C in air for 100 h are shown in Fig. 2. The oxide scales formed on all alloys were only approximately 150 nm thick. The Z-contrast images (Fig. 2(c), (d), (g), (h)) showed that the oxide scale consisted of a duplex structure. The outer oxide layer was thicker than the inner layer. The outer layer thickness tended to decrease with increasing Cr content, whereas the inner layer thickness tended to increase. Small precipitates were observed in the oxide scale near the interface between the outer and

inner layers. Representative EDS maps of the oxide scale formed on the 10Cr and 25Cr alloys revealed that the outer layer formed on the 10Cr alloy was Al-rich oxide and contained Cr and Fe (Fig. 3(a)). In the outer layer, Cr was homogeneously distributed but Fe was locally distributed in the grains in the outer layer. The thin inner layer was relatively pure Al_2O_3 , and other elements were not detected. Similar element distributions were observed in the oxide scale formed on the 25Cr alloy. There was a continuous Cr layer above the interface between the outer and inner layers and local Fe distribution was also observed above the Cr-rich band (Fig. 3(b)). Fig. 4 shows the STEM-EDS maps of the oxide scale formed on the 10Cr and 25Cr alloys near the outer and inner layers. The precipitate size with the ranging of several to 15 nm were formed. The precipitates consisted mainly of Cr, Mn, and Nb. Fe was also detected in large precipitates. No apparent difference in element distribution was observed in the precipitate in the Al_2O_3 scale formed on alloys with different Cr contents.

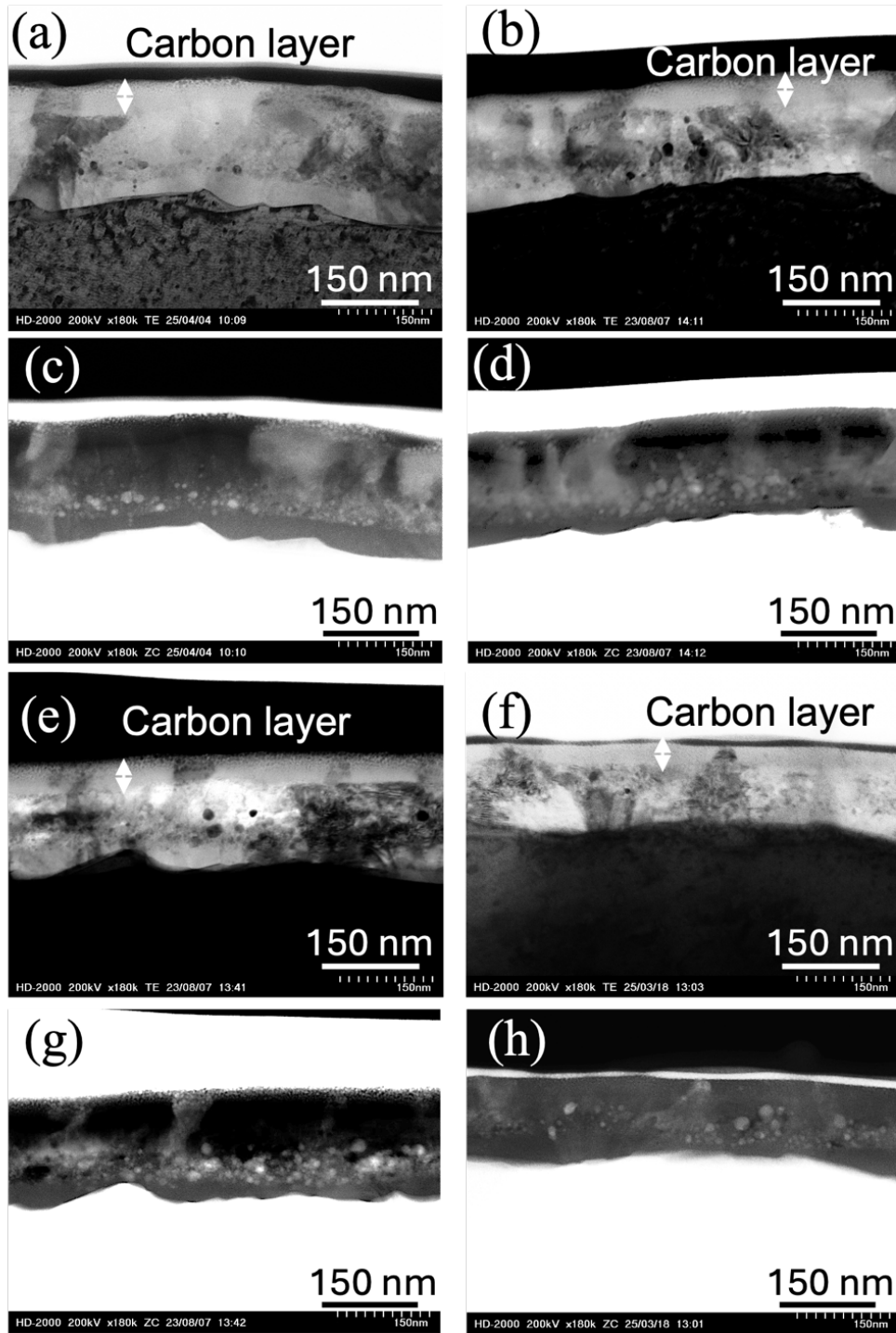


Fig. 2 STEM cross-sections of the oxide scale formed on Fe-1Al-0.35Nb alloys with (a)(c)10, (b)(d)15, (e)(g)20 and (f)(h)25 wt% Cr oxidized at 850°C for 100 h by TGA. (c)(d)(g), and (h) are corresponding Z-contrast images of (a)(b)(e) and (f), respectively

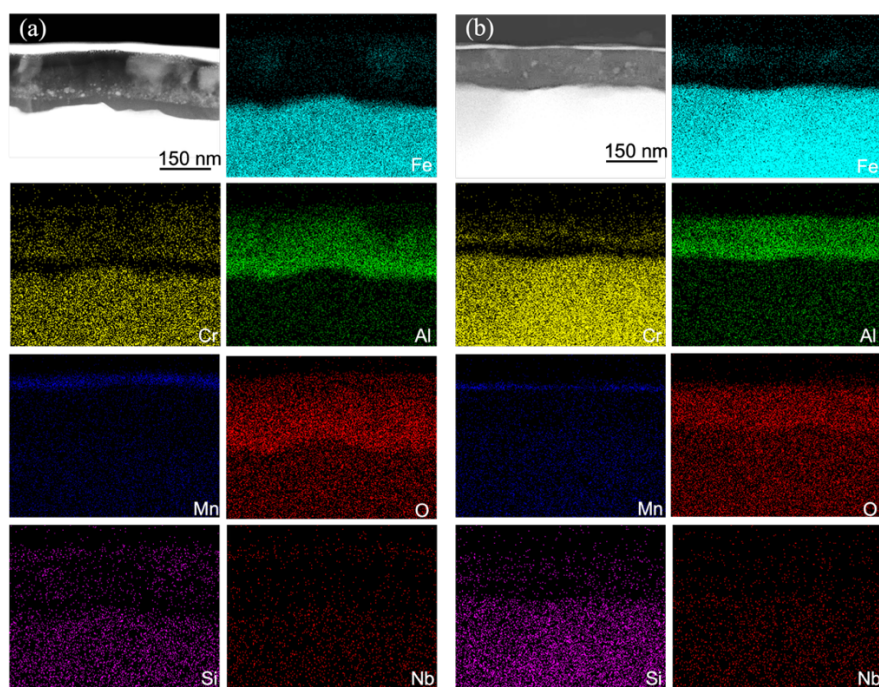


Fig. 3 Element maps of the oxide scale formed on Fe-1Al-0.35Nb: -(a)10Cr and -(b) 25Cr alloys oxidized at 850°C for 100 h by TGA

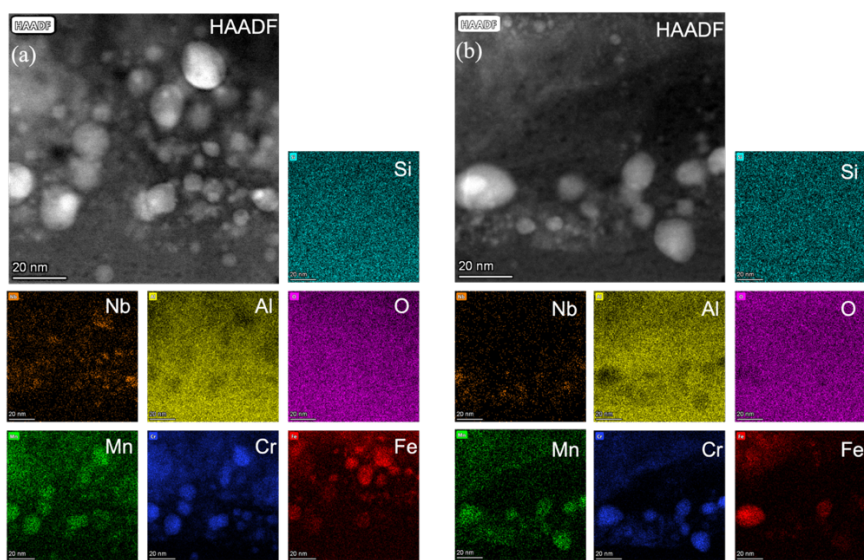


Fig. 4 HAADF- STEM images and corresponding element maps of precipitates with bright contrast in the oxide scale formed on Fe-1Al-0.35Nb: -(a)10Cr and -(b) 25Cr alloys oxidized at 850°C for 100 h by TGA

Figures 5 and 6 show the cross-sectional microstructures and element maps of the oxide scale formed on the 10Cr and 25Cr alloys after 5 and 25 h of oxidation, respectively. The duplex oxide scale had already developed on the 10Cr and 25Cr alloys after 5 h of oxidation. The oxide scale structure formed on both alloys were the same. The Cr and Fe-rich outer oxide layer formed on the 10Cr alloy was much thicker than that of the 25Cr alloy, consistent with the oxidation kinetics. However, the inner Al_2O_3 layer formed on the 10Cr alloy tended to be thinner than that on the 25Cr alloy, suggesting that the establishment of a continuous inner Al_2O_3 layer was delayed on the 10Cr alloy. The outer layer was thinner, and the inner layer was thicker for the 25Cr alloy than for the 10Cr alloy even after 25 h of oxidation.

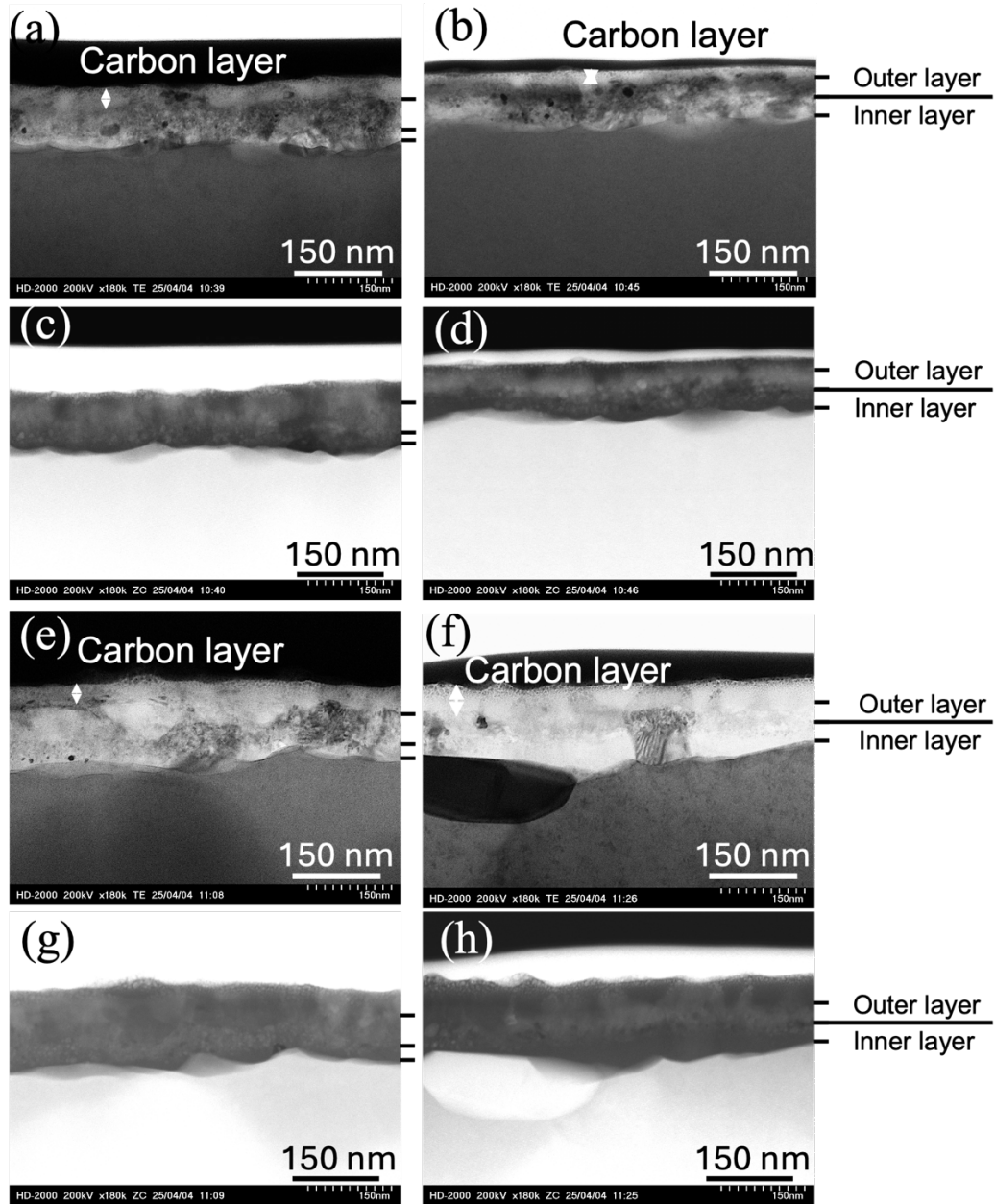


Fig. 5 STEM cross-sections of the oxide scale formed on Fe-1Al-0.35Nb alloys with (a)(c) 10 and (b)(d) 25Cr after 5 h of oxidation, (e)(g) 10 and (f)(h) 25Cr after 25h of oxidation, respectively. (c)(d)(g), and (h) are corresponding Z-contrast images of (a)(b)(e) and (f), respectively

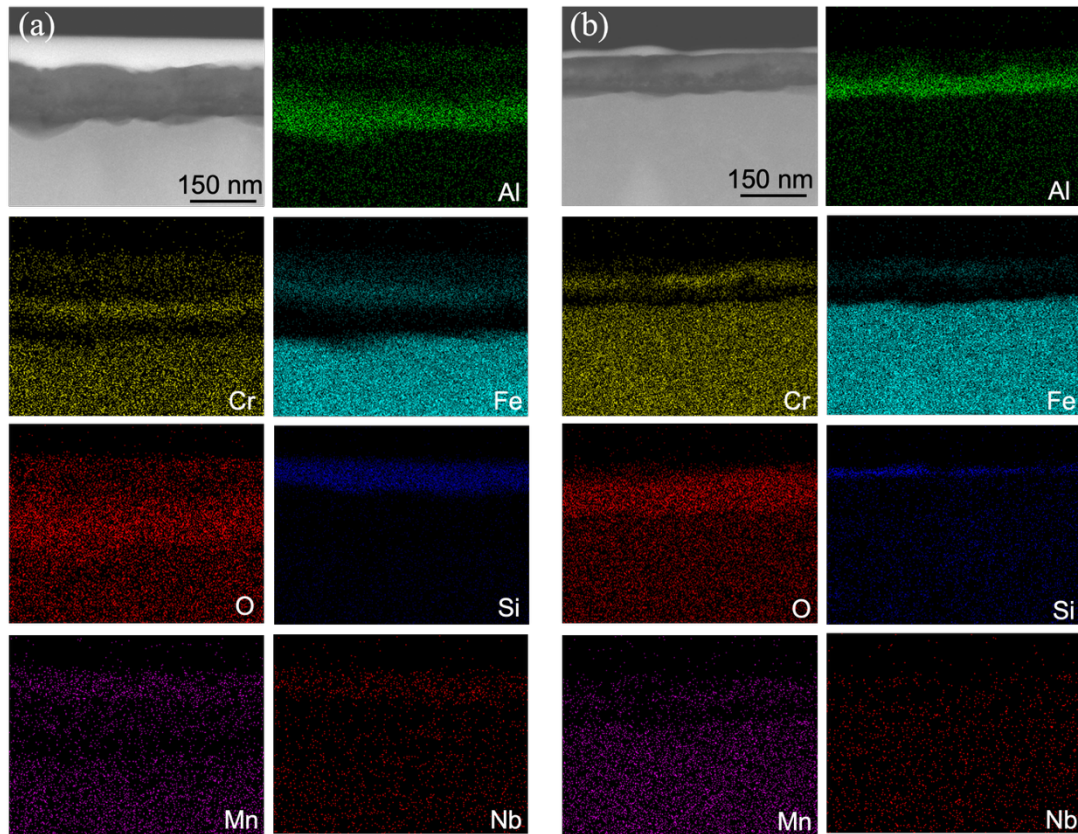


Fig. 6 Element maps of the oxide scale formed on Fe-1Al-0.35Nb: -(a)10Cr and -(b) 25Cr alloys oxidized at 850°C for 5 h by TGA

The long-term oxidation kinetics of the alloys were obtained by oxidation in a box furnace up to 1000 h. Three specimens of each composition were oxidized simultaneously. Fig. 7 shows the oxidation kinetics of the 10Cr, 20Cr, and 25Cr alloys up to 1000 h, and the long-term oxidation kinetics were parabolic. The 10Cr alloy showed the largest oxidation mass gain at the initial transient oxidation stage, although the oxidation rate of the 10Cr alloy was similar to those of the 20Cr and 25Cr alloys until about 400 h of oxidation. Thereafter, the rate was smaller than those of the other alloys in the long-term oxidation stage. Table 2 shows the parabolic rate constants of

the alloys in the long-term oxidation stage, obtained from Fig. 7, which were within the range of t α -Al₂O₃ growth [9].

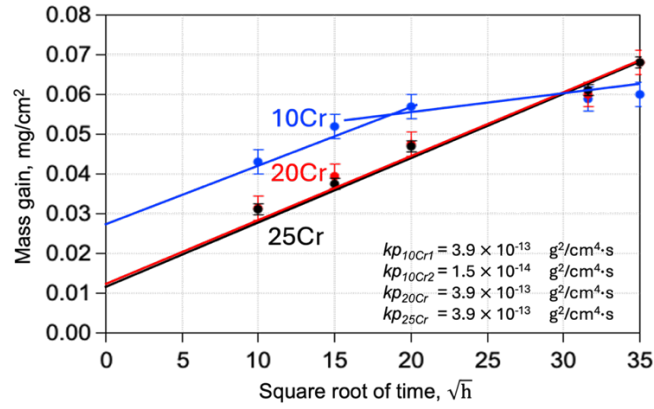


Fig. 7 Oxidation kinetics of the alloys at 850°C in air for up to 1000 h

Table 2 The k_p value of Fe-xCr-1Al-0.35Nb alloys oxidized at 850°C for 1225h by the box furnace ($\text{g}^2/\text{cm}^4 \cdot \text{sec}$)

Alloy	k_p
10Cr(1)(~400h)	3.9×10^{-13}
10Cr(2)(400h~)	1.5×10^{-14}
20Cr	3.9×10^{-13}
25Cr	3.9×10^{-13}

Figure 8 shows the cross-sectional microstructures of the oxide scale formed on the 10Cr and 25Cr alloys after 500 and 1000 h of oxidation. Both inner and outer layers grew thicker, and the outer layer formed on the 25Cr alloy still tended to be thinner than that formed on the 10Cr alloy. Small Cr-rich precipitates were still observed in the inner layer formed on both alloys. Laves phase precipitates were also observed in both

alloys. The thickness of the oxide scale, particularly that of the inner layer formed above the Laves phase precipitates, was thin.

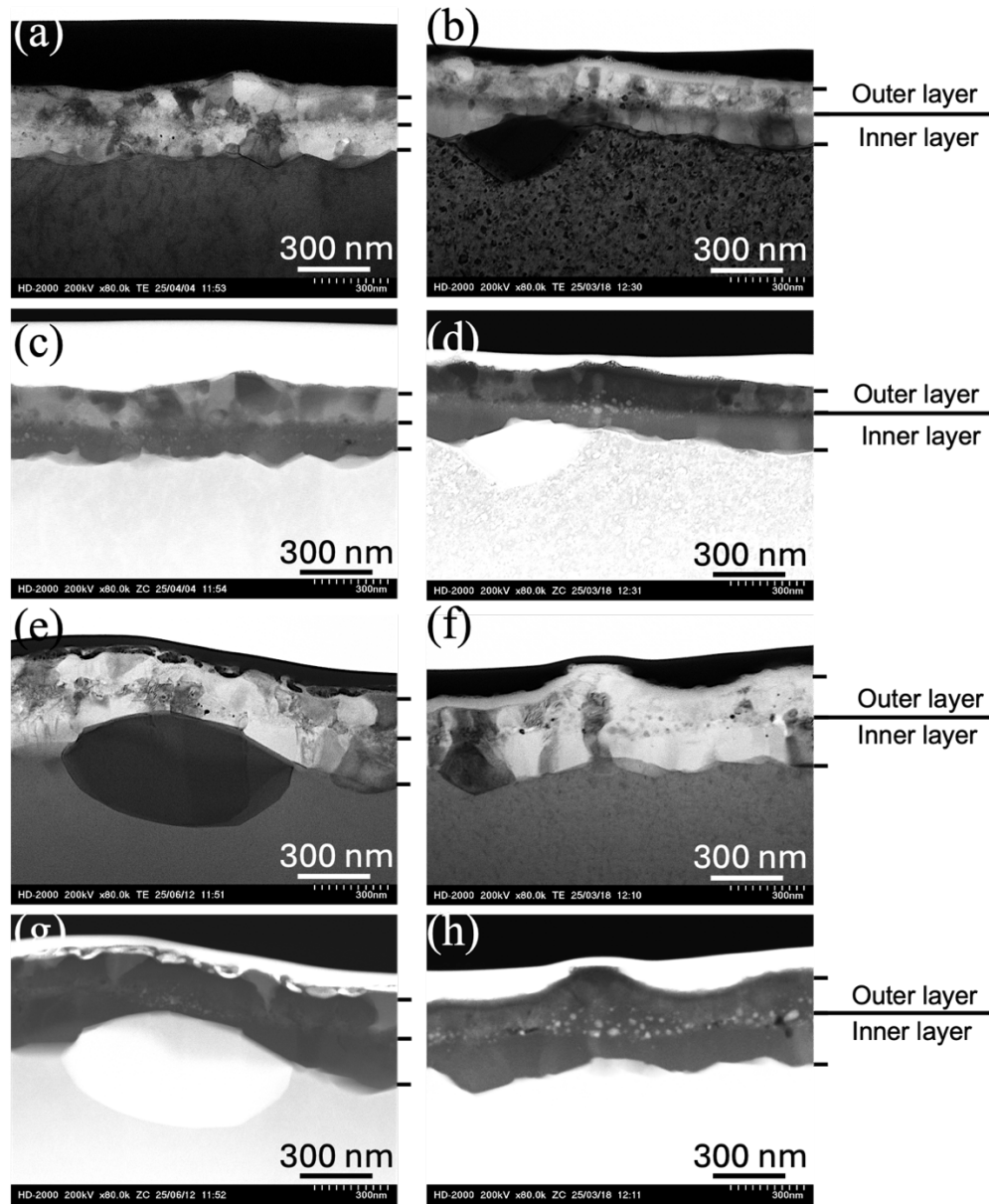


Fig. 8 STEM cross-sections of the oxide scale formed on Fe-1Al-0.35Nb alloys with (a)10 and (b)25Cr after 500 h of oxidation, (c)10 and (f)25Cr after 1000 h of oxidation, respectively. (c)(d) and (g)(h) are corresponding Z-contrast images of (a), (b), (e) and (f)

Figure 9 shows the SEM cross-sectional microstructures of the 10Cr, 20Cr, and 25Cr alloys oxidized for 400 and 1225 h. The formation of the Laves phase at the scale/alloy interface tended to increase as the Cr content decreased after 1225 h of oxidation. Fig. 10 shows the fraction of the Laves phase formed at the oxide scale and substrate interface on the 10Cr, 20Cr, and 25Cr alloys oxidized for 400 and 1225 h. After 400 h, the average Laves phase fractions in the three alloys were similar and around 2.5%. However, the fraction for the 10Cr alloy increased significantly to 33.5% after 1225 h, which was much larger than those of the 20Cr (12%) and 25Cr (10.1%) alloys. It was reported that Cr depletion due to Cr_2O_3 scale formation can promote the formation of the Laves phase at the oxide scale/alloy interface in Cr_2O_3 -forming alloys [10]. Therefore, low-Cr alloys could be more prone to form Laves phase precipitates at the scale alloy interface. Because the growth rate of the Al_2O_3 scale was found to decrease above the Laves phase, the higher Laves phase fraction on the 10Cr alloy could be one of the reasons for the decrease in the parabolic rate constant after longer oxidation time.

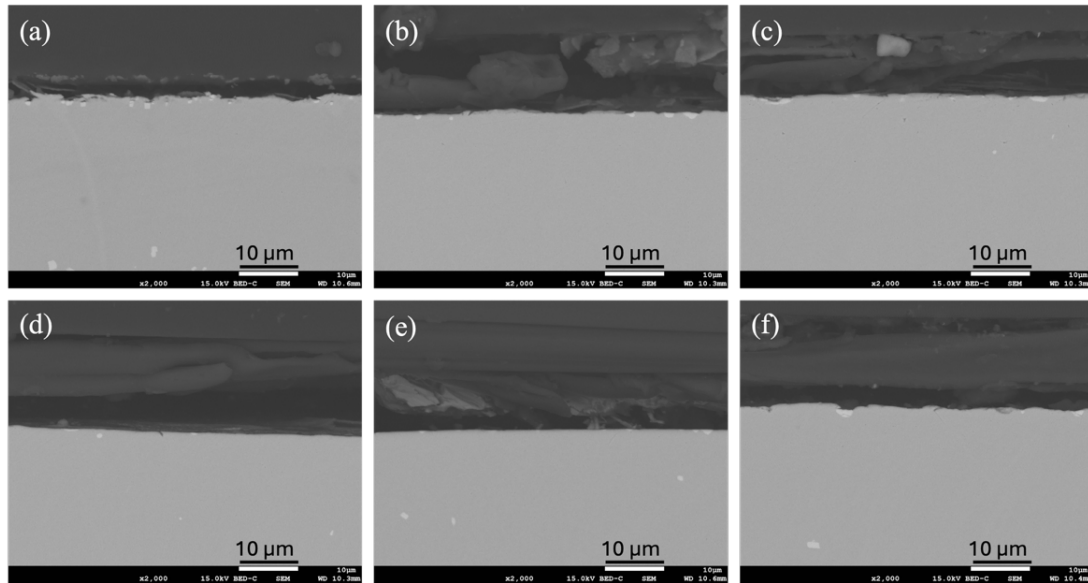


Fig. 9 Cross-sectional microstructures of near the interface of Fe-1Al-0.35Nb alloys with (a)(d)10, (b)(e)20Cr and (c)(f)25Cr after (a)(b)(c)1225 h and (d)(e)(f) 400 h of oxidation

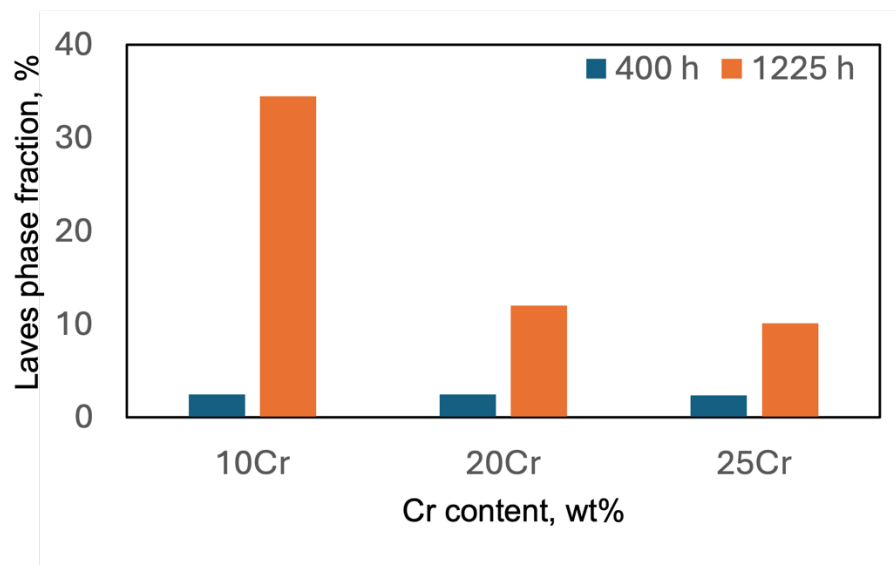


Fig. 10 The fraction of Laves Phase formed at the oxide/alloy interface of 10, 20 and 25Cr alloys oxidized for 400 and 1225 h

2.4 Discussion

Fe-(10, 15, 20, 25) Cr-1Al-0.35Nb alloys formed a protective Al_2O_3 scale at 850°C in air. Although 1 wt % Al is insufficient to form a protective Al_2O_3 scale in the ternary ferritic Fe-Cr-Al system [1], Nb promoted the exclusive Al_2O_3 scale formation on these alloys. Hayashi et al. [8] reported that the addition of Nb promotes the formation of a continuous Cr_2O_3 scale in the transient oxidation stage. The rapid establishment of the Cr_2O_3 scale favors an exclusive Al_2O_3 scale formation. In the present study, Nb had a similar effect on Al_2O_3 scale formation not only in low-Cr alloys but also in the high-Cr alloy (~25% Cr), which had sufficient Cr content to form a continuous Cr_2O_3 scale in the initial oxidation stage. Therefore, Nb might have additional effects on promoting an exclusive Al_2O_3 scale on the low-Al alloy; however, there was no Nb detected in the oxide scale from the current analysis, except in the precipitates formed within the Al_2O_3 scale. The additional effect of Nb on Al_2O_3 scale formation was unclear in this study.

The Al_2O_3 scale formed on alloys consisted of a duplex structure. The outer Al_2O_3 layer contained Fe and Cr and the inner layer was relatively pure Al_2O_3 . A similar oxide scale structure has frequently been reported in oxidation studies of Fe-Cr-Al alloys [26-30]. Yoneda et al. [11–13] reported the amorphous Al_2O_3 scale formation beneath a Cr- or Fe/Cr-rich oxide layer at lower temperatures between 650°C and 800°C. They mentioned that this amorphous layer protected the alloy substrate during the early transient oxidation stage until a protective $\alpha\text{-Al}_2\text{O}_3$ scale had developed upon heating to 900°C. They also discussed the effect of Cr content on the formation of an Al_2O_3 and proposed not only decreasing the oxygen potential at the alloy surface by formation of

Cr_2O_3 but also increasing the outward Al flux toward the alloy surface due to Cr depletion. Therefore, higher Cr content is beneficial for rapid establishment of a continuous Al_2O_3 scale. In the present work, Cr content is not essential for the formation of an Al_2O_3 scale since 25Cr alloy does not form an Al_2O_3 scale without Nb. However, it was suggested that higher Cr content promoted the formation of the protective Al_2O_3 scale quickly during the initial oxidation stage. The alloys with lower Cr content also formed an Al_2O_3 scale, but it needed more time to form an Al_2O_3 scale. Therefore, the transient outer oxide scale grew thicker on the alloys with lower Cr content.

Figure 11 shows the change in Al, Cr and Fe contents in the outer and inner parts of the Al_2O_3 scale formed on the 10Cr and 25Cr alloys with oxidation time. The Fe and Cr contents in the outer part of the outer layer were high in the short-term oxidation period and then decreased rapidly with oxidation time, which revealed that the initial Fe- and/or Cr-rich oxides formed on both alloys were transformed to an Al-rich oxide in a short time. The Fe content in the outer layer formed on the 10Cr alloy during the initial oxidation period was much higher than that of the 25Cr alloy. The Cr content in the outer layer formed on the 10Cr alloy during the initial oxidation period (~5h) was lower than that in the oxide scale formed on the 25Cr alloy. These results suggest that the growth rate of the initial transient oxide scale was faster for the 10Cr alloy than for the 25Cr alloy, which explained the initial higher oxidation mass gain and rapid growth kinetics of the outer layer on the 10Cr alloy.

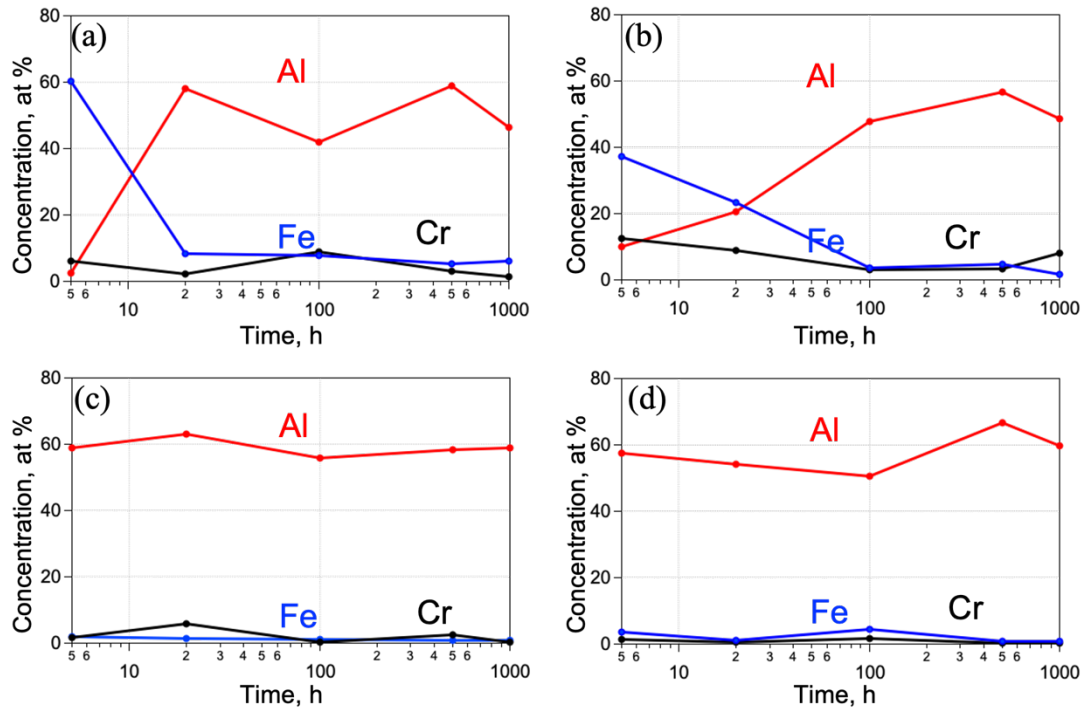


Fig. 11 Al, Cr and Fe contents in the oxide scale formed on (a)(c)10Cr and (b)(d)25Cr alloys. (a)(b) outer layer and (c)(d) inner layer in the oxide scale after 5, 20, 100, 500 and 1000 h of oxidation

Figure 12 shows a schematic of the development and growth of the Al_2O_3 scale. In the initial stage of oxidation, the transient oxide scale was formed on low- and high-Cr alloys. Alloys with higher Cr contents formed a continuous Cr-rich layer during a shorter oxidation period, which caused the early development of Al_2O_3 scale. However, alloys with lower Cr contents formed an Fe-rich transient oxide scale with a faster growth rate, and thus the transient Fe-rich oxide grew thicker until a continuous Al_2O_3 scale was established. When a continuous Al_2O_3 scale developed, the oxidation stage transitioned to the steady-state stage. In the steady-state oxidation period, the Al_2O_3 layer grew both outward and inward. Al ions dissolved in the outer Fe- and Cr-rich

oxide scale, and the composition of the outer layer gradually changed to be an Al_2O_3 that contained Fe and Cr. Because of the lower solubility of Fe, Nb, Cr, and Mn in Al_2O_3 , the oxide composed of these elements remained undissolved or formed precipitates at the bottom of the outer Al_2O_3 layer. In case of Fe-Cr-Al alloy with Nb addition, Nb promoted the Al_2O_3 scale even with low Cr alloys, therefore the effect of Cr on oxidation behavior was confirmed only in the initial transient oxidation period. In addition, because Cr content strongly affects the stability of Laves phase, Laves phase was formed on 10Cr alloy at the scale/alloy interface with a higher volume fraction. It was also found that the growth rate of the Al_2O_3 scale formed on Laves phase was low. Therefore, the oxidation kinetics of low-Cr alloy decreased in the long-term oxidation period after Laves phase precipitation.

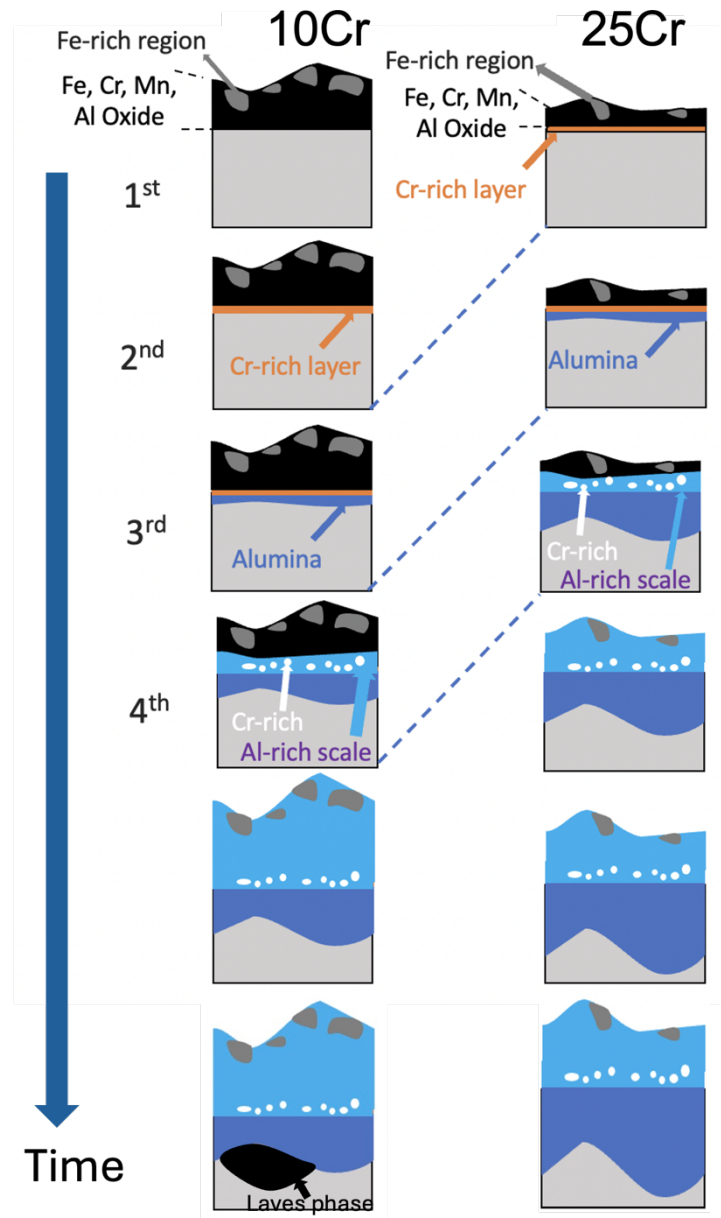


Fig. 12 Schematic illustration of oxidation process for alloys with high and low Cr

2.5 Conclusion

The effect of Cr on the oxidation behavior of ferritic Fe-Cr-Al-Nb alloys with different Cr contents was investigated at 850°C in air. The results can be summarized as follows.

- (1) Nb addition promoted the Al_2O_3 scale formation on ferritic Fe-Cr-Al alloys. An Al content of 1 wt % and a Cr content of 10 wt % were sufficient to form a continuous

Al₂O₃ scale.

- (2) The mass gain increased with decreasing Cr content during the initial oxidation stage; however, the oxidation kinetics were similar among alloys until about 400 h of oxidation. For further longer oxidation periods, the oxidation kinetics of 10Cr alloy decreased significantly, which was probably due to the formation of the Laves phase at the scale/alloy interface.
- (3) The oxide scale consisted of a duplex layer with an outer layer of Al₂O₃ scale containing Fe and Cr and an inner layer of relatively pure Al₂O₃ scale. The outer layer that formed on the low-Cr alloy was thicker than that of the high-Cr alloy, whereas the inner layer on the low-Cr alloy was thinner than that on the high-Cr alloy. This structural difference resulted from different oxidation behavior in the initial oxidation stage.

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Chapter 3.

The effect of niobium on the growth behavior of alumina scale on aluminum-containing ferritic stainless steel

3.1 Introduction

In the previous chapter, the effect of Cr on the growth of alumina scale was discussed. Generally, the critical Al content for the formation of a protective Al_2O_3 scale on ferritic Fe-Cr-Al alloys that contain 15 wt% Cr is about 2 wt% [1]. However, it was shown that only 1wt% Al addition is sufficient to form a continuous Al_2O_3 scale on Fe-xCr-Al alloys with 0.35 wt% Nb in Chapter 2. Hayashi et al. also reported that Nb addition promotes a protective Al_2O_3 scale on austenitic steels as well. Nb was also found to promote the formation of a Cr_2O_3 scale on Ni-Fe-Cr alloys [2]. Kuo et al. proposed that the beneficial role of Nb on the Cr_2O_3 scale formation on Ni-Fe-Cr alloys was attributed to the formation of a CrNbO_4 layer, which acts as a barrier for inward oxygen penetration, promoting the transition from internal to external scale formation [3]. This beneficial effect of Nb on Cr_2O_3 scale formation is considered to decrease the critical Al content for Al_2O_3 scale formation on austenitic steels; that is, the rapid establishment of the Cr_2O_3 scale in the early oxidation stage on Nb-containing alloys is beneficial for the formation of Al_2O_3 scale [3]. In Chapter 2, the effect of Cr on the growth of Al_2O_3 scale was discussed; however, the effect of Nb on the growth behavior of Al_2O_3 scale formed on Nb-modified alloys is still unclear. In this chapter, the effect of Nb on the

oxidation behavior of Al₂O₃-forming ferritic Fe-Cr-Al-Nb alloys at 1000 °C was investigated.

3.2 Experimental procedures

Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys (in wt%) were prepared by argon arc melting with high-purity metals (99.99%). Table 1 shows the nominal composition of alloys used in this study. All alloy ingots were homogenized at 1200°C for 48 h in a vacuum. Specimens with approximately 1mm thickness were cut from homogenized ingots and polished down with a 3µm diamond paste. Before the oxidation experiment, the specimens were ultrasonically cleaned in acetone. Since 1 wt% Al is not sufficient to form an Al₂O₃ scale on the Nb-free alloy, alloys with higher Al contents, 3 and 5 wt% were prepared to evaluate the growth behavior of the Al₂O₃ scale on Nb-free alloys.

Table 1 The chemical composition of alloys (nominal in wt%)

Alloy	Fe	Cr	Al	Si	Mn	Nb
1	Bal.	10	1	0.1	0.1	0.35
2	Bal.	10	1	0.1	0.1	0.7
3	Bal.	10	3	0.1	0.1	0
4	Bal.	10	3	0.1	0.1	0.35
5	Bal.	10	3	0.1	0.1	0.7
6	Bal.	10	5	0.1	0.1	0
7	Bal.	10	5	0.1	0.1	0.35
8	Bal.	10	5	0.1	0.1	0.7

The isothermal oxidation test was performed in a box furnace in air at 850°C and 1000°C for up to 100 h and 400 h. Some specimens were oxidized using Thermo-Gravimetric Analysis (TGA). For the oxidation in a box furnace, samples were hung on an Al₂O₃ rod in an Al₂O₃ crucible and placed in the center of a box furnace. The furnace was then heated from room temperature to 850°C or 1000°C at a rate of 10°C/min and held for designated time. After the oxidation experiment, the sample was cooled down to room temperature in the furnace. For the oxidation by TGA, the specimen was heated at the same heating rate, 10°C /min but cooled at a rate of 20°C/min after the oxidation test. After the experiment, the sample mass was measured using an electronic balance capable of weighing to a precision of 0.001 mg at room temperature. Surface and cross-sectional microstructures of the samples were observed using a Scanning Electron Microscope (SEM). To observe the detailed microstructure of the oxide scale, samples were analyzed using Scanning Transmission Electron Microscopy (STEM) equipped with an Energy-Dispersive X-ray spectrometer (EDS) and a Cs-corrected Scanning Transmission Electron Microscope (Titan). The TEM specimens were prepared using a Focused Ion Beam (FIB). The image analysis of the microstructure of the oxide scale was performed using ImageJ software.

3.3 Results

3.3.1 Oxidation kinetics

Figure 1 shows the oxidation kinetics of Fe-10Cr-1Al-(0.35, 0.7) Nb alloys (Fig. 1(a)) and Fe-10Cr-3Al-(0, 0.35, 0.7) Nb alloys (Fig. 1(b)) at 850°C in air for up to 100 h by

TGA. For 1Al alloys, both alloys oxidized rapidly in the initial oxidation stage, followed by the slow parabolic oxidation stage. The mass gain of 1Al-0.7Nb was found to be slightly higher than that of 1Al-0.35Nb alloy. For 3Al alloys, the oxidation kinetics also followed the parabolic law, however, the mass gain of 3Al with and without Nb addition is close to each other. The initial mass gain of 3Al-0.7Nb alloy was smaller than that of the 3Al-0Nb and 3Al-0.35Nb alloys, but the growth rate was higher, thus the mass gain crossed over at about 30 h of oxidation. The mass gain of alloys after 100 h of oxidation was in the order of $0.7 > 0.35 > 0\text{Nb}$.

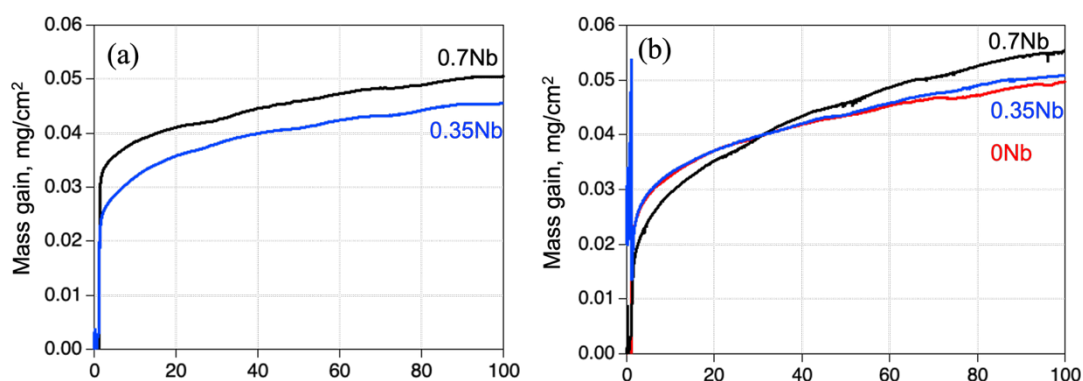


Fig. 1 Oxidation kinetics of (a) Fe-10Cr-1Al-(0.35, 0.7)Nb and (a) Fe-10Cr-3Al-(0, 0.35, 0.7)Nb alloys at 850°C in air for 100h by TGA

Figure 2 shows the oxidation kinetics of Fe-10Cr-(1, 3) Al-(0.35, 0.7) Nb alloys oxidized at 850°C in air for up to 10 h by TGA. For 1Al alloys, as mentioned in Fig. 1, both alloys oxidized rapidly in the initial oxidation stage, followed by the slow parabolic oxidation stage. The initial mass gain of 1Al-0.7Nb was higher than that of 1Al-0.35Nb alloy. For 3Al alloys, the oxidation kinetics also followed the parabolic law, however, the mass gain of 3Al with and without Nb addition was close to each

other. The oxidation kinetics of the 3Al alloys shown in Figs. 1(b) and 2 are not consistent because the reproducibility of the oxidation kinetics and the difference of oxidation mass gain within alloys with/without Nb were smaller than the variability in such low mass gain $\sim 0.01 \text{ mg/cm}^2$. To obtain a clear effect of Nb clearly, the oxidation temperature was increased to 1000°C .

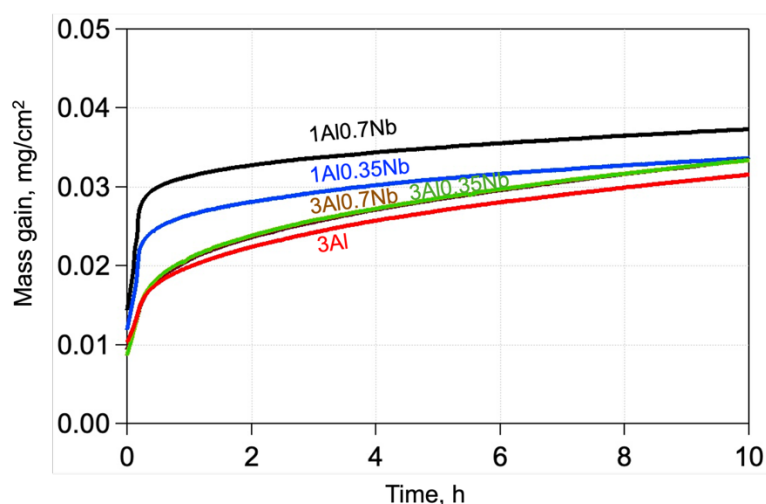


Fig. 2 Oxidation kinetics of Fe-10Cr-(1, 3)Al-(0, 0.35, 0.7)Nb alloys at 850°C in air for 10h by TGA

Figure 3 shows the oxidation kinetics of Fe-10Cr-1Al-(0.35, 0.7) Nb alloys (Fig. 3(a)) and Fe-10Cr-3Al-(0, 0.35, 0.7) Nb alloys (Fig. 3(b)) at 1000°C in air for up to 100 h by TGA. For 1Al alloys, both alloys with/without Nb oxidized rapidly in the initial oxidation stage, followed by the slow parabolic oxidation stage. The mass gain of 1Al-0.7Nb was found to be higher than that of 1Al-0.35Nb alloy. For 3Al alloys, the oxidation kinetics also followed the parabolic law, however, the effect of Nb on the oxidation mass gain was not clearly confirmed. In this study, kinetics curves were adjusted for the mass gain measured at room temperature after the oxidation test. The

mass gain kinetic curves of 3Al alloys did not start from 0, because of buoyancy effects during heating in air in TGA.

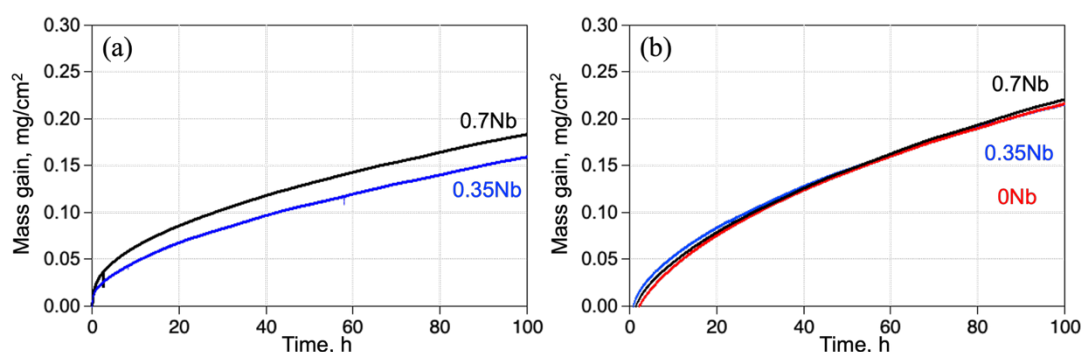


Fig. 3 Oxidation kinetics of Fe-10Cr-xAl-(0, 0.35, 0.7)Nb alloys at 1000°C in air by TGA, (a) 1Al and (b) 3Al

Figure 4 shows the oxidation kinetics of Fe-10Cr-(1, 3, 5) Al-(0, 0.35, 0.7) Nb alloys oxidized at 1000°C in air for up to 400 h by a box furnace. The oxidation curves followed the same trend as results obtained by TGA. For 1Al alloys, both alloys oxidized parabolically, and the mass-gain was larger for 0.7Nb than 0.35Nb, and this difference became larger after a longer oxidation time. It was also found that the oxidation mass gain increased with increasing Al content. The oxidation mass gain of 3Al alloys tended to increase with increasing Nb content for the longer oxidation stage, however, the difference of the oxidation mass gain of 3Al alloys with different Nb content was still small. No apparent effect of Nb on the oxidation mass-gain was confirmed for 5Al alloys even after a longer oxidation time, 400h.

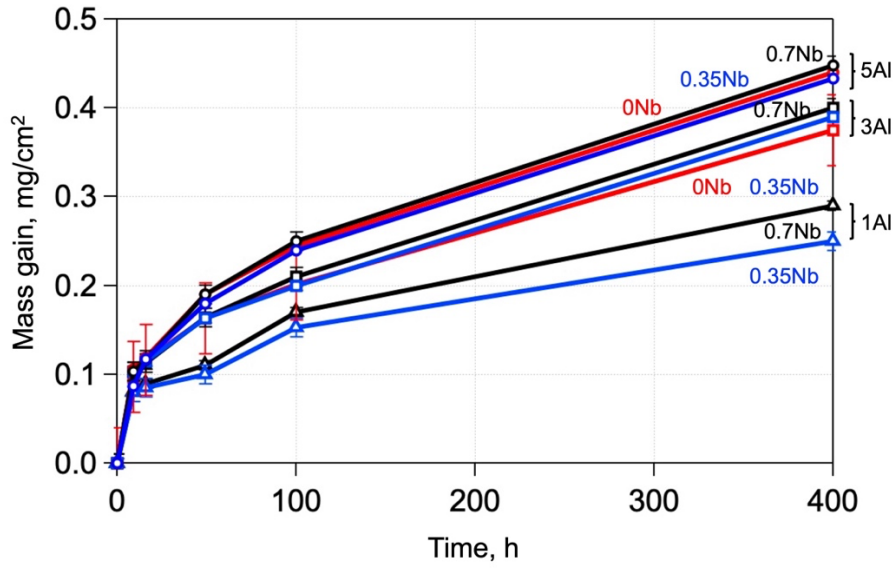


Fig. 4 Oxidation kinetics of Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys at 1000°C in air for 100h by a box furnace

3.3.2 Cross-sectional microstructures of oxide scale

The cross-sectional microstructures of the oxide scale formed on Fe-10 Cr-(1, 3) Al-(0, 0.35, 0.7) Nb alloys oxidized at 850°C in air for 10 h are shown in Fig. 5. The oxide scale formed on all alloys consisted of a duplex structure with both the outer and inner layers. The outer and inner layers were composed of equiaxed and columnar grains, respectively. The thickness of the Al_2O_3 scale formed on 1Al or 3Al alloys with different Nb content was similar, but the Al_2O_3 scales formed on 3Al alloys were thinner than those formed on 1Al alloys.

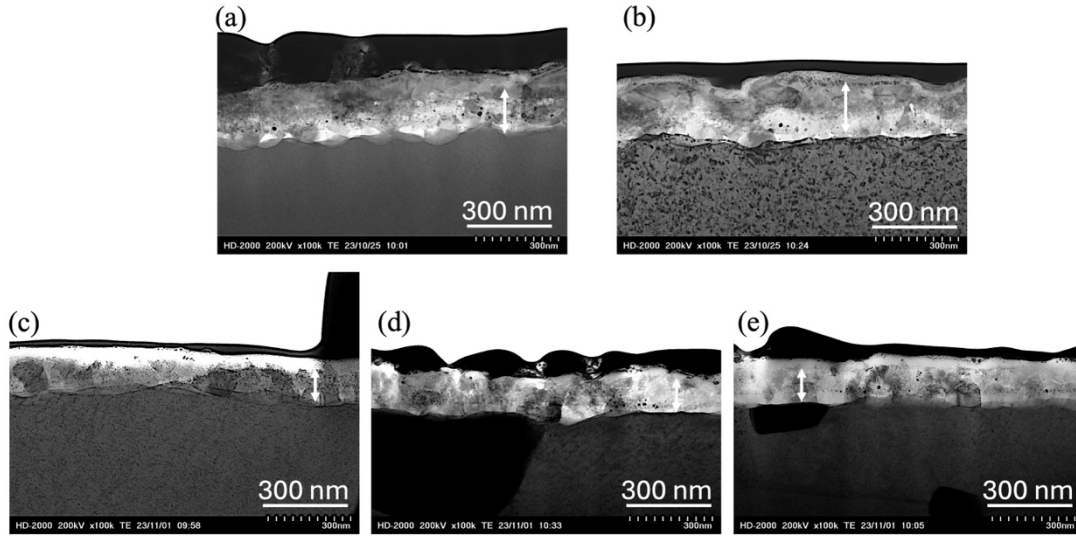


Fig. 5 STEM cross-sections of the oxide scale formed on Fe-10Cr-(1, 3)Al-(0, 0.35, 0.7)Nb alloys oxidized at 850°C for 10h by TGA, (a) 1Al-0.35Nb, (b) 1Al-0.7Nb, (c) 3Al, (d) 3Al-0.35Nb and (e) 3Al-0.7Nb

The cross-sectional microstructures of oxide scale formed on Fe-10Cr-(1, 3)Al-(0, 0.35, 0.7)Nb alloys oxidized at 850°C in air for 100 h are shown in Fig. 6. The oxide scale structure was the same as those formed after 10 h of oxidation. For 1Al alloys, the thickness of the oxide scale was almost the same. The thickness of the oxide scale formed on 3Al alloys with different Nb content was also almost the same. However, the Al_2O_3 scale formed on 3Al alloys became thicker than that on 1Al alloys after 100 h of oxidation.

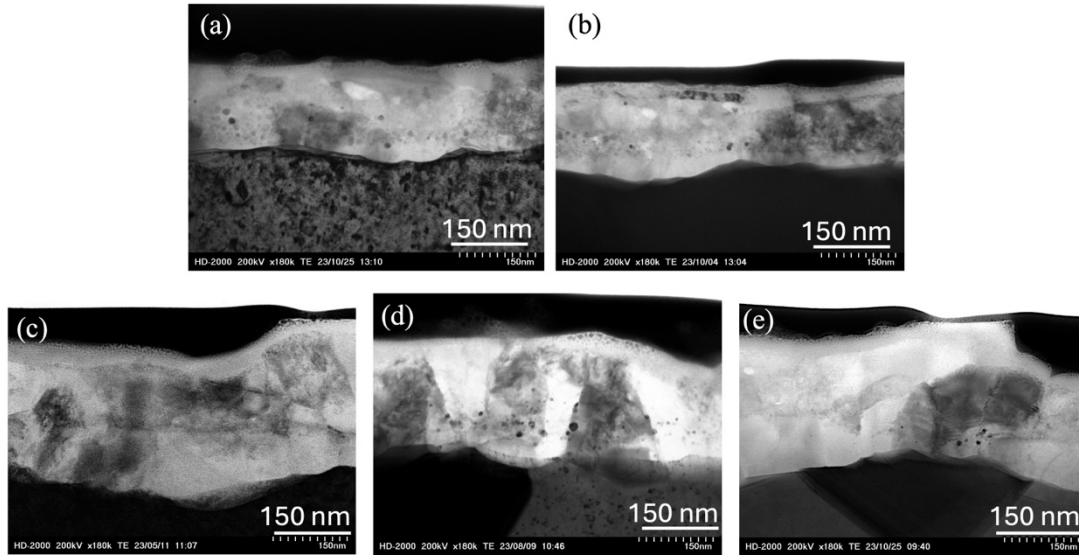


Fig. 6 STEM cross-sections of the oxide scale formed on Fe-10Cr-(1, 3)Al-(0, 0.35, 0.7)Nb alloys oxidized at 850°C for 100h by TGA, (a) 1Al-0.35Nb, (b) 1Al-0.7Nb, (c) 3Al, (d) 3Al-0.35Nb, and (e) 3Al-0.7Nb

The cross-sectional microstructures of oxide scale formed on Fe-10 Cr-(1, 3, 5) Al-(0, 0.35, 0.7) Nb alloys oxidized at 1000°C in air for 100 h are shown in Fig. 7. The oxide scale formed on all alloys consisted of a duplex structure with both the outer and inner layers. At 1000°C, the grain structure of the oxide scale was clearly observed. The outer and inner layers were composed of equiaxed and columnar grains, respectively. The thickness of the outer layer formed on 1Al alloys with different Nb content was similar, however, the inner layer thickness was not homogeneous and increased locally with increasing Nb content. The thickness of the outer layer formed on 3Al alloys was also almost the same, but the inner layer thickness tended to increase with increasing Nb content. The thickness of both the inner and outer oxide layers formed on 5Al alloys

was similar among alloys, indicating that the effect of Nb disappeared in 5Al alloys. It is also observed that the Al_2O_3 scale became thicker with increasing Al content.

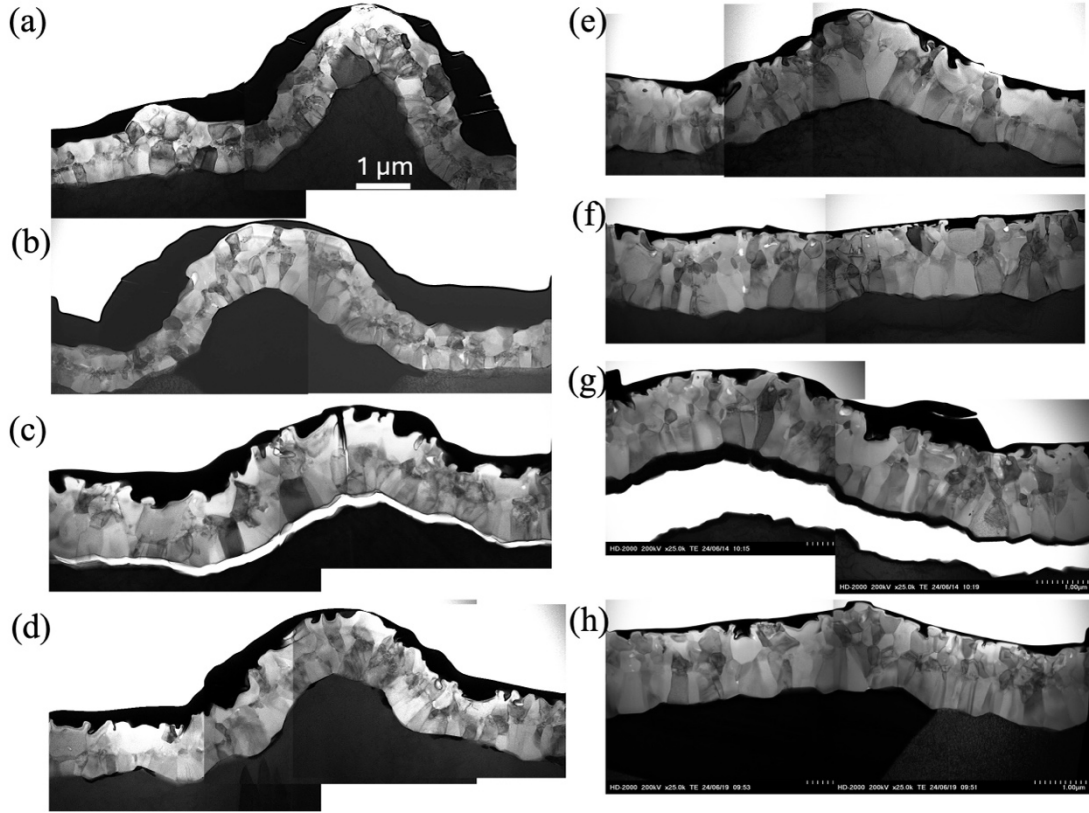


Fig. 7 STEM cross-sections of the oxide scale formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys oxidized at 1000°C for 100h by a box furnace, (a) 1Al-0.35Nb, (b) 1Al-0.7Nb, (c) 3Al, (d) 3Al-0.35Nb, (e) 3Al-0.7Nb, (f) 5Al, (g) 5Al-0.35Nb and (h) 5Al-0.7Nb

Figure 8 shows the cross-sectional microstructures of Fe-10 Cr-(1, 3, 5) Al-(0, 0.35, 0.7) Nb alloys oxidized at 1000°C in air for 400 h. The thickness of the oxide scale appeared to increase with increasing Al content. The thicknesses of the inner layer formed on 1 and 3Al alloys were confirmed to increase with increasing Nb content, however, no apparent Nb effect on the oxide scale thickness was observed in 5Al alloys.

No apparent difference in the thickness of the outer layer formed on each 1, 3 or 5Al alloys with different Nb content was also confirmed.

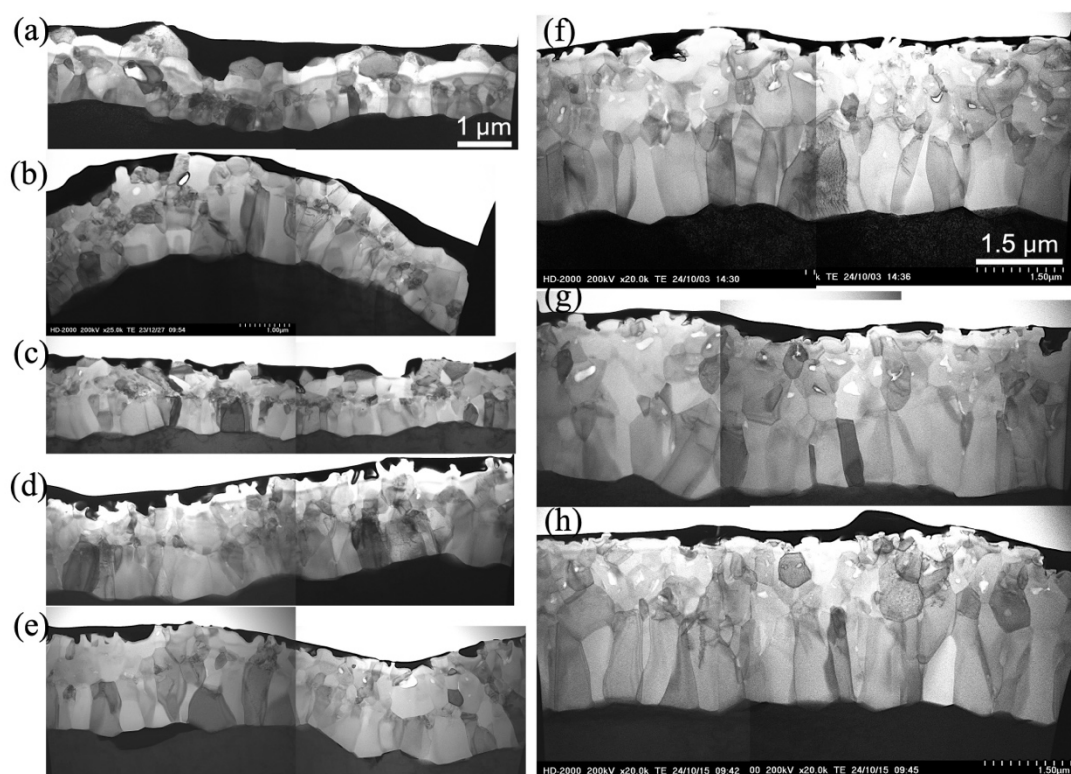


Fig. 8 STEM cross-sections of the oxide scale formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys oxidized at 1000°C for 400h by a box furnace, (a) 1Al-0.35Nb, (b) 1Al-0.7Nb, (c) 3Al, (d) 3Al-0.35Nb, (e) 3Al-0.7Nb, (f) 5Al, (g) 5Al-0.35Nb and (h) 5Al-0.7Nb

EDS maps of the oxide scale formed on Fe-10Cr-(1, 3) Al-(0, 0.35, 0.7) Nb alloys oxidized at 850°C in air for 100 h, are shown in Figs. 9-13. The outer layer formed on 1 and 3Al alloys with 0.35Nb and 0.7Nb was an Al_2O_3 containing Fe and Cr, and the inner layers were a relatively pure Al_2O_3 . A discontinuous Cr-rich band was observed between the inner and outer layers. No Nb-oxide was detected within the oxide scale

from this analysis. The Laves phase was observed to form at the subsurface region of 1Al-0.7Nb, 3Al-0.35Nb and 3Al-0.7Nb alloys.

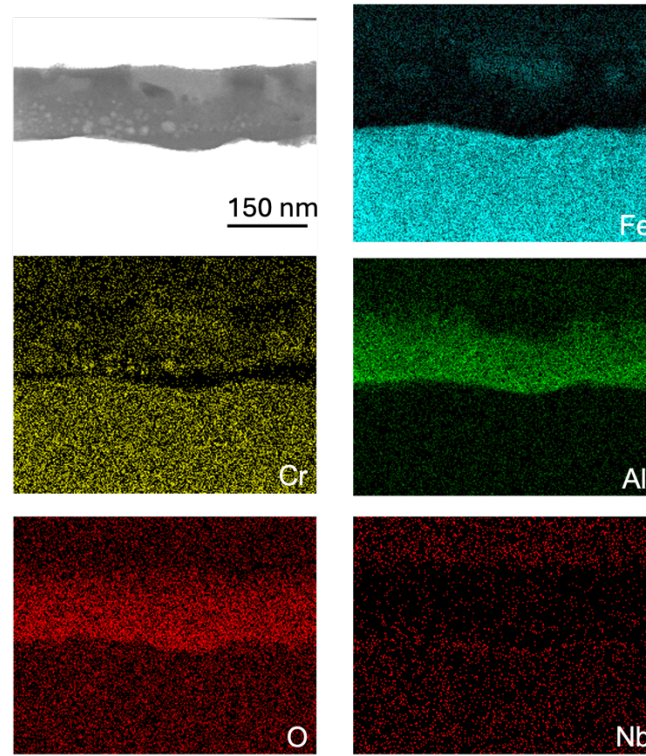


Fig. 9 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb alloy oxidized at 850°C for 100h by TGA

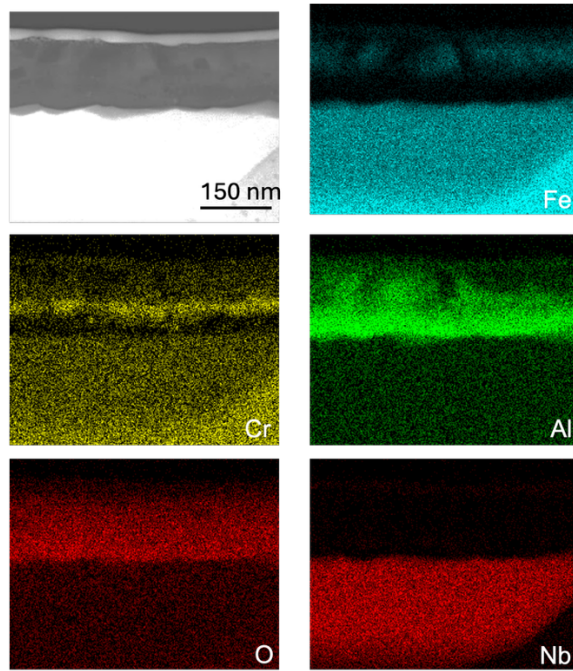


Fig. 10 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb alloy oxidized at 850°C for 100h by TGA

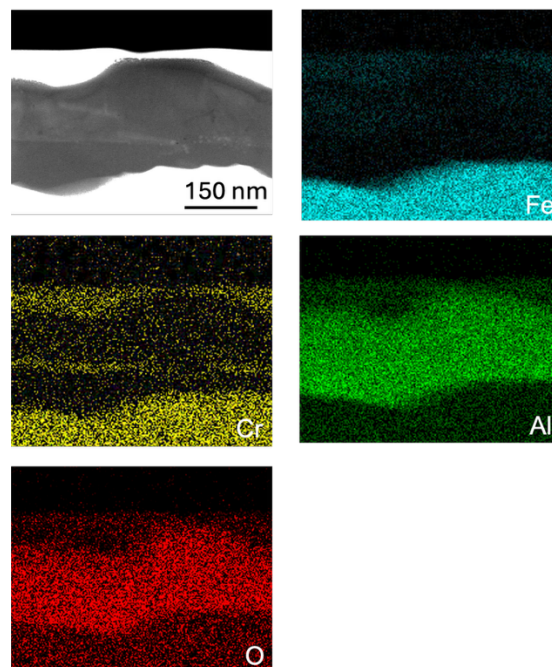


Fig. 11 Element maps of the oxide scale formed on Fe-10Cr-3Al alloy oxidized at 850°C for 100h by TGA

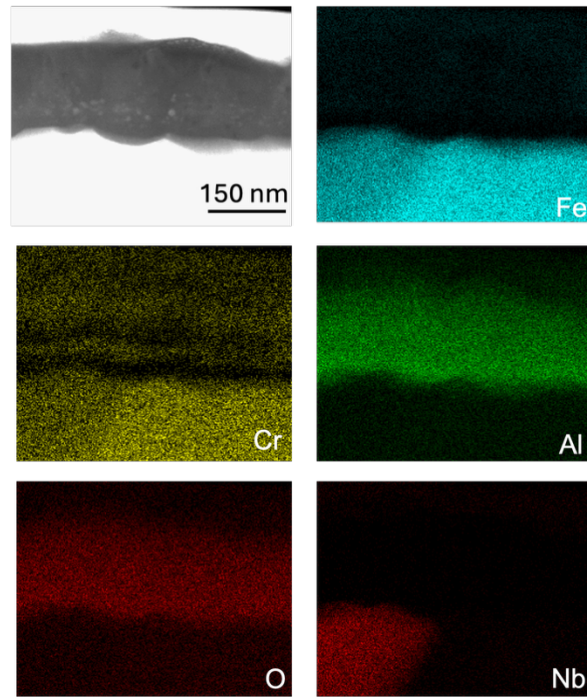


Fig. 12 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.35Nb alloy oxidized at 850°C for 100h by TGA

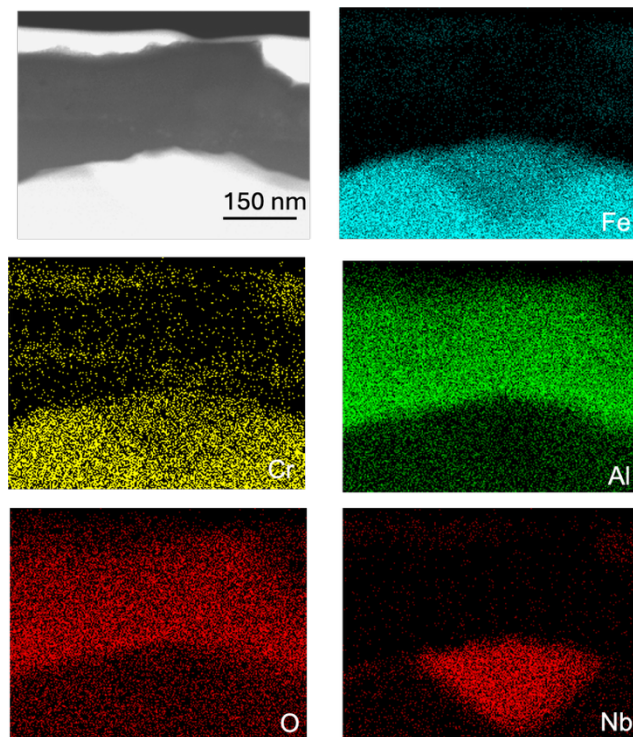


Fig. 13 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.7Nb alloy oxidized at 850°C for 100h by TGA

Representative EDS maps of the oxide scale formed on Fe-10Cr-1Al with different Nb content oxidized at 1000°C for 400 h, are shown in Figs. 14, 15. The outer layer formed on 0.35Nb and 0.7Nb alloys was an Al_2O_3 containing Fe and Cr, and the inner layers were a relatively pure Al_2O_3 . A discontinuous Cr-rich band was observed between the inner and outer layers. No Nb-oxide was detected within the oxide scale from this analysis. The Laves phase was observed to form at the subsurface region of 0.7Nb alloy. Figs. 16-18 show the EDS maps of the oxide scale formed on Fe-10Cr-3Al with and without different Nb content after 400 h of oxidation. The outer layer formed on both alloys was an Al_2O_3 that contains Fe and Cr and the inner layer was a relatively pure Al_2O_3 layer, which is very similar to the oxide scale formed on the 1Al alloy. A Cr-rich band formed between the inner and outer layers was continuous on 3Al alloys. Compared to the Nb free alloy, the Fe and Cr content in the outer layer formed on 0.7Nb alloy tended to be low from the quantitative line analysis shown in Fig. 19. Furthermore, no Nb oxide was detected in the oxide scale of 0.7Nb alloy.

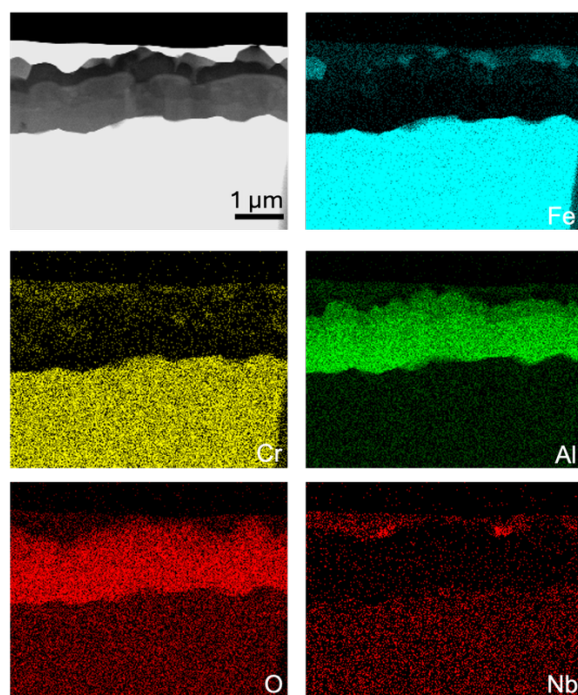


Fig. 14 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb alloy oxidized at 1000°C for 400h by box furnace

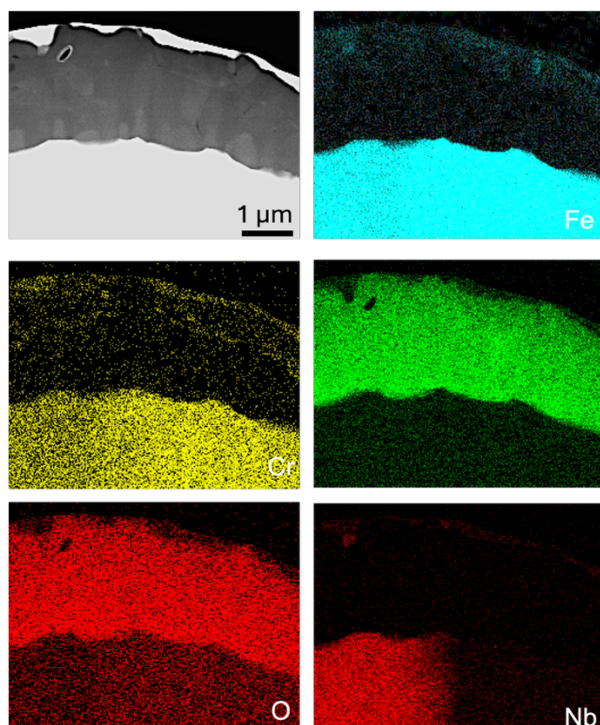


Fig. 15 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb alloy oxidized at 1000°C for 400h by box furnace

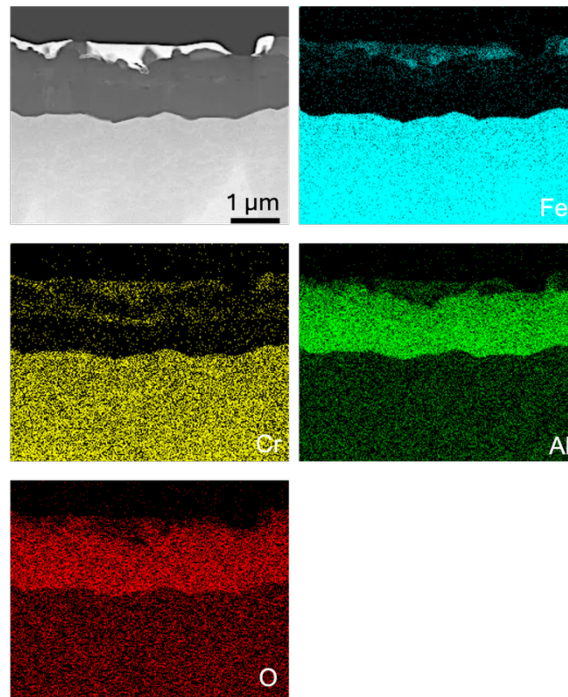


Fig.16 Element maps of the oxide scale formed on Fe-10Cr-3Al alloy oxidized at 1000°C for 400h by box furnace

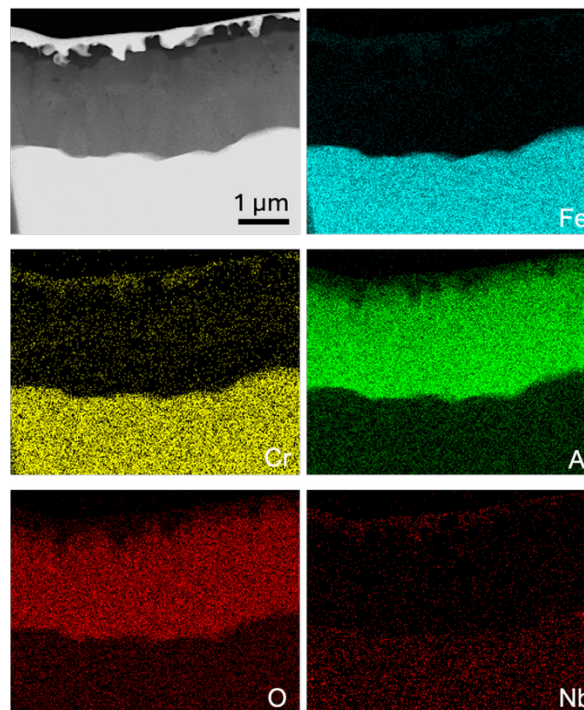


Fig. 17 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.35Nb alloy oxidized at 1000°C for 400h by box furnace

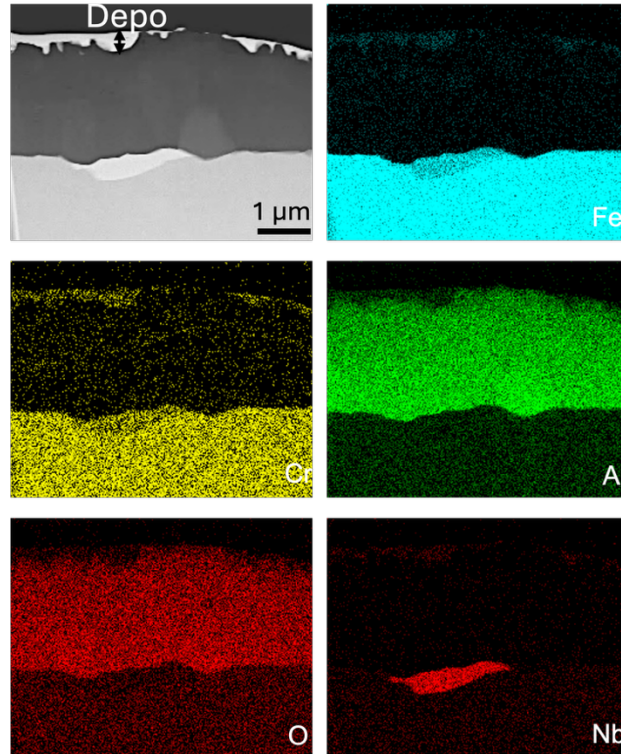


Fig. 18 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.7Nb alloy oxidized at 1000°C for 400h by box furnace

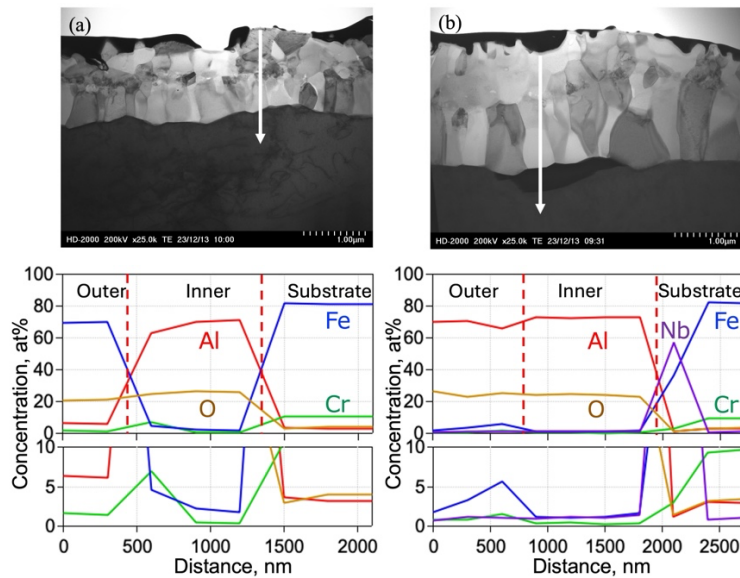


Fig. 19 STEM images and EDS line profiles of each element in the oxide scale formed on Fe-10Cr-3Al-xNb, (a)0Nb and (b) 0.7Nb alloys after 400 h of oxidation

3.3.3 Growth kinetics of the outer and inner layers

Figure 20 shows the growth kinetics of the outer and inner oxide layers formed on 1Al, 3Al and 5Al alloys. The thickness of the outer layer increased with increasing Al content (Fig. 20(a)). However, for the alloys with the same Al content, the growth kinetics of the outer layer was independent of Nb content. The thickness of the inner layer formed on 1Al alloys appeared to increase with increasing Nb content (Fig. 20(b)). The same effect of Nb on the thickness of the inner layer was also confirmed for 3Al alloy (Fig. 20(c)). However, no effect of Nb on the thickness of the inner layer formed on 5Al alloy was confirmed even after a longer oxidation period.

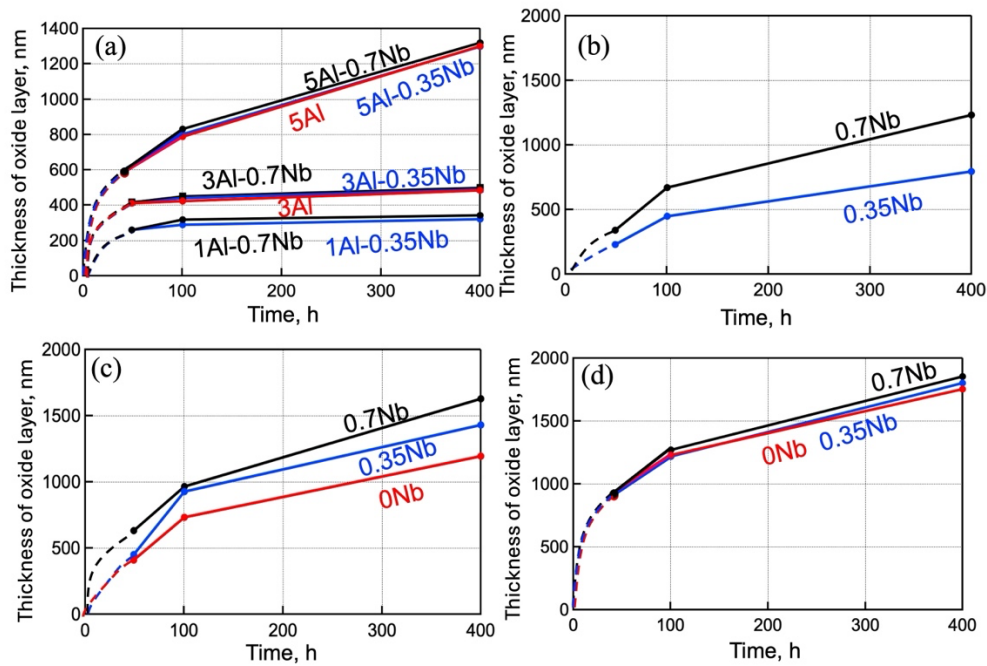


Fig. 20 Growth kinetics of the outer and inner Al_2O_3 layers formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys oxidized at 1000°C for 49, 100 and 400h by a box furnace, (a) outer layer thickness, (b) inner layer thickness of 1Al alloys, (c) inner layer thickness of 3Al alloys and (d) inner layer thickness of 5Al alloys

3.4 Discussion

As was mentioned in the introduction, the Nb addition promotes a continuous Al_2O_3 scale formation and decreases the critical Al content on ferritic Fe-Cr-low Al alloys. In this chapter, it was also found that the Nb addition increases the growth rate of Al_2O_3 scale, particularly for the inner layer formed on low Al alloys. The growth of the inner layer is controlled by the inward diffusion of oxygen, and the outer layer is controlled by the outward diffusion of aluminum along grain boundaries which are schematically illustrated in Fig. 21 [4]. Because Nb is considered to affect mainly the growth of the inner layer, it affects the inward diffusion of oxygen along grain boundaries of the oxide scale. Under the assumption that the flux of the oxygen within the Al_2O_3 scale is controlled by diffusion along grain boundaries, the density of grain boundaries, i.e., grain size, r_G , in the Al_2O_3 layer and the grain boundary diffusion coefficient, D_{GB} , might be affected by Nb addition. The effective diffusion coefficient of oxygen, D_{eff} is given by Eq. 1 with the simple assumption that the grains are square-shaped.

$$D_{eff} = \frac{2D_{GB}\delta_{GB}}{r_G} \quad (\text{Eq. 1})$$

Here, δ_{GB} is the grain boundary width, and r_G is the average grain diameter. Fig. 22 and Table 2 show the average grain size of the outer (Table 2) and inner (Fig. 22) Al_2O_3 layers formed on alloys oxidized for 400 h in a box furnace. Because the outer layer consisted of equiaxed grains, the average grain size of the Al_2O_3 was evaluated, however, since the inner layer had a columnar grain structure, the average grain size was evaluated as the diameter of columnar grains as a function of the distance from the outer/inner layer interface to the scale/alloy interface. The grain size of equiaxed grains

in the outer layer with different Nb content was almost the same among the alloys with the same Al content and it tended to slightly increase with increasing Al content (Table 2). The grain size of the inner layer linearly increased with increasing distance from the outer/inner layers interface for all alloys and tended to increase with increasing Al content. The proportional constants, k_{av} shown in Table 3 were almost the same among alloys with different Nb and Al contents, indicating the shape of the columnar grain is independent of Al and Nb contents. Additionally, the average grain size of the inner Al_2O_3 layer formed on 1, 3Al, or 5Al alloys with and without different Nb content was very similar, indicating that the average grain size of the inner Al_2O_3 layer is also independent of Nb content. Therefore, the reason for the increase in the growth rate of the inner layer on alloys with higher Nb addition is most likely due to an increase in the grain boundary diffusion coefficient of oxygen D_{GB} . Because the grain size of the outer and inner layers was independent of Nb content and Nb affected the growth rate of the inner layer, the characterization was focused only on the inner layer in the following discussion.

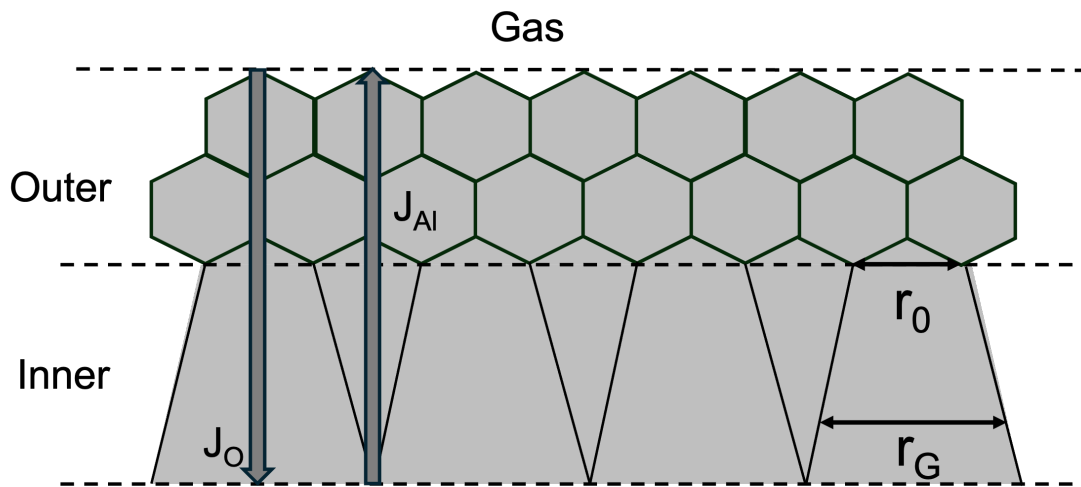


Fig. 21 Schematic illustration of grain structure of an Al_2O_3 scale

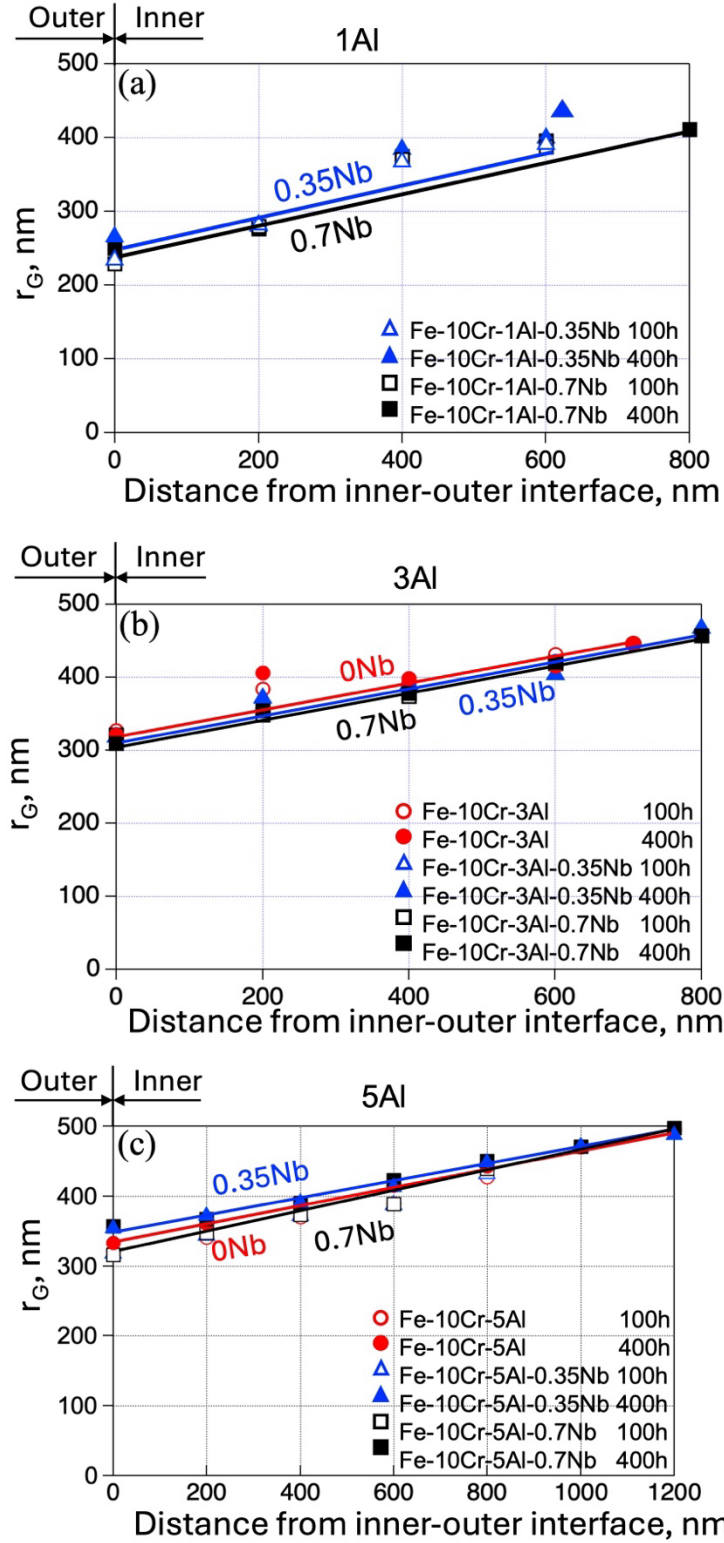


Fig. 22 Average grain size of the inner Al_2O_3 layer formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys after 400h of oxidation at 1000°C by a box furnace: (a) 1Al, (b) 3Al and (c) 5Al alloys

Table 2 The average grain size of the outer layer formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys after 400h of oxidation at 1000°C by a box furnace

	(in nm)		
Composition	0Nb	0.35Nb	0.7Nb
1Al		319	321
3Al	333	332	329
5Al	339	345	341

Table 3 The proportional constants of the average grain size of columnar grains of inner layer formed on Fe-10Cr-(1, 3, 5)Al-(0, 0.35, 0.7)Nb alloys after 400h of oxidation by a box furnace

Composition	0Nb	0.35Nb	0.7Nb
		nm/h	
1Al		5.7×10^{-4}	5.5×10^{-4}
3Al	4.5×10^{-4}	4.4×10^{-4}	4.5×10^{-4}
5Al	4.2×10^{-4}	4.2×10^{-4}	4.2×10^{-4}

In order to confirm the segregation of elements at the grain boundaries, the line analysis and element mapping were conducted across the grain boundaries of the inner layer formed on 1Al, 3Al and 5Al alloys and the results are shown in Figs. 23-27. Figs. 23 and 24 represent the Nb and Fe segregation at the grain boundaries in the oxide scale formed on 1Al alloys which are confirmed by both line analysis and element mapping. Similar segregation was confirmed in 1 or 2 grain boundaries out of 6 or 7 grain boundaries of the Al_2O_3 scale formed on 0.35 or 0.7Nb alloys, respectively. For 3Al

alloys, 4 and 5 grain boundaries were analyzed for 0 and 0.7Nb alloys, respectively. Fig. 25 shows the element mapping of the inner layer formed on 3Al-0, and 3Al-0.7Nb alloys. Fe segregation was confirmed in 1 of 4 grain boundaries of the Al_2O_3 scale formed on the 3Al-0Nb alloy. Fe and weak Nb segregation were also detected from 2 of 5 grain boundaries of the Al_2O_3 scale formed on the 3Al-0.7Nb alloy. In the case of 5Al alloys, neither Nb nor Fe segregation was confirmed in any of the 8 grain boundaries of the Al_2O_3 scale formed on the 5Al-0.7Nb alloy as shown in Figs. 26 and 27. The results regarding the segregation behavior of Nb and Fe at the grain boundaries of the Al_2O_3 scale formed on alloys with different Al and Nb contents suggest that the inward oxygen diffusion might be enhanced due to the segregation of Nb and/or Fe. The reason for the different segregation behavior of Fe and Nb in the Al_2O_3 scale formed on alloys with different Al content can be related to the oxygen potential at the scale/alloy interface. Because the oxygen potential at the scale/alloy interface is expected to decrease with increasing Al content in the alloy, Nb and Fe can be oxidized on alloys with lower Al content. Because there are no thermodynamic data, such as the activity or activity coefficient of Nb and Fe in Fe-Cr-Al alloys, it was not possible to evaluate and compare the free energy change of the different oxide formation of oxides. It was found that the growth rate of Al_2O_3 scale increased with increasing Al content, and it was the fastest on 5Al which formed the Al_2O_3 scale without segregation of Fe and Nb, Fe segregation might have an effect on decrease the grain boundary diffusion coefficient of oxygen.

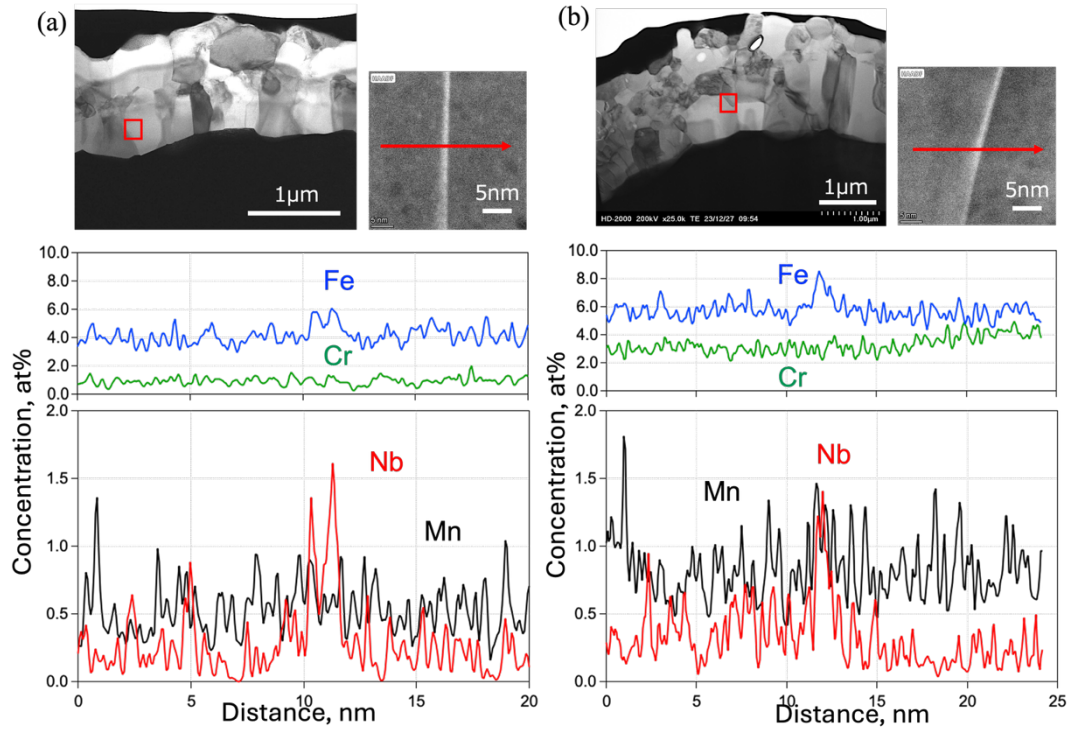


Fig. 23 Line profiles of Fe, Cr, Mn, and Nb across grain boundaries of Al_2O_3 scale formed on Fe-10Cr-1Al: -(a) 0.35Nb and -(b) 0.7Nb alloys after 400 h of oxidation

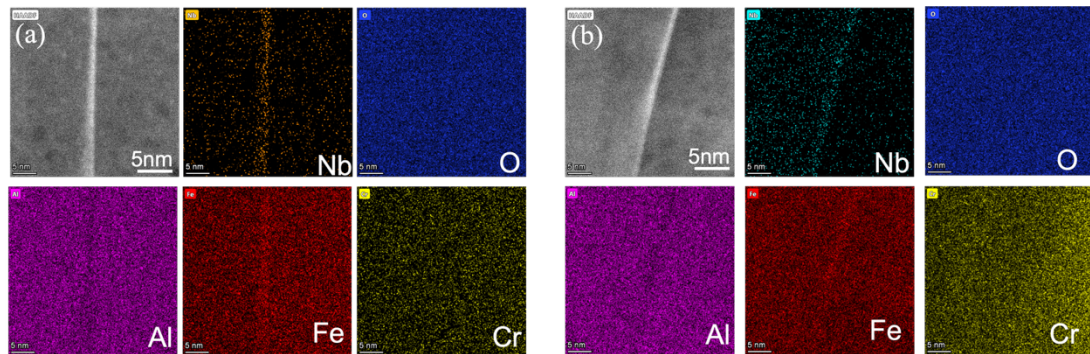


Fig. 24 Element maps of the grain boundaries of Al_2O_3 scale formed on Fe-10Cr-1Al with -(a) 0.35Nb and -(b) 0.7Nb alloys after 400 h of oxidation

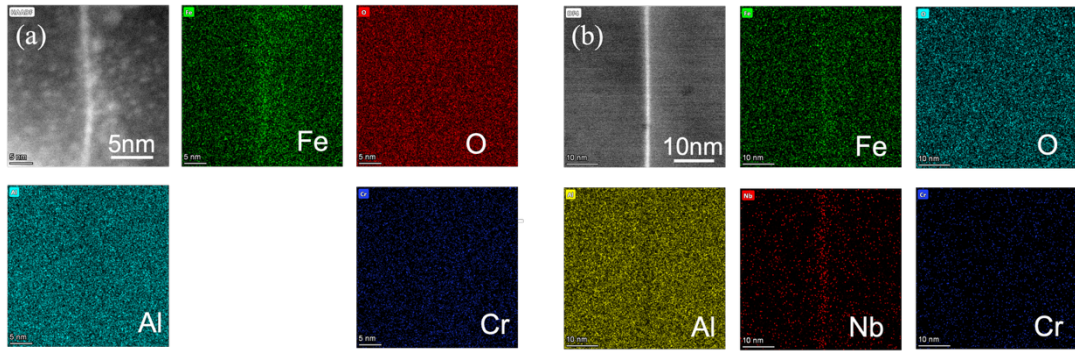


Fig. 25 Element maps of the grain boundaries of Al_2O_3 scale formed on Fe-10Cr-3Al with -(a)0Nb and -(b) 0.7Nb alloys after 400 h of oxidation

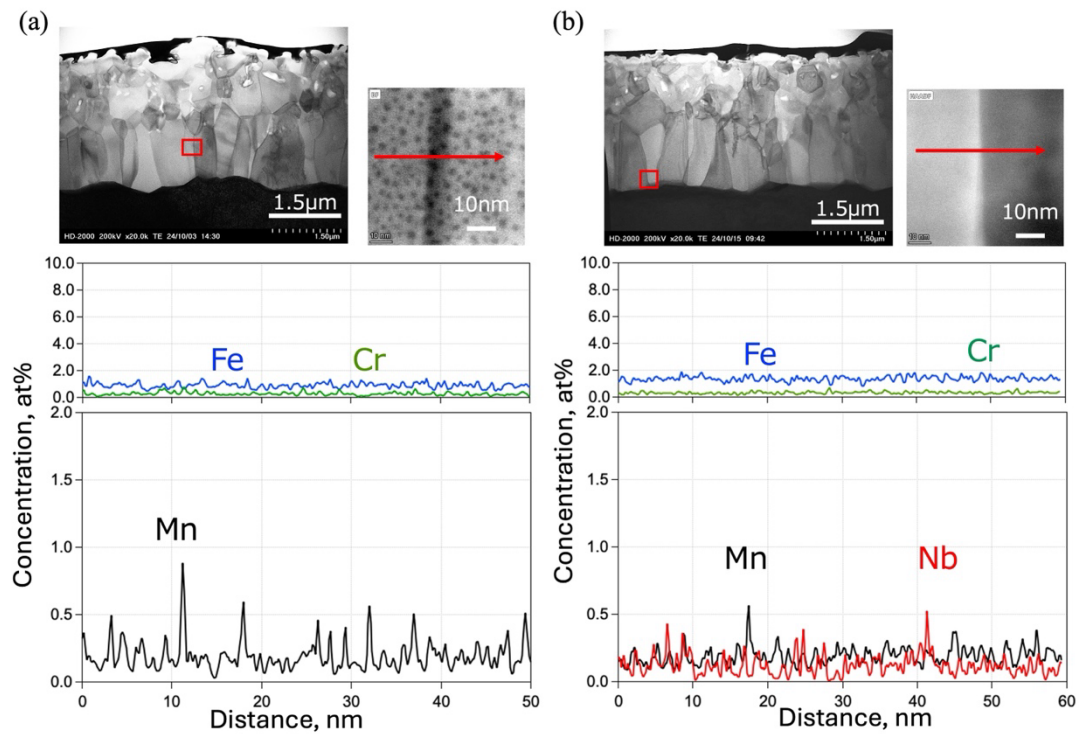


Fig. 26 Line analysis of the grain boundaries of Al_2O_3 scale formed on Fe-10Cr-5Al: -(a)0Nb and -(b) 0.7Nb alloys after 400 h of oxidation

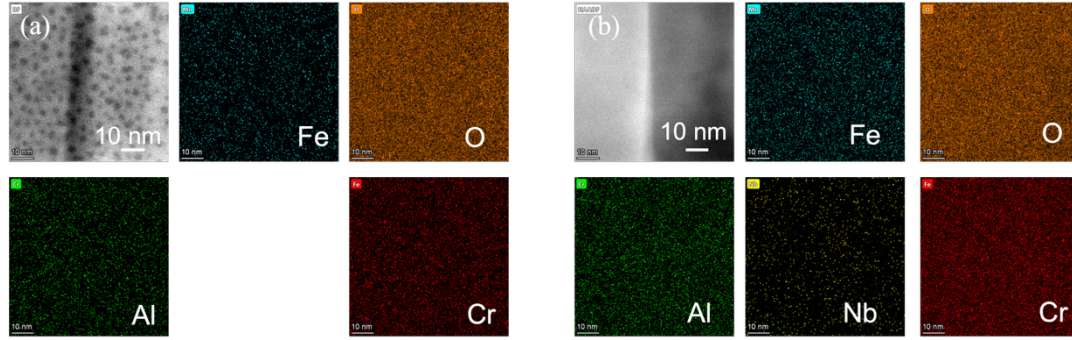


Fig. 27 Element maps of the grain boundaries of Al_2O_3 scale formed on Fe-10Cr-5Al with -(a) 0Nb and -(b) 0.7Nb alloys after 400 h of oxidation

Segregation of different elements, particularly reactive elements (RE), such as Zr, Y, and Hf at the grain boundaries of Al_2O_3 scale is known to have an effect on the growth rate of Al_2O_3 and Cr_2O_3 scales [5, 6]. Based on the dynamic RE segregation theory [7], RE ions with larger sizes, such as Zr, Y and Hf, are considered to have an effect on suppressing outward diffusion of Al ions because larger ions diffuse at a slower rate at grain boundaries and occupy more of the diffusion pathway in grain boundaries. Several studies also reported that Zr could segregate as ZrO_2 at grain boundaries of the Al_2O_3 scale formed on the Fe-22Cr-10Al-0.06wt%Z alloy. Segregation of Zr as ZrO_2 hinders the outward diffusion of Al ions, but enhances the inward diffusion of oxide ions [6-8]. Similar segregation behavior of Hf was also reported [9-11].

In this study Fe and Nb segregation was confirmed along the grain boundaries of the inner Al_2O_3 layer formed on alloys with lower Al concentration. Compared to Zr, Y and Hf, Nb ions are smaller, therefore, a Nb ion may not inhibit the outward Al ion diffusion [7]. In fact, it was found that Nb addition does not affect the growth rate of

the outer layer in this study (Fig. 8). Nb segregation at grain boundaries of the Al_2O_3 scale formed on Fe-Cr-Al and Ni-Al alloys has been reported [6-7, 12-14]. The former study using Fe-Cr-Al alloys reported no effect of Nb on the growth of Al_2O_3 scale, but the study on Ni-Al alloys showed a decrease in the growth rate of the Al_2O_3 scale by the addition of Nb, but no explanation for the effect of Nb was reported. In this study, in order to understand the mechanism of Nb effects, EELS analysis was conducted to confirm the state of segregated Nb.

Figure 28 shows the result of EELS analysis at the grain boundary of the Al_2O_3 scale formed on 1Al-0.35Nb, 3Al-0.35Nb and 3Al-0.7Nb alloys oxidized for 400 h at 1000°C . Compared with the standard valence state [15], the peak positions suggest the possible valence states of Nb are Nb^{5+} and Nb^{4+} . Nb^{4+} was also confirmed, but only from the 3Al-0.7Nb alloy. Although NbO_2 was not observed from the STEM observation (Figs. 19-23), the EELS results suggested the formation of NbO_2 , which has the rutile crystal structure and is known to have a lot of oxygen vacancies. Under this assumption of the formation of NbO_2 based on EELS analysis, Nb segregation might increase the diffusivity of oxygen [12-15], enhancing the inward oxygen diffusion along grain boundaries, which increases the growth rate of the inner layer formed on low-Al alloys containing Nb.

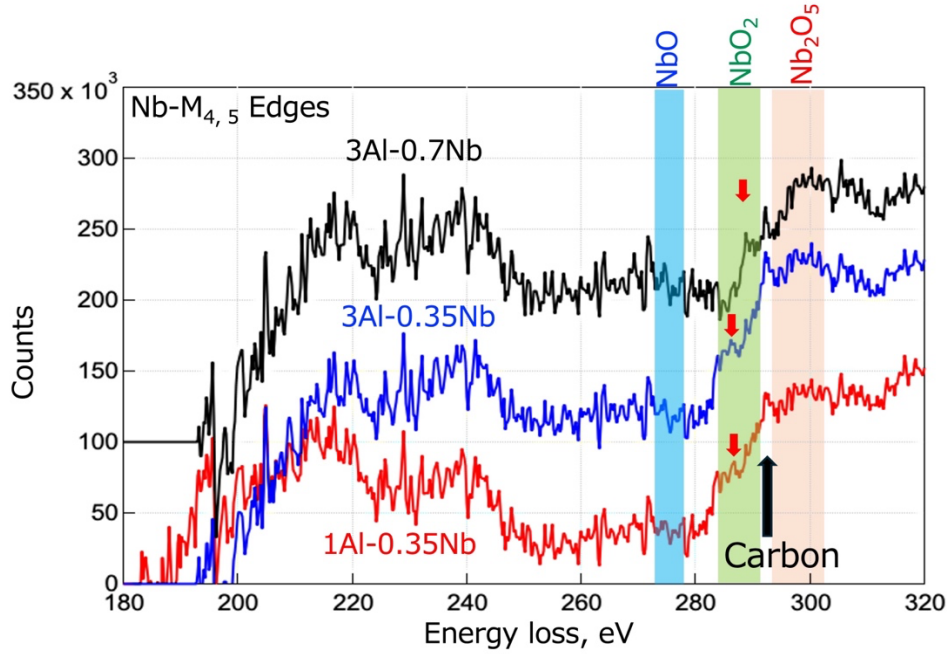


Fig. 28 EELS analysis at the grain boundary of Al_2O_3 scales formed on (a) 1Al-0.35Nb, (b) 3Al-0.35Nb and (c) 3Al-0.7Nb alloys after 400 h of oxidation

In this study, it was also found that the thickness of the outer and inner layers increased with increasing Al content, although the difference of the growth rate of the inner layer was smaller compared to that of the outer layer. As mentioned earlier, this effect might be caused by Fe segregation at grain boundaries. Because Nb is considered to increase the oxygen inward diffusion, the higher growth rate of the Al_2O_3 scale without Fe and Nb segregation on the 5Al alloy suggested that Fe segregation decreases the diffusivity of Al and oxygen ions. There are several reports of Fe segregation at the grain boundaries of the Al_2O_3 scale, but no apparent effect of Fe was reported in those studies [8]. Although the effect of the Fe/Al on the growth rate of Al_2O_3 scale is important, the effect of Fe segregation on the growth of Al_2O_3 scale was not evaluated in this study.

3.5 Conclusion

The oxidation behavior of Fe-10Cr-(1, 3, 5) Al alloys with different Nb contents (0, 0.35 and 0.7 wt%) in air at 1000°C was investigated to understand the effect of Nb on the long-term growth behavior of the Al₂O₃ scale. Alloys with higher Al content were used for the assessment of alloys with and without Nb addition, since 1 wt% Al is not sufficient to form a continuous Al₂O₃ scale without Nb addition. The results can be summarized as follows:

- (1) The mass gain of low-Al alloys increased with increasing Nb content. However, this Nb effect was not clearly observed in the high Al alloy, 5Al.
- (2) The Al₂O₃ scale consisted of a duplex layer, and the thickness of the inner layer formed on 1 and 3Al alloys increased with increasing Nb content. However, no apparent effect of Nb was confirmed on the growth of the outer layer.
- (3) Nb and Fe segregation were confirmed at the grain boundaries of the inner layer formed on 1 and 3Al alloys. EELS analysis suggested the valence states of Nb would be Nb⁵⁺ and/or Nb⁴⁺, indicating enhanced oxygen diffusion due to a higher concentration of oxygen vacancies in the oxide with the rutile structure, NbO₂. This enhanced inward oxygen diffusion may be one of the reasons for the faster growth rate of the inner layer of the Al₂O₃ scale formed on low-Al alloys with Nb.

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Chapter 4.

The effect of titanium addition on growth of the oxide scale formed on niobium modified aluminum-containing ferritic stainless steel

4.1 Introduction

In the previous chapter, the effect of Nb on the growth rate of the Al_2O_3 scale was investigated. Nb was found to increase the growth rate of the inner Al_2O_3 layer. This Nb effect is thought to be attributable to Nb segregation along the grain boundaries of the Al_2O_3 scale. EELS analysis suggested that the valence state of the Nb at grain boundaries was Nb^{4+} or Nb^{5+} . If Nb was segregated as a Nb^{4+} , which has an equivalent structure to TiO_2 , a lot of vacancies could be generated, which could increase oxygen inward diffusion [1-2]. In fact, Ti is known to be a detrimental element for high temperature oxidation resistance to increase the growth rate of Al_2O_3 scale [3-4]. J. M. X. Wo et al. reported that the growth kinetics (k_p) of Al_2O_3 scale formed on Ni-17Cr-7Al alloy increased with increasing Ti addition at 800°C and 1000°C [3]. R. P. Oleksak reported that the growth rate and thickness of Al_2O_3 formed on Ni-13Al alloy increased with 2.99 wt% Ti addition at 1100°C [4]. In those studies, Ti addition was reported to increase the growth rate of the Al_2O_3 . However, the mechanism of this detrimental effect of Ti addition has not been clearly elucidated. As Nb was found to segregate as a Nb^{4+} and to increase the growth rate of Al_2O_3 scale, it is possible to evaluate the effect of Ti on the growth of an Al_2O_3 scale. Thus, in this chapter, the effect of Ti addition on

the oxidation behavior of Al₂O₃-forming Nb-modified ferritic stainless steel was investigated.

4.2 Experimental procedures

Fe-10Cr-(1, 3)Al-(0.35, 0.7)Nb-(0, 0.35)Ti alloys (in wt%) were prepared by argon arc-melting with high-purity metals (99.99%). Table 1 shows the nominal composition of the alloys used in this study. All alloy ingots were homogenized at 1200°C for 48 h in a vacuum. Specimens with approximately 1 mm thick were cut from homogenized ingots and polished down to a 3 μm diamond paste. Before oxidation experiments, the specimens were ultrasonically cleaned in acetone.

Table 1 The chemical compositions of alloys (nominal in wt%)

Fe	Cr	Al	Si	Mn	Nb	Ti
Bal.	10	1	0.1	0.1	0.35	0
Bal.	10	1	0.1	0.1	0.35	0.35
Bal.	10	1	0.1	0.1	0.7	0.35
Bal.	10	3	0.1	0.1	0.35	0.35

The isothermal oxidation test was performed in a box furnace in air at 850°C for up to 100 h. Some specimens were oxidized using Thermo-Gravimetric Analysis (TGA). For isothermal oxidation tests, the specimen was heated at a rate of 10 °C/min and cooled at the rate of 20 °C/min as shown in Fig. 1(a). For short-term oxidation tests,

the specimen was heated at the same heating rate, 10 °C/min to the target temperature and immediately cooled at the rate of 20 °C/min as shown in Fig. 1(b).

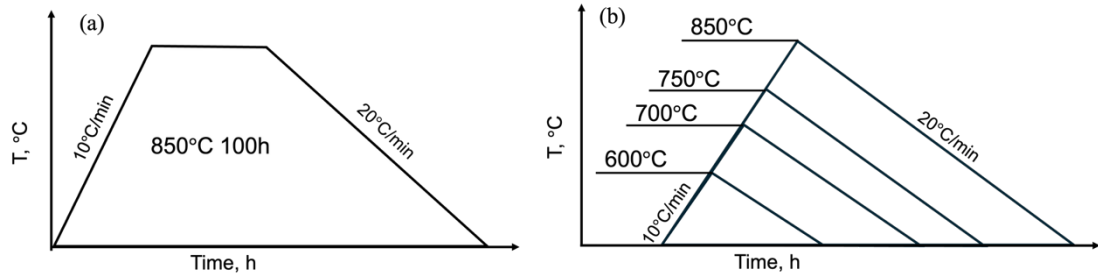


Fig. 1 Oxidation tests: (a) Isothermal long-term oxidation experiment procedure and (b) heating process oxidation experiment procedure

After the experiment, the sample mass was measured by an electronic balance capable of weighing to a precision of 0.001 mg at room temperature. To observe the detailed microstructure of the oxide scale, samples were analyzed by Scanning Transmission Electron Microscopy (STEM) equipped with Energy-Dispersive X-ray spectrometer (EDS). The TEM specimens were prepared by a Focused Ion Beam System (FIB). Image analysis of the microstructure of the oxide scale was performed using ImageJ software.

4.3 Results

4.3.1 Oxidation kinetics

Figure 2 shows the oxidation kinetics of Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys oxidized at 850°C in air. All alloys oxidized rapidly in the initial oxidation stage, followed by a slow steady-state oxidation stage, in which the oxidation proceeded slowly as indicated in Fig. 2(a). The oxidation mass gain of 0.35Ti alloy was larger than that of Ti free alloy. The time for the transition from rapid to steady-state oxidation stages occurred at 75 min for Ti free alloy but it was about 4 h for 0.35Ti alloy (Fig. 2(b)). Fig. 2(c) shows the instantaneous parabolic rate constant (k'_p) obtained from Fig. 2(a). In the initial oxidation stage, the k'_p of 0.35Ti alloy was significantly larger than that of Ti free alloy, but it decreased rapidly and became slightly larger than that of 0.35Ti alloy in the long-term oxidation stage. Fig. 2(d) shows the oxidation kinetics of Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys oxidized at 850°C for 400 h in air using a box furnace. The difference of the oxidation mass gain of Ti free and 0.35Ti alloy became larger after 400 h of oxidation, confirming that the growth rate of Al_2O_3 scale on Ti free alloy in the long-term oxidation stage was larger than that on 0.35Ti alloy. Fig. 3 shows the oxidation kinetics of Fe-10Cr-1Al-(0.35, 0.7) Nb-0.35Ti alloys oxidized at 850°C in air for up to 100 h. The oxidation behavior of the two alloys was similar, i.e., higher oxidation rates at the initial oxidation stage, followed by a slow steady-state oxidation stage. However, a higher Nb addition slightly decreased the initial oxidation mass gain. Fig. 4 shows the oxidation kinetics of Fe-10Cr-(1, 3)Al-0.35Nb-0.35Ti alloys oxidized at 850°C in air for up to 100 h. The mass gain, in particular the initial oxidation mass gain, of 3Al alloys was much smaller than that of 1Al, and the detrimental effect of Ti was not confirmed for the oxidation of 3Al-0.35Nb alloys.

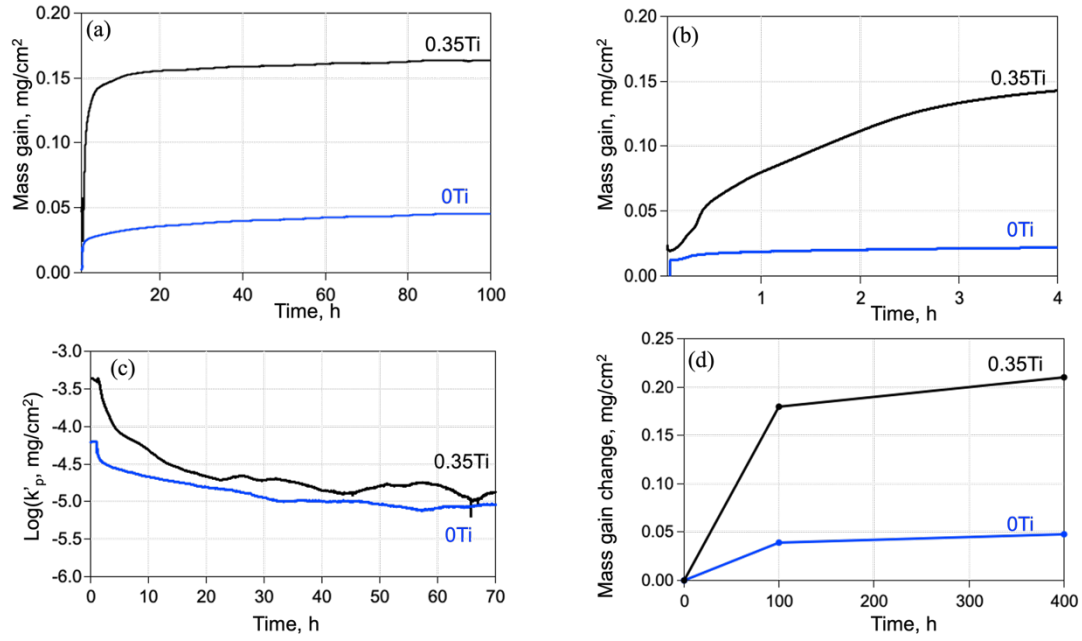


Fig. 2 Oxidation kinetics of Fe-10Cr-1Al-0.35Nb-(0, 0.35)Ti alloys oxidized at 850°C in air for (a)100 h, (b)4 h and (c) instantaneous parabolic rate constant (k'_p) calculated from data in (a), (d) is for 400 h by box furnace

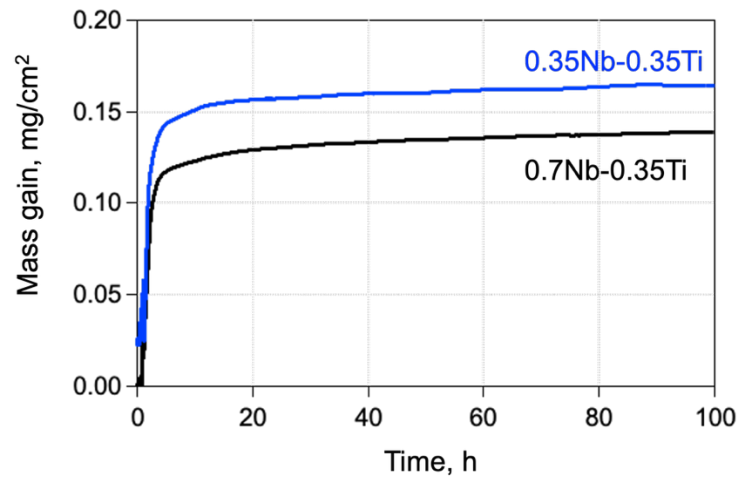


Fig. 3 Oxidation kinetics of Fe-10Cr-1Al-(0.35, 0.7)Nb-0.35Ti alloys at 850°C in air for 100 h

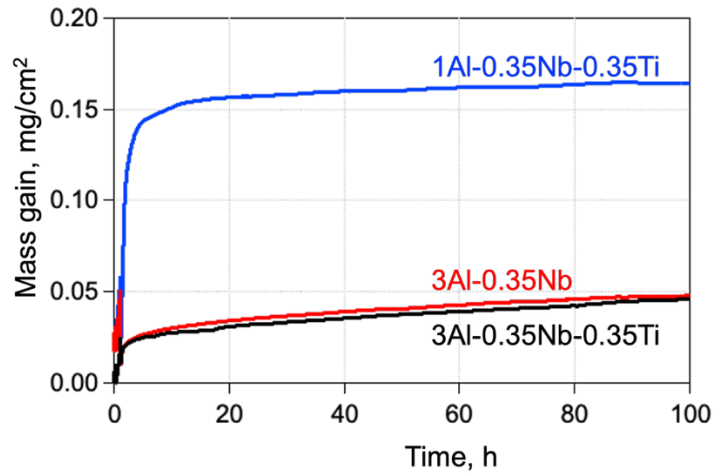


Fig. 4 Oxidation kinetics of Fe-10Cr-(1, 3)Al-0.35Nb-0.35Ti alloys at 850°C in air for 100 h

4.3.2 Surface morphologies of oxide scale

Figures 5 and 6 represent the surface morphologies of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-(0, 0.35)Ti alloys oxidized for 100 h at 850°C. The surface of Ti free alloy was homogeneous, however that of 0.35Ti alloy was uneven, and many nodules were randomly formed. Fig. 7 shows the surface morphology of Fe-10Cr-1Al-0.7Nb-0.35Ti alloy oxidized for 100 h at 850°C. Compared with the alloy with lower Nb content, nodule formation was suppressed. Fig. 8 shows the surface morphology of Fe-10Cr-3Al-0.35Nb-0.35Ti alloy oxidized for 100 h at 850°C. The surface was smooth and the surface morphology was similar to that formed on Ti free alloy.

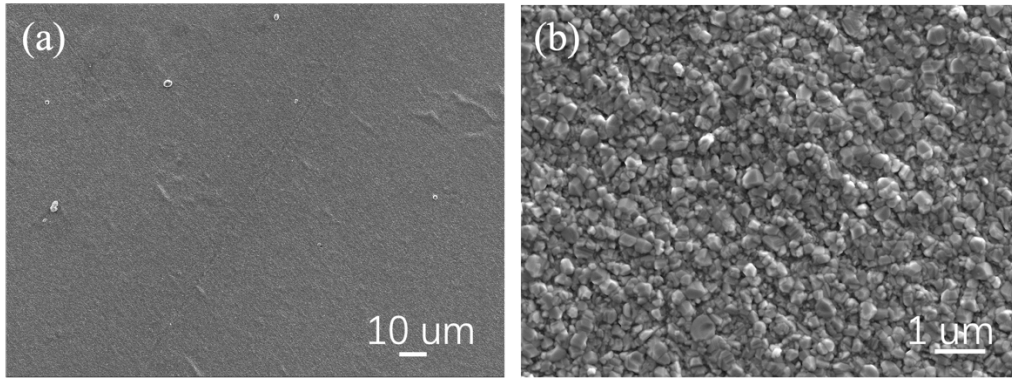


Fig. 5 Surface morphology of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-0Ti alloys oxidized at 850°C for 100 h. (b) is enlarged image of (a)

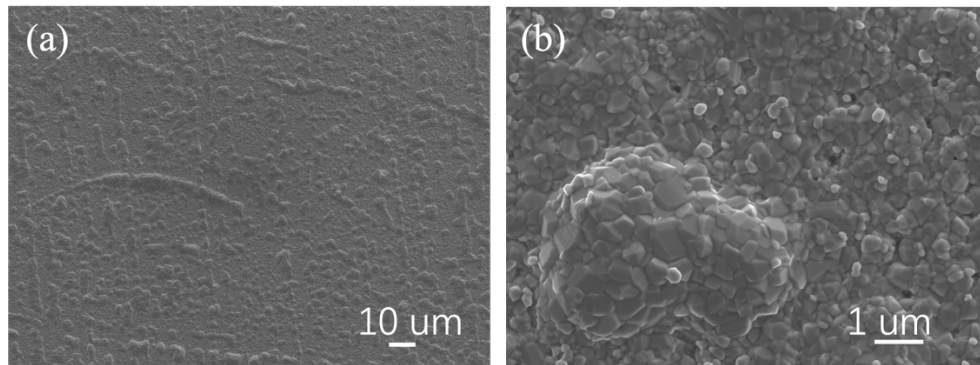


Fig. 6 Surface morphology of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-0.35Ti alloys oxidized at 850°C for 100 h. (b) is enlarged image of (a)

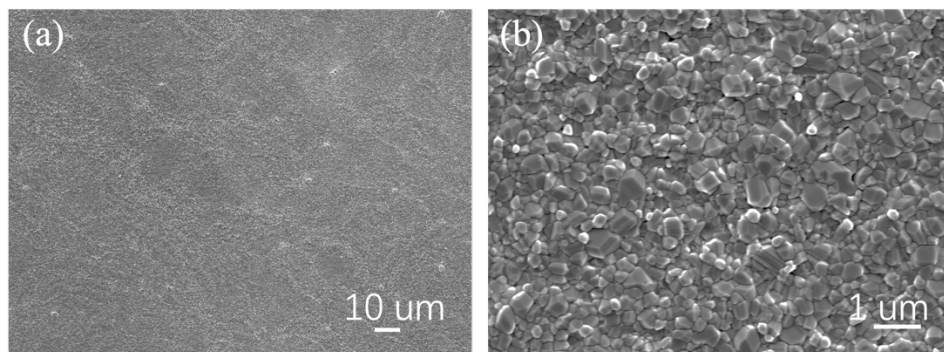


Fig. 7 Surface morphology of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloys oxidized at 850°C for 100 h. (b) is enlarged image of (a)

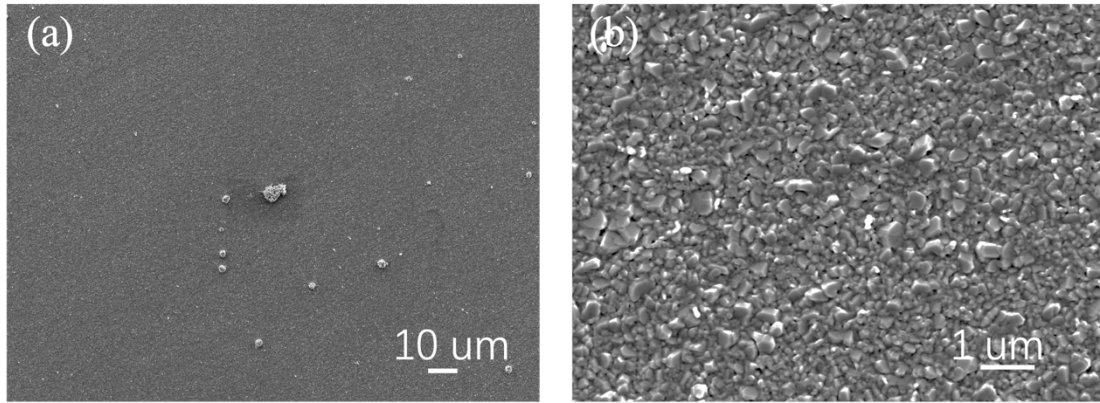


Fig. 8 Surface morphology of the oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloys oxidized at 850°C for 100 h. (b) is enlarged image of (a)

The cross-sectional microstructures of Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys oxidized at 850°C in air for 4 h are shown in Fig. 9. The oxide scale formed on both alloys consisted of a duplex structure. The oxide scale formed on Ti free alloy was very thin, ~150nm, but both the outer and inner layers formed on 0.35Ti alloy were thick. The oxide nodule formed on 0.35Ti alloy also consisted of a duplex structure, and the outer and inner layers of the nodule were much thicker than those of the oxide scale formed in homogeneous area. Many voids were confirmed in the inner part of the nodule formed on 0.35Ti alloy.

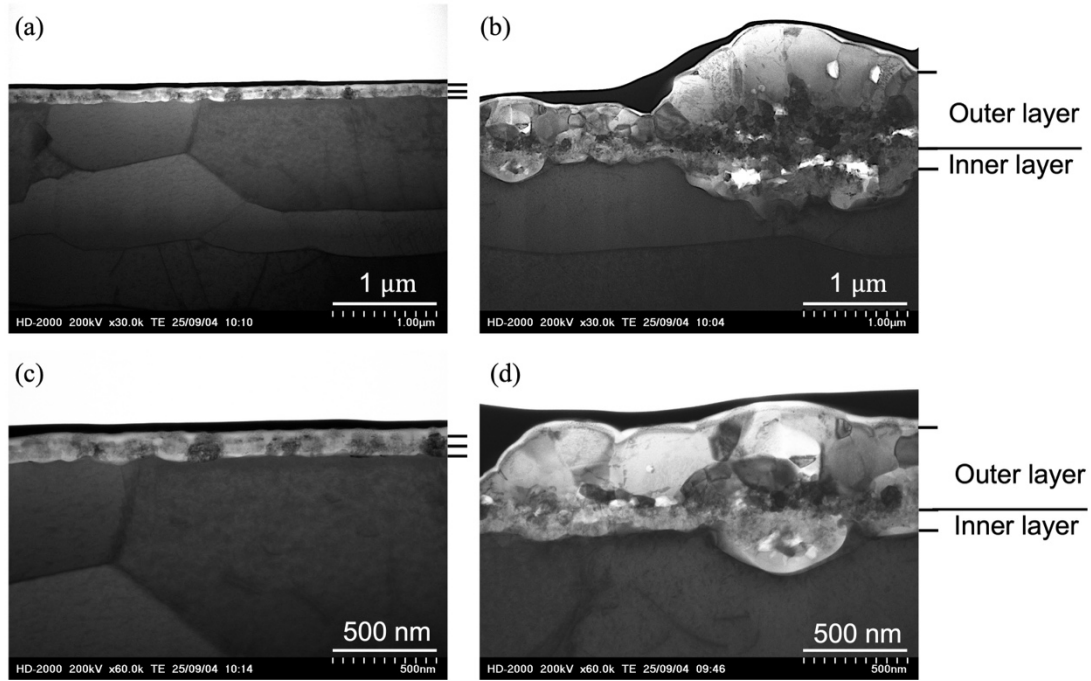


Fig. 9 Cross-sections of the oxide scale formed on (a)Fe-10Cr-1Al-0.35Nb and (b)Fe-10Cr-1Al-0.35Nb-0.35Ti alloys oxidized at 850°C for 4 h. (c) and (d) are the corresponding enlarged figures of (a) and (b)

The cross-sectional microstructures of the oxide scale formed on Fe-10Cr-(1, 3) Al-(0.35, 0.7) Nb-(0, 0.35) Ti alloys oxidized at 850°C in air for 100 h are shown in Fig. 10. The oxide scale formed on Ti free alloy was still thinner than those formed on alloys with Ti. The thickness of the oxide scale in homogeneous area on 1Al-0.35Ti alloy was similar to that formed after 4 h, suggesting that the growth rate of the oxide scale was low after the establishment of an Al₂O₃ scale. However, the nodule eventually grew larger and thicker.

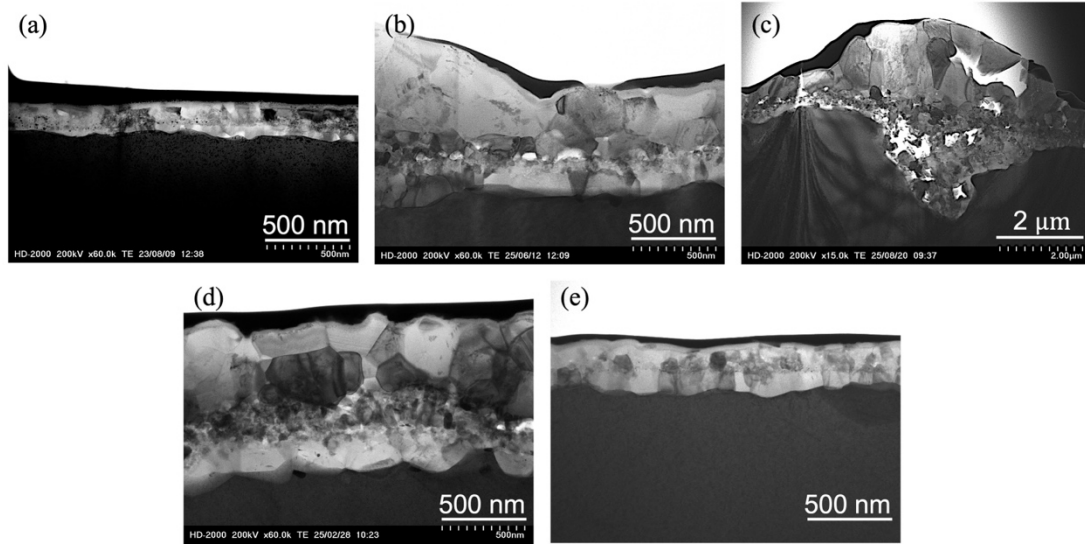


Fig. 10 Cross-sections of the oxide scale formed on (a)Fe-10Cr-1Al-0.35Nb , (b)Fe-10Cr-1Al-0.35Nb-0.35Ti thinner part, (c)Fe-10Cr-1Al-0.35Nb-0.35Ti thicker part, (d)Fe-10Cr-1Al-0.7Nb-0.35Ti and (e)Fe-10Cr-3Al-0.35Nb-0.35Ti alloys oxidized at 850°C for 100 h

The oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloy was homogeneous, but it was thick and the thickness of the oxide scale was similar to that formed in the homogeneous area of Fe-10Cr-1Al-0.35Nb-0.35Ti alloy. It was also confirmed that the thickness of inner layer tended to increase with increasing Nb content. The oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloy was thin, but it was thicker than the oxide scale formed on Ti free Fe-10Cr-1Al-0.35Nb alloy, which may be due to higher Al as discussed in Chapter 3.

Figure 11 represents the thickness of oxide scales formed on Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys oxidized for 4 and 100 h at 850°C. The thickness of the Al_2O_3 formed

on Ti-free alloys was about half of that formed on 0.35Ti alloy, which confirmed that the growth rate of Al_2O_3 scale increased with Ti addition.

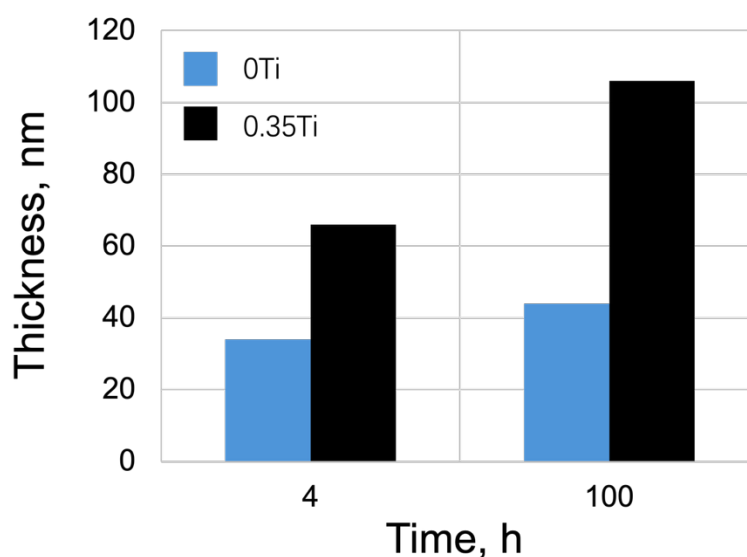


Fig. 11 The thickness of inner Al_2O_3 layer formed on Fe-10Cr-1Al-0.35Nb-(0, 0.35)Ti alloys oxidized at 850°C for 4 and 100 h

Figures 12-14 show the element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys oxidized for 100 h at 850°C. The outer layer of oxide scale formed on Ti free alloy was Fe and Cr-rich and the inner layer was a pure Al_2O_3 layer. No Nb was detected in the oxide scale. The oxide scale of the homogeneous area formed on 0.35Ti alloy exhibited a similar structure to that of the oxide scale formed on Ti free alloy, but the outer Fe and Cr-rich layer contained Ti. Nb and Ti oxides were also detected at the interface between the outer and inner layers. The inner part of the oxide nodule formed on 0.35Ti alloy contained a high amount of Ti oxide within the inner Al_2O_3 layer. The outer part of the nodule was Fe and Cr-rich oxide mixed with Ti oxide.

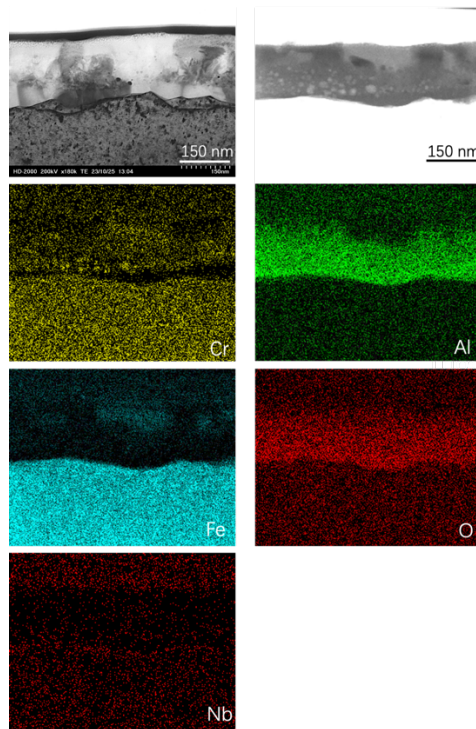


Fig. 12 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-0Ti alloy oxidized at 850°C for 100 h

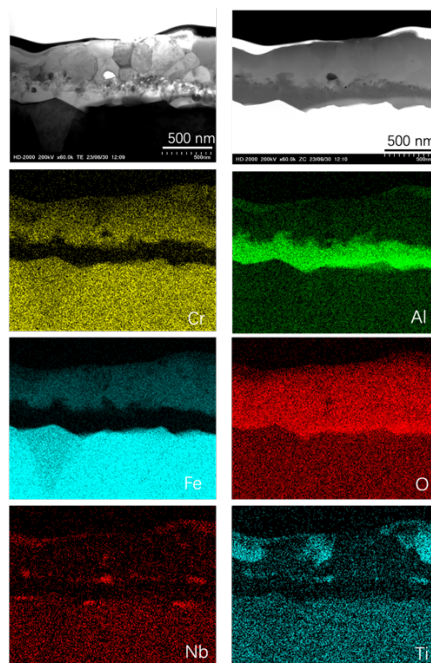


Fig. 13 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-0.35Ti alloy oxidized at 850°C for 100 h (thinner part)

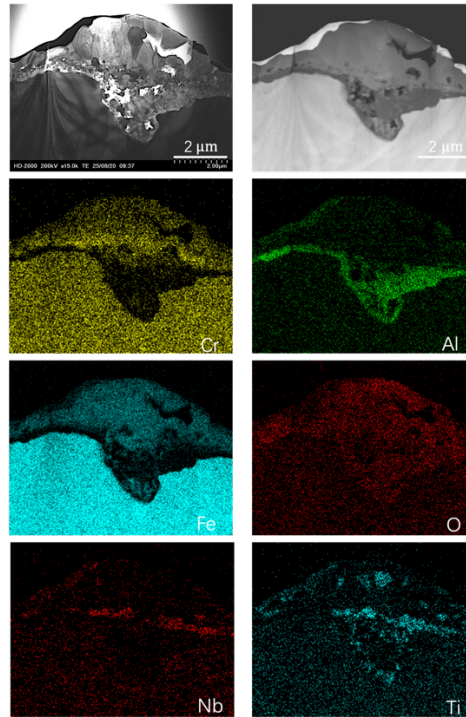


Fig. 14 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-0.35Ti alloy oxidized at 850°C for 100 h (thicker part)

Figure 15 shows the element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloys oxidized at 850°C for 100 h. The outer oxide layer was a Fe- and Cr-rich layer, and the inner layer was pure Al_2O_3 layer. Compared with the element maps of 0.35Nb-0.35Ti alloy, the distribution of Ti and Nb were similar, and no apparent difference was confirmed. Fig. 16 shows the element maps of the oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloys oxidized for 100h at 850°C. The outer layer was Al_2O_3 , and Fe and Cr were also detected. The inner layer was pure Al_2O_3 . The Laves phase formed in the subsurface region contained Ti. No Ti or Nb oxides were detected in the oxide scale.

Figure 17 shows the element maps of the inner part of the Al_2O_3 scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloys after for 400 h of oxidation at 850°C. The distribution of Ti and Nb in the inner Al_2O_3 layer was detected.

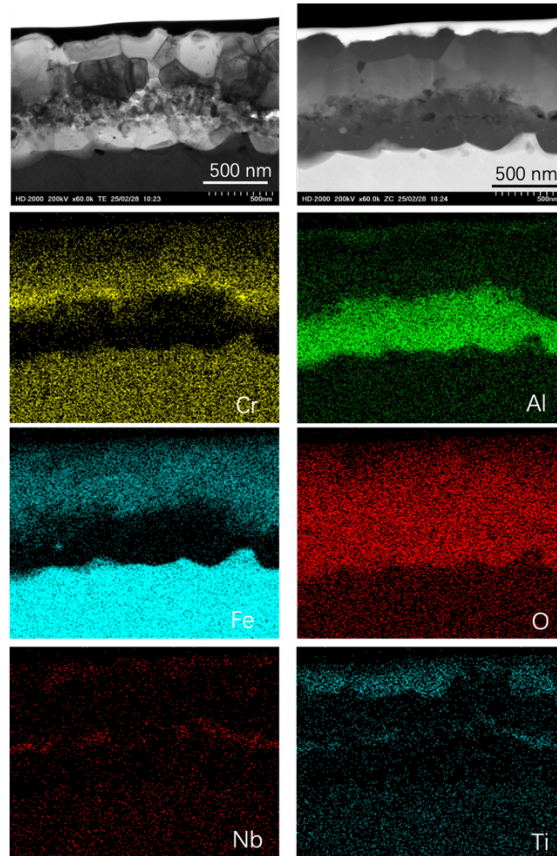


Fig. 15 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloys oxidized at 850°C for 100 h

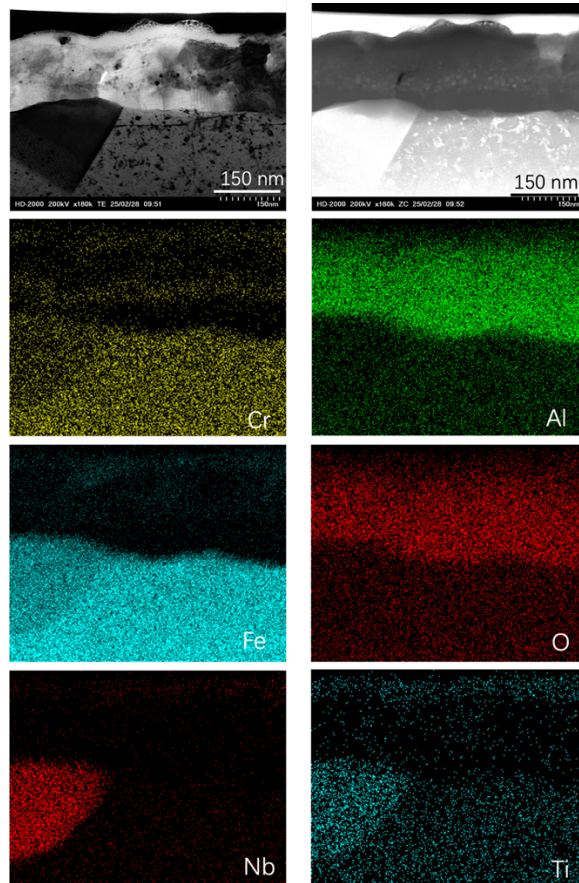


Fig. 16 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloy oxidized at 850°C for 100 h

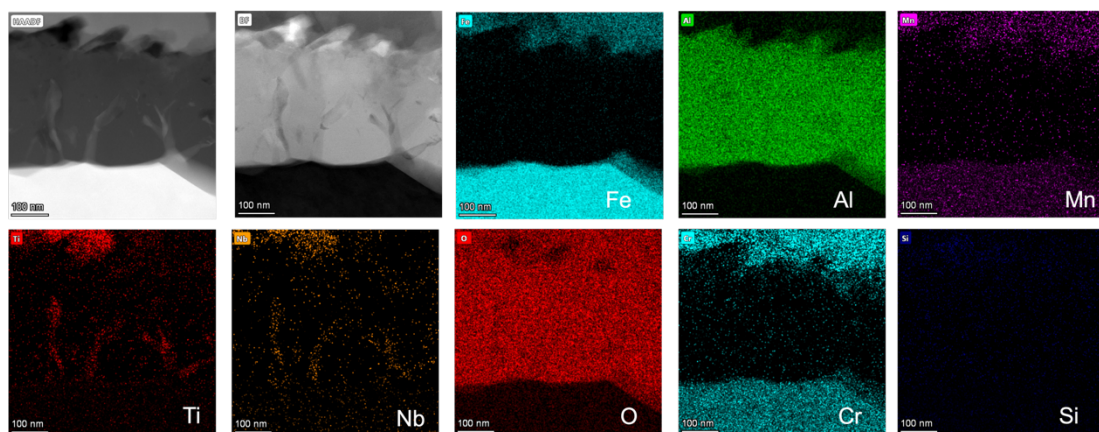


Fig. 17 Element maps of inner oxide layer grain boundary of Fe-10Cr-1Al-0.7Nb-0.35Ti alloys oxidized at 850°C for 400 h by Titan

4.3.3 Initial oxidation behavior

In order to confirm the initial oxidation behavior, the oxidation of the alloys during heating was evaluated. Fig. 18 shows the mass gain of Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys as a function of temperature in air during heating. The oxidation mass gain of 0 and 0.35Ti alloys were almost the same until heating to 700°C. However, the mass gain of 0.35Ti alloy at 750°C became larger than that of Ti free alloy. When the samples were heated to 850°C, the difference of the mass gains of 0 and 0.35Ti alloys became larger suggesting that the oxidation rate of the 0.35Ti alloy increased during the transient oxidation period.

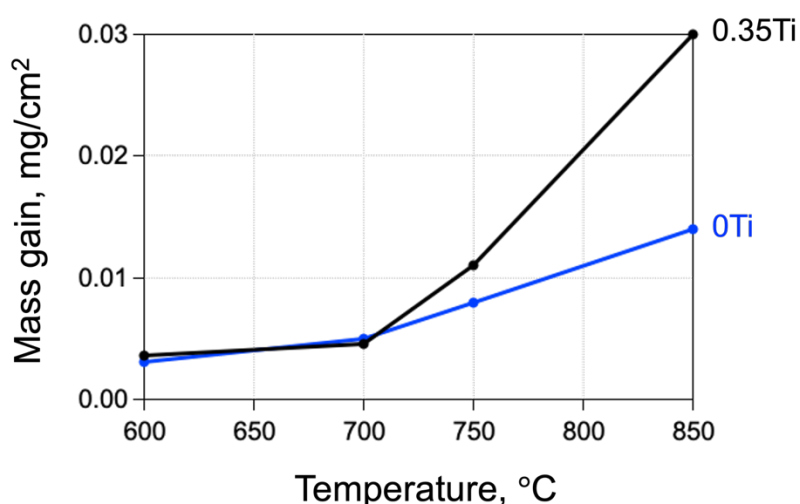


Fig. 18 Mass gain of Fe-10Cr-1Al-0.35Nb-(0, 0.35)Ti alloys as a function of temperature in air during heating

The cross-sectional microstructures of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys during heating to 600°C, 700°C, 750°C, and 850°C are shown in Fig. 19. At 600°C, the scale structure of 0 and 0.35Ti alloys was almost the

same, and consisted of an outer Fe- and Cr-rich oxide scale and an inner amorphous Al_2O_3 larger [5-7]. When the temperature increased to 700°C , both alloys formed internal Al_2O_3 precipitates. The internal Al_2O_3 zone was not observed in the Ti free specimen after heating to 750°C , and a continuous protective Al_2O_3 scale had developed. The disappearance of the internal oxidation zone in the specimen heated to 750°C might be due to experimental variations in the specimens, suggesting that the Ti free alloy has a high ability to form a continuous Al_2O_3 scale from the initial oxidation stage. In contrast, internal Al_2O_3 zone became thicker in 0.35Ti alloy after heating to 750°C . With increasing temperature, a continuous Al_2O_3 scale remained on Ti free alloy, but the internal oxidation zone became thicker in most regions, except for some parts where a continuous Al_2O_3 layer had developed on 0.35Ti alloy.

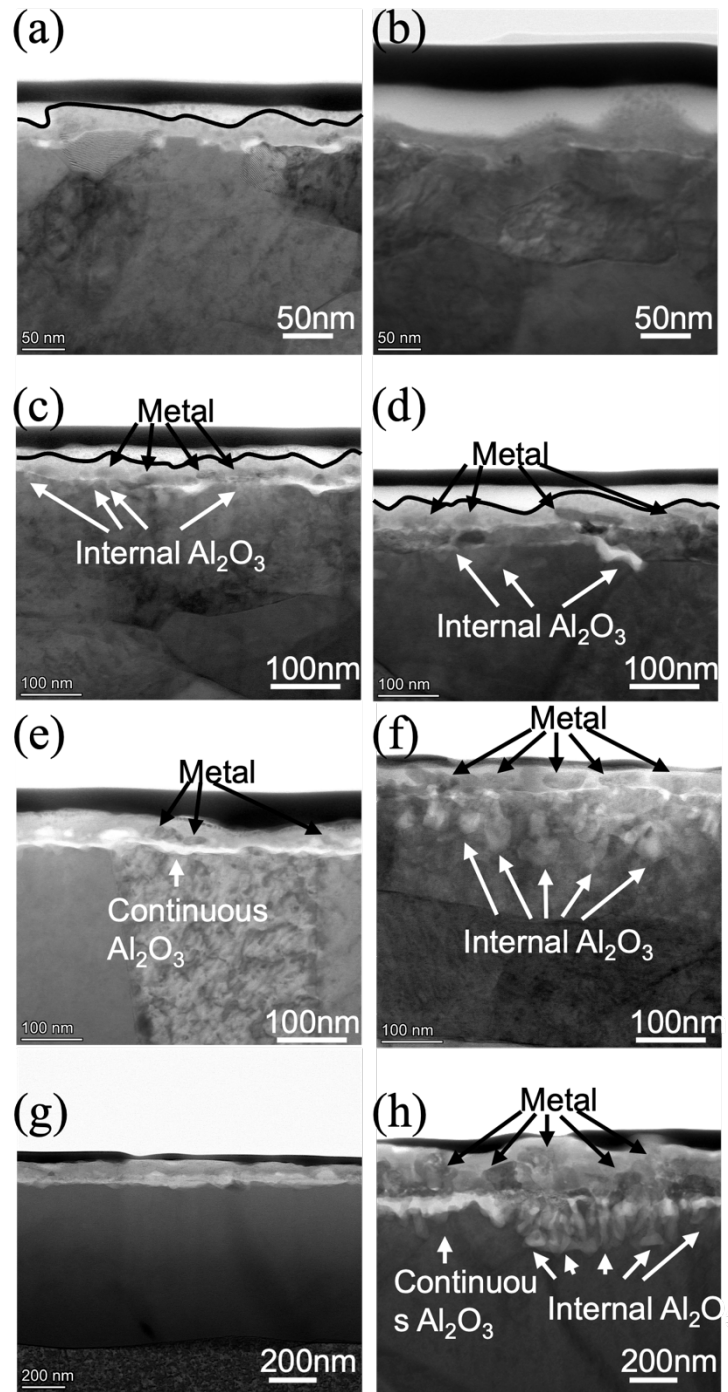


Fig. 19 Cross-sections of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-xTi alloys containing (a)(c)(e)(g)0 and (b)(d)(f)(h)0.35 wt% Ti oxidized during heating. (a)(b)600°C, (c)(d)700°C, (e)(f)750°C and (g)(h)850°C

Figure 20 shows the element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-xTi alloys with and without 0.35Ti after being heated to 700°C. Nb was detected below the Cr and Fe rich oxide layer on Ti free alloy, but it was widely distributed around the internal Al₂O₃ precipitates in the alloy with 0.35Ti. A similar Nb distribution was also confirmed after heating to 750°C as shown in Fig. 21. An Nb-rich layer was observed below the Cr₂O₃ layer on Ti free alloy, but it was observed together with the internal Al₂O₃, suggesting that Ti promotes the initial Al₂O₃ precipitation, which might be caused by the consumption of Nb through its incorporation into the Ti oxide. The cross-sectional microstructure and the element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloy after being heated to 850°C are shown in Figs. 22 and 23, respectively. Both Nb and Ti were detected below the Cr-rich oxide layer. Figs. 24 and 25 show the cross-sectional microstructure and element maps of oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloy heated to 850°C. The outer layer was Al₂O₃ rich in Cr. A continuous Ti-rich metal layer was observed below the Al₂O₃ layer.

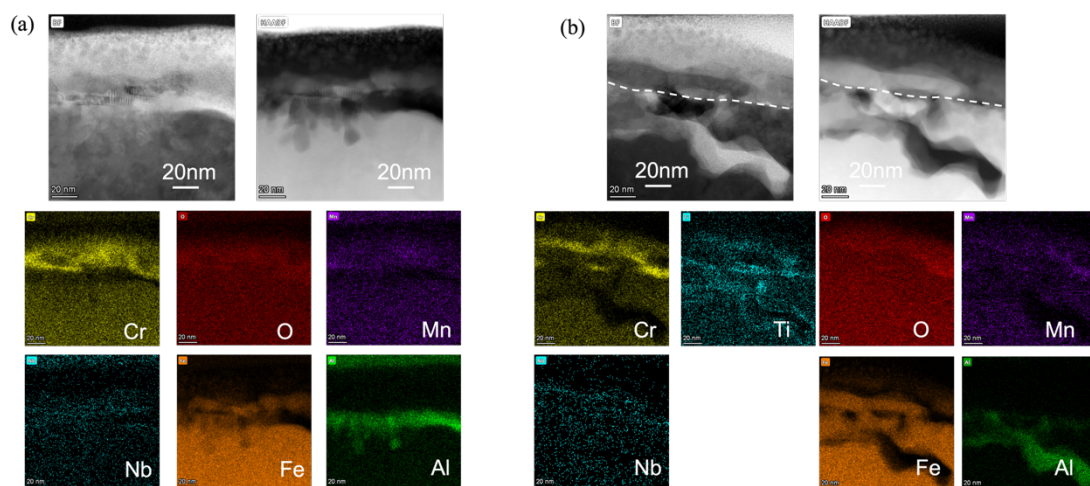


Fig. 20 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-xTi alloys containing (a) 0 and (b) 0.35 wt% Ti oxidized to 700°C

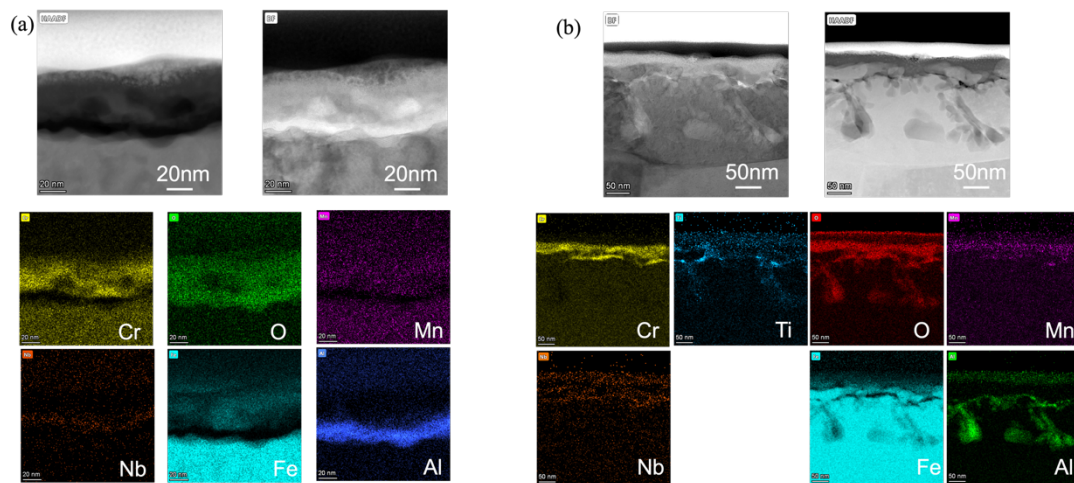


Fig. 21 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.35Nb-xTi alloys containing (a) 0 and (b) 0.35 wt% Ti oxidized to 750°C

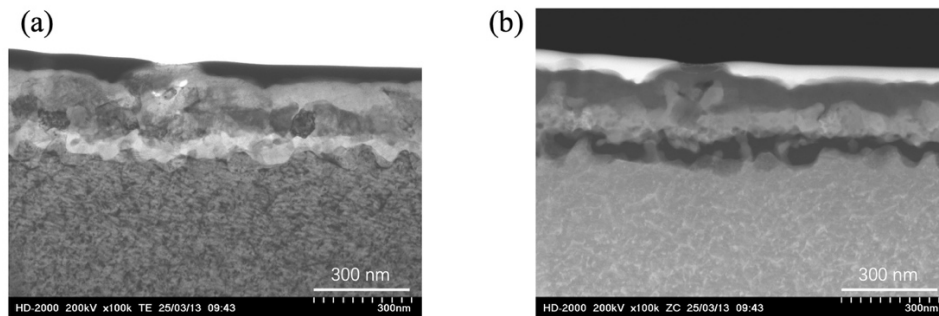


Fig. 22 Cross-sections of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloy oxidized to 850°C: (a) TE mode and (b) ZC mode

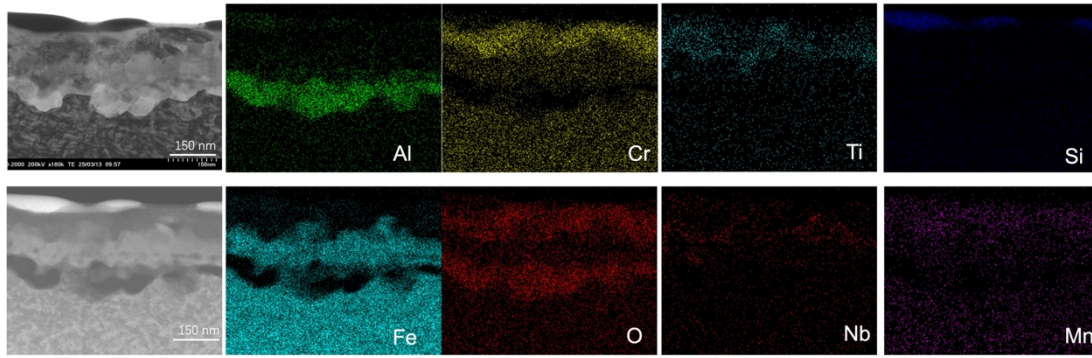


Fig. 23 Element maps of the oxide scale formed on Fe-10Cr-1Al-0.7Nb-0.35Ti alloy oxidized to 850°C

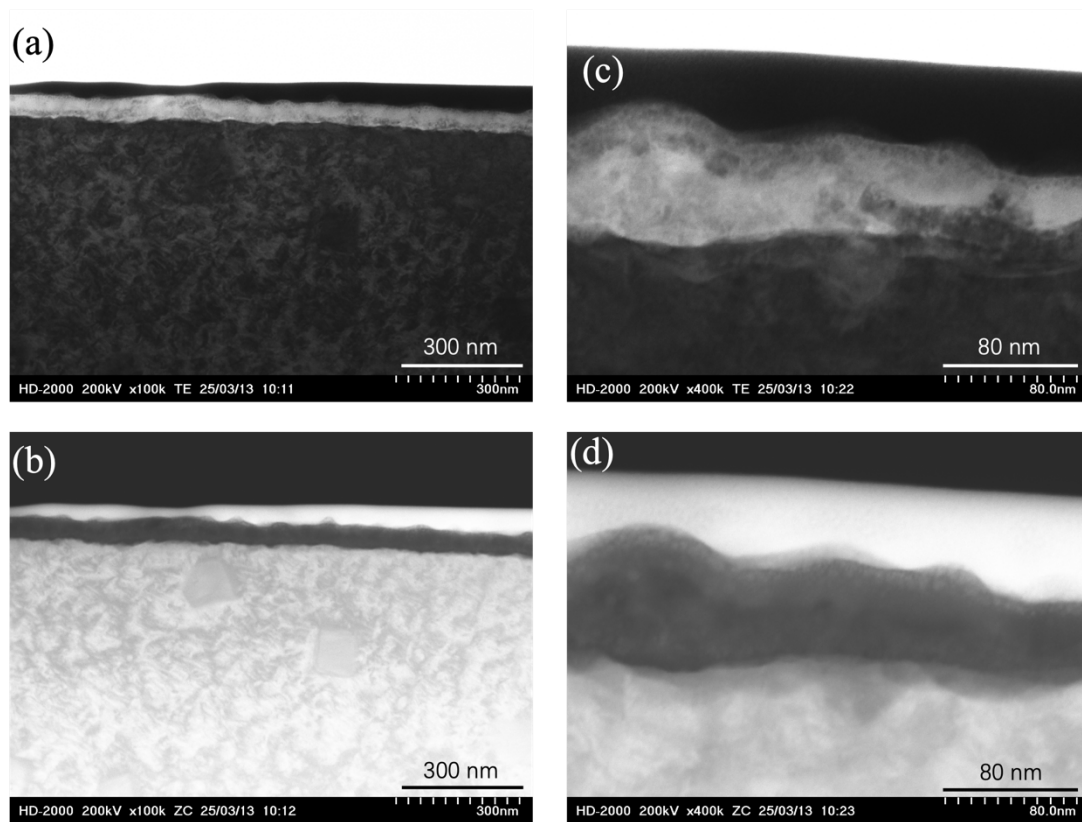


Fig. 24 Cross-sections of the oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti (a) TE mode and (b) ZC mode, (c) and (d) are with higher magnification alloys oxidized to 850°C

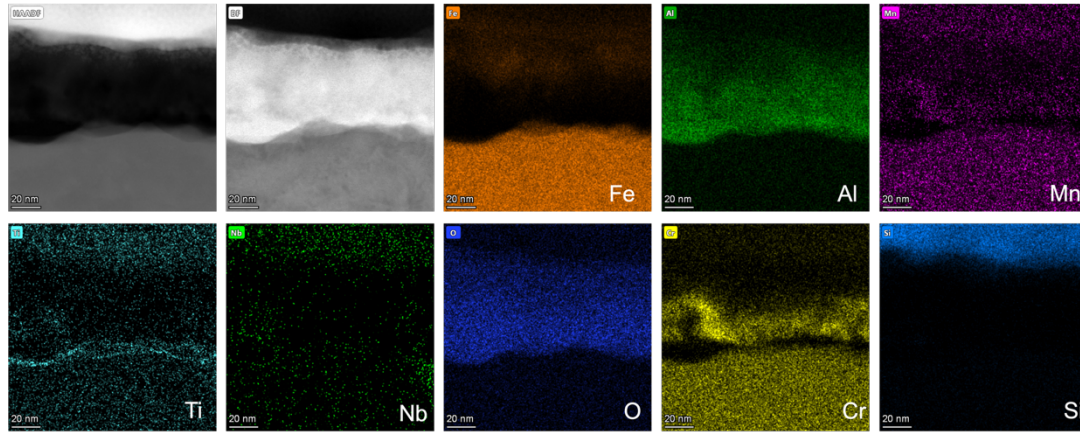


Fig. 25 Element maps of the oxide scale formed on Fe-10Cr-3Al-0.35Nb-0.35Ti alloy oxidized to 850°C

4.4 Discussion

4.4.1 Initial stage of oxidation

Fe-10Cr-1Al-0.35Nb-(0, 0.35) Ti alloys formed a protective Al_2O_3 scale at 850°C in air for 100 h, but the oxidation mass gain was larger for 0.35Ti alloy. This larger oxidation mass gain was mainly due to the higher mass gain in the initial oxidation stage. Hayashi et al. reported that Nb promotes the formation of a continuous Cr_2O_3 scale in the initial transient oxidation stage, and the rapid establishment of the Cr_2O_3 scale favors an exclusive Al_2O_3 scale formation [5]. The CrNbO_4 layer was proposed to form and to promote the Cr_2O_3 scale formation. In this study, a continuous Nb oxide layer was observed below the continuous Cr-rich oxide layer in the element maps of Ti free alloy after heating to 750°C, which suggests the formation of CrNbO_4 . However, such an Nb oxide layer was not observed on 0.35Ti alloy. Nb was always detected with Ti as an oxide. Apparently, Nb was consumed by the formation of Ti oxide, which might suppress the beneficial effect of Nb for promoting the initial Cr_2O_3 formation.

Figure 26 shows the model for Ti free and 0.35Ti alloys. At 600°C, both alloys formed Cr- and Fe-rich oxide scale, below this Cr-rich oxide, a CrNbO₄ layer may form. An amorphous Al₂O₃ scale developed below the CrNbO₄ layer and protected the substrate to some extent. When the temperature increased to 600-700°C, internal Al₂O₃ precipitates formed beneath the amorphous Al₂O₃ layer in both alloys. But the area of internal Al₂O₃ zone in the Ti free alloy was considered to be much smaller than that in the 0.35Ti alloy. After heating to 750°C, Ti free alloy developed a continuous Al₂O₃ scale, but the internal Al₂O₃ zone accompanied by Ti oxide grew thicker in the 0.35Ti alloy. Nb was also oxidized with Ti and consumed, which decreased the protectiveness of the CrNbO₄ layer due to insufficient Nb supply from the substrate. Therefore, 0.35Ti alloy formed a thick internal Al₂O₃ zone, and the formation of a continuous Al₂O₃ scale formation was delayed, which caused the initial higher mass gain. With increasing temperature, Al₂O₃ precipitates grew larger, eventually connecting each other to form a continuous layer in 0.35Ti alloy. Because inward oxygen diffusion in the 0.35Ti alloy was expected to be high due to internal Ti oxide [6-10], the transition to the continuous Al₂O₃ scale was delayed.

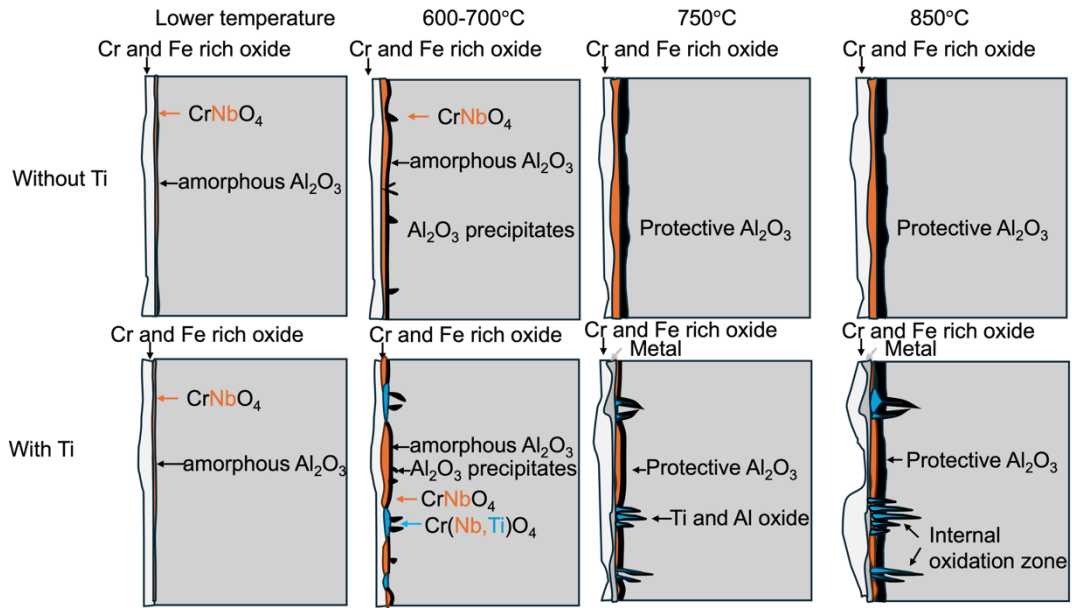


Fig. 26 Growth model of alloys without and with Ti addition during heating process

The 1Al-0.7Nb-0.35Ti alloy formed a continuous protective homogeneous inner Al_2O_3 layer. The initial oxidation mass gain was lower than that of the 0.35Ti-0.35Nb alloy, which indicates that the higher Nb addition can decrease the detrimental effect of Ti on low Al alloys. This is because Nb could be still retained, which promotes the formation of an Al_2O_3 scale.

The 3Al-0.35Nb-0.35Ti alloy formed a thinner protective homogenous Al_2O_3 layer, and the initial oxidation mass gain significantly decreased. This decreased oxidation mass gain of 3Al alloy suggests that sufficient Al addition for the formation of a continuous Al_2O_3 scale can mitigate the detrimental effect of Ti on the alloy during the initial stage oxidation stage.

4.4.2 Long-term oxidation

In the steady-state, long-term oxidation stage, the growth rate of the Al_2O_3 scales formed on Ti free and 0.35Ti alloys was low, however, the growth rate of Al_2O_3 scale formed on 0.35Ti alloy was slightly higher than that on Ti free alloy (Fig. 3(c)). The STEM-EDS analysis indicated Ti oxide formation in the inner Al_2O_3 layer (Fig. 17). Ti oxide was formed perpendicular to the surface. Nb was always detected in the Ti oxide formed within the inner Al_2O_3 layer (Fig. 17). Such Ti oxide formation in the inner Al_2O_3 layer has been frequently reported for Fe-Cr-Al alloys with 0.5~1 wt% Ti [11-12]. For example, the thickness of Al_2O_3 scale formed on Fe-22Cr-5Al-3Mo alloy increased with 0.5Ti addition at 1000°C in air. The alloy was also reported to form nodules [11]. Up to 1 wt% Ti addition in the Fe-18Cr-3Al alloy also increased the oxidation mass gain in air due to the enhanced growth rate of Al_2O_3 scale [12]. The Ti oxide detected in the inner Al_2O_3 layer in the present study could be pathways for inward diffusion of oxygen, due to the higher oxygen diffusion in TiO_2 , which contains a large number of oxygen vacancies [6-10]. The Ti oxide in the Al_2O_3 scale could be formed from Ti-rich oxide precipitates which formed during a heating period as shown in Figs. 21 and 22. The inner Al_2O_3 layer grew inwardly and became thicker with time. The internal precipitates of Ti-rich oxide could be incorporated in the inner Al_2O_3 layer due to inward growth of the inner Al_2O_3 layer.

4.5 Conclusion

The effect of Ti addition on the oxidation behavior of Nb modified Al_2O_3 -forming ferritic stainless steels was investigated at 850°C in air. The results can be summarized as follows.

- (1) Ti addition increased the oxidation mass gain of Fe-10Cr-1Al-0.35Nb alloys. The higher mass gain of the alloys with Ti addition was mainly due to the higher mass gain of 0.35Ti alloy in the initial oxidation stage. Higher Nb addition decreased the initial oxidation mass gain of 1Al alloys. Sufficient Al addition (3Al) resulted in a rapid formation of a continuous Al_2O_3 scale, suggesting that the detrimental effect of Ti during the initial stage of oxidation can be suppressed.
- (2) Nb was always found with Ti in the oxide. Because Nb was consumed by the formation of TiO_2 and resulted in the formation of $\text{Cr}(\text{Nb}, \text{Ti})\text{O}_4$, the ability to sustain the amorphous Al_2O_3 layer decreased, which caused severe internal oxidation in 1Al alloys.
- (3) After longer oxidation time, the mass gain and the thickness of both the outer and inner layers increased with increasing Ti content for 1Al alloys, but no effect of Ti on the oxidation mass gain and scale structure was confirmed for 3Al alloys.
- (4) Ti oxide was found in the inner Al_2O_3 layer of 1Al-0.7Nb alloy, which could be one of the reasons for the increased growth rate of the inner Al_2O_3 layer after longer oxidation time.

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Chapter 5.

General summary

This study investigates the effect of Cr content, Nb content and Ti addition on the high temperature oxidation behavior of Nb-modified ferritic Fe-Cr-Al steels, with particular emphasis on how these elements influence the growth of the oxide scale. To clarify these effects and the underlying mechanisms, detailed microstructural analyses were conducted, based on STEM observations of the oxide scales formed from the initial stages of oxidation through long-term exposure. The dissertation consists of five chapters and the main findings obtained in this study are summarized below.

In Chapter 1, an overview of stainless steels is briefly presented, including their classification and applications. This chapter also introduces heat-resistant stainless steels, including Cr_2O_3 -forming and Al_2O_3 -forming stainless steels, and reviews the current understanding of the roles of alloying elements in improving high-temperature oxidation resistance of steels. The chapter concludes with the motivation and objective of the present study.

In Chapter 2, the effect of Cr content on the oxidation behavior of Al_2O_3 scale on Fe-(10, 15, 20, 25) Cr-1Al-0.35Nb alloys was investigated. The oxidation mass gain was found to increase with decreasing Cr content. The oxide scale exhibited a duplex structure. The thickness of the outer layer increased as the Cr content decreased, whereas that of the inner Al_2O_3 layer increased with increasing Cr content. The higher oxidation mass gain at the lower Cr contents was attributed to the larger mass gain

during the initial oxidation stage. Laves phase precipitates were confirmed at the scale/alloy interface, and their interfacial volume fraction increased with decreasing Cr content. The growth rate of the inner Al_2O_3 layer was low on the Laves phase, which reduced the oxidation kinetics of the low-Cr alloys during prolonged oxidation.

In Chapter 3, the effect of Nb on the growth behavior of Al_2O_3 scale on Fe-10Cr-(1, 3, 5) Al-(0, 0.35, 0.7) Nb alloys was investigated. The oxidation mass gain was confirmed to increase with increasing Nb content. This Nb effect was apparent in alloys with lower Al content. No Nb effect was confirmed in 5Al alloys. STEM observations demonstrated that the higher oxidation mass gain in higher-Nb alloys was attributed to the higher growth rate of the inner Al_2O_3 layer. Nb segregation at grain boundaries was proposed to be responsible for the enhanced growth of the inner Al_2O_3 layer.

In Chapter 4, the effect of Ti on the growth of the oxide scale formed by Fe-10Cr-(1, 3) Al-(0.35, 0.7) Nb-(0, 0.35) Ti alloys was investigated. Ti addition consistently increased the oxidation mass gain in the 1Al alloys, irrespective of Nb content. STEM-EDS analysis showed that Ti appeared together with Nb as oxides and that $\text{Cr}(\text{Nb}, \text{Ti})\text{O}_4$ formed beneath the Cr-rich transient oxide scale during the initial oxidation stage. Because Nb was consumed in the formation of Ti-containing oxides, the beneficial effect of Nb—namely, promoting Al_2O_3 scale through the formation of a CrNbO_4 layer—was suppressed by Ti addition. This Nb consumption by Ti diminished the ability of low Al alloys to form a protective Al_2O_3 scale, since sufficient Nb is necessary to develop a continuous Al_2O_3 scale. In addition, Ti increased the growth rate of the inner

Al₂O₃ layer during long-term oxidation through the formation of Ti-rich oxides within the inner Al₂O₃ layer.

In Chapter 5, the general conclusion of this study is presented. The results show that increasing Nb and Ti additions in ferritic Fe-Cr-low Al alloys enhances the growth rate of Al₂O₃ scale through segregation of these elements to the grain boundaries. Therefore, optimizing the concentration of Nb and Ti is expected to improve the high-temperature oxidation resistance of ferritic Al₂O₃-forming stainless steels.

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