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Citation	Oxidation of Metals, 78(3-4), 167-178 https://doi.org/10.1007/s11085-012-9298-2
Issue Date	2012-10
Doc URL	http://hdl.handle.net/2115/50353
Rights	The final publication is available at www.springerlink.com
Type	article (author version)
File Information	OoM78-3-4_167-178.pdf



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Formation of Exclusive Al₂O₃ scale on Nb and Nb-Rich Alloys by Two-Step Oxygen-Aluminum Diffusion Process

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Keywords: Nb based alloy, oxidation resistance, exclusive Al₂O₃ scale formation, Oxygen-Aluminum diffusion treatment,

Abstract

External Al₂O₃ scale formation behavior by an aluminum diffusion process on Nb and Nb-X (X=Mo, Re, and Ta) alloys with different oxygen solubilities was investigated. The oxygen content in Nb and Nb-X alloys was controlled by oxygen diffusion treatment at 1100 °C using Nb/NbO mixture. Nb-aluminide, NbAl₃ and Nb₂Al, layers were developed on the low-oxygen Nb substrate by an aluminum diffusion treatment using Al/Al₂O₃/NH₄Cl mixture at 1100 °C; whereas an adhesive Al₂O₃ scale developed on the Nb substrate with higher oxygen content. The alloy oxygen content decreased by an addition of Ta, Mo and Re, in this order, and the decrease in alloy oxygen content resulted in the transition of Al₂O₃ formation from external scale to internal precipitates. This transition was not observed when low Al activity powder mixture, Ni50Al/Al₂O₃/NH₄Cl, was used for Al diffusion process, and only external Al₂O₃ scale was developed on all samples. In the present study, the effects of oxygen solubility limit, oxygen content, and the activity of Al in diffusion process on the formation of Al₂O₃ scale will be discussed.

Introduction

The temperature capability of Ni-based superalloys has been improved significantly over the last few decades [1], however, it is now approaching limits due to requirements of further increase in the operation temperature of heat exchanging plants to meet the recent strong demands of increasing efficiency in order to reduce CO₂ emissions, and reduce the use of fossil fuels.

Nb-based alloys are one of the candidate materials to replace Ni-based superalloys in high-temperature applications. Since the melting temperatures of

Nb-based alloys are much higher than Ni or Fe-based alloys, Nb-based alloys are expected to have excellent mechanical performance at very high temperatures, more than 1200 °C. However, one of the biggest issues of high temperature application of Nb-alloys is extremely poor oxidation resistance. Very rapid oxidation occurs due to the formation of non-protective and powder-like Nb oxide Nb_2O_5 when Nb alloys are oxidized at high temperatures. To increase the oxidation resistance by forming a protective oxide scale of Al_2O_3 , Cr_2O_3 or SiO_2 on Nb-based alloys, very large additions of alloying elements, such as Al, Cr or Si are required. For example, 75at.% Al would be required to form Al_2O_3 scale on a binary Nb-Al alloy. However, even such a high Al addition is still not sufficient to protect the substrate for longer time exposures [2, 3] and causes the alloy substrate to be very brittle. Previous studies have been conducted to improve the oxidation resistance with reduced Al content by multiple element additions [4-6], however sufficient improvement of oxidation resistance of Nb-based alloys has not yet been achieved.

There are several reasons for the very poor oxidation resistance of Nb-based alloys, such as relative stability of Nb oxide preventing the selective oxidation of Al, and the higher solubility product of Al_2O_3 in Nb compared to Ni or Fe based alloys due to the high oxygen solubility in Nb, about 2.5at.% at 1200°C [7, 8]. Of those reasons, the latter must be taken into account when forming the protective oxide scale rapidly and then maintaining for longer-term oxidation.

The present work initially started to investigate the thermodynamic stability of Al_2O_3 on Nb by studying the Nb-Al-O ternary system. To prepare Nb samples with different Al and O content for evaluating the equilibrium content of Al and O, oxygen and aluminum-diffusion treatments were used. It was found that Al_2O_3 scale was formed after Al diffusion treatment of an oxygen saturated Nb substrate. It appeared possible that the Al_2O_3 scale formed by this two-step treatment could be used for providing oxidation protection of Nb-based alloys. The aim of this study was to investigate the formation behavior of Al_2O_3 scale on Nb alloys with different oxygen content and will introduce the concept of formation of protective Al_2O_3 scale on Nb-based alloys by the two-step oxygen-aluminum diffusion process. The effect of oxygen content and aluminum activity used by the two-step process on the Al_2O_3 scale formation will also be discussed.

Experimental Procedure

Pure Nb (200 mass ppm O_2) and Nb-15, 30at.%X (X=Mo, Ta, Re) alloys were prepared by argon-arc melting the pure constituent metals (~99.99% pure). The

alloying elements were used to decrease the solubility limit of oxygen in Nb [9, 10]. The resulting alloy ingots, approximately 50 mm long and 13 mm diameter, were homogenized in vacuum at 1200°C for 48 h. Approximately 1.5 mm thick test samples were cut from the homogenized ingots and ground to a 1200-grit finish using SiC abrasion paper, followed by ultrasonic cleaning in acetone.

The prepared samples were embedded in Nb/NbO powder mixture and sealed in an evacuated quartz capsule, and for the oxygen-diffusion process were heated to 1100 °C, then held for 100 h in order to saturate the oxygen content in the alloys. The oxygen partial pressure, P_{O_2} , in the quartz capsule will be 2.0×10^{-22} atm in Nb/NbO equilibrium at 1100°C. In the aluminum-diffusion process, samples were embedded in either an Al/Al₂O₃/NH₄Cl high Al-activity mixture, or Ni-50Al/Al₂O₃/NH₄Cl low Al-activity mixture in an Al₂O₃ crucible and heat-treated at 1100°C under a dynamic vacuum condition for 64hr. This two-step oxygen-aluminum diffusion process is illustrated in Fig. 1.

After the diffusion process, the surface and the cross-section of samples were examined by a scanning electron microscope (SEM). Element distributions were measured by an electron probe micro-analyzer (EPMA). Since the accuracy of measuring oxygen content by EPMA is poor, thus oxygen content in EPMA profiles was only used for checking the oxygen distribution in the samples in the present study. In order to evaluate the oxygen content in the different alloy quantitatively, an oxygen-nitrogen analyzer (LECO TC-500) was used to measure oxygen content in the alloy substrate.

Results and Discussion

Table 1 shows the alloy oxygen content in the different alloys after an oxygen diffusion treatment analyzed by an oxygen-nitrogen analyzer. Those oxygen contents can be regarded as oxygen solubility in the alloys at 1100 °C. The oxygen content in pure-Nb, 2.62at.%, agreed with the oxygen solubility in Nb, ~2.3% at 1100 °C [7]. The oxygen content in the alloys decreased with an addition of various elements. Among the elements used in the present study, Re was found mostly effective to decrease the alloy oxygen contents. Addition of 15%Mo also decreased oxygen content, however further increase in Mo content resulted in increasing oxygen content. This increase in oxygen content with the addition of 30%Mo does not agree with the data from Bryant [9], and the reason was not clear.

Figure 2 shows cross-sections and EPMA profiles of pure-Nb after an aluminum diffusion treatment with and without a pre-oxygen diffusion treatment. A duplex aluminized layer with outer thick NbAl₃ and inner thin Nb₂Al layers was formed

on the pure-Nb without prior oxygen diffusion treatment. In the binary Nb-Al system shown in Fig. 3, three aluminide phases exist, NbAl₃, Nb₂Al, and Nb₃Al, however Nb₃Al was not clearly observed in the present study. The absence of Nb₃Al may be due to the different diffusivity of Al in different Nb-Al compounds [11, 12]. On the pure-Nb with prior oxygen diffusion treatment, no aluminide layer was formed, but a thin Al₂O₃ scale was found to develop over the entire surface of the sample. Aluminum profiles of both the samples with and without an oxygen treatment, Fig. 2(c) and (d), show no aluminum penetration into the Nb substrate. Oxygen content was a minimum in the outermost NbAl₃ layer, and increased stepwise across the inner Nb₂Al layer and Nb substrate, indicating that oxygen solubility decreases in the higher Al compounds. It must be noticed that the oxygen content of the Nb with an oxygen treatment, ~10at.%, in Fig. 2(c) was much higher than the solubility in pure-Nb, ~2.3at.% at 1100°C, and the absolute values of oxygen content in the alloy substrate obtained from the EPMA analysis were quite different to Table 1. As mentioned in experimental procedure, measuring oxygen content by EPMA is less accurate, therefore oxygen profiles cannot be used for the comparison between the samples, but only used to assess the distribution of oxygen in the alloy substrate.

Figures 4-6 show cross-sections and EPMA profiles of Nb-Ta (Fig. 4), -Mo (Fig. 5), and -Re (Fig. 6) alloys after the two-step diffusion treatment using the higher Al activity Al/Al₂O₃ mixture. Thin exclusive Al₂O₃ scale was developed on the Nb-15Ta, -30Ta, and -15Mo alloys (Figs. 4(a), (b) and 5(a)). Beneath the exclusive Al₂O₃ scale in the Nb substrate, neither Al penetration nor oxygen depletion were observed from EPMA profiles (Figs. 4(c), (d) and 5(c)). However, on the Nb-30Mo, -15Re, and -30Re alloys, no external Al₂O₃ scale formation was observed (Figs. 5(b) and 6(a)(b)). On the Nb-30Mo and -15Re alloy, internal Al₂O₃ precipitates were formed in the subsurface region, and an Al₂O₃ layer was developed at the bottom of the internal oxidation zone. The number density of internal Al₂O₃ precipitates in Nb-15Re tended to be lower than in Nb-30Mo. The matrix of the internal Al₂O₃ region was confirmed to be NbAl₃. Re-Al precipitate formation was also observed in this internal Al₂O₃ region in the Nb-15Re alloy, however the size of the precipitates was too small to accurately identify by EPMA. On the Nb-30Re alloy although no oxide formation was observed, a duplex layer with different size and distribution of precipitates was developed. Because of the high density of small particles in both layers, it was difficult to identify the phases. Presumably, the outer and inner layer formed on Nb-30Re alloy consisted of Re-Al particles in an NbAl₃ matrix, and Re-Al rich particles in an (Nb, Re)₂Al matrix, respectively.

As mentioned in the introduction, the addition of Mo and Re has been reported to decrease the oxygen solubility in Nb, and supporting results were obtained in this study as shown in Table 1 except a Nb-30Mo alloy which showed high oxygen content. Figure 7 is the re-arranged plot of Table 1. The oxygen solubility in Nb-Mo, Re obtained from the references at 1000°C [9] and pure-Nb at 1100°C [7] was also plotted for the comparison. Although some deviation from the references exists, the oxygen content/solubility obtained here agreed with the data from the references, and decreased with the addition of Mo and Re. Figure 7(a) indicates that exclusive Al₂O₃ scale was formed only when the alloy oxygen solubility/content was high. With decreasing alloy oxygen solubility/content, the formation behavior of Al₂O₃ changed from an external scale to internal precipitates + inner Al₂O₃ layer. Further decreasing oxygen content resulted in no Al₂O₃ formation. Without external Al₂O₃ scale formation, the Al content in the subsurface region increased to about 75at.%, i.e., NbAl₃ formation. However, when a lower Al activity diffusion treatment was used, thin exclusive Al₂O₃ scale was developed on all alloys as shown in Figs. 7(b) and 8.

In conventional high-temperature oxidation studies, it is well known that the transition from internal oxidation to external scale formation occurs when the alloying element that forms the protective oxide scale, such as Al, Cr, and Si, exceeds a critical concentration. In this study the inward diffusing species, Al, and the alloying element, O, are opposite to conventional oxidation systems, but the same internal to external transition was found to occur with increasing alloy oxygen content. Oxygen in solution in the Nb-alloy reacted with Al, which inwardly diffused into the substrate during the Al diffusion treatments, and formed Al₂O₃ as internal oxides in the Nb substrate, or as an external scale in this system. Moreover, an external Al₂O₃ scale was developed on all the alloys without any internal oxide formation when the low Al diffusion treatment was used. This is due to the critical oxygen content for external Al₂O₃ scale formation decreasing for the lower Al activity treatment, as expected from Wagner's model of the transition from the internal oxidation to external scale formation [13]. However, Wagner's model contains several assumptions that the solubility product of oxide, K_{sp} , is vanishingly small, ~ 0 , and N_O and N_B are extremely dilute at the front of internal oxidation zone. Therefore, Wagner's model is apparently not applicable to the present Nb-O-Al system, since Nb has higher oxygen solubility, i.e., higher solubility product of Al₂O₃. Figure 9 shows the model of the formation behavior of Al₂O₃, which is essentially similar to Wagner's transition model. With higher Al activity treatment and higher alloy oxygen content, since the diffusivity of oxygen in Nb is much higher than that of Al [11-15], much higher outward oxygen flux

than inward Al flux is expected. Under this condition, oxygen in the substrate can be enriched as oxides at the surface region, forming external Al_2O_3 scale. However with low alloy oxygen content the total outward oxygen flux decreases and sufficient enrichment of oxygen cannot occur, resulting in the formation of internal Al_2O_3 . In the case of the lower activity Al diffusion treatment, even though the alloy oxygen content is lower, the relative outward oxygen flux compared to the Al flux increases, causing the formation of an external Al_2O_3 scale. Another factors, which may affect the transition from internal to external scale formation, are the change in diffusivities of Al and O in the alloys by third element additions. However, further discussion was not possible due to the lack of diffusivities of Al and O in Nb-X alloys. Figure 10 shows the cross-sections of the binary “Nb-O” alloys with different oxygen content after Al diffusion process with different Al activities. Al_2O_3 scale was developed on the alloy with higher oxygen content (Fig. 10b), but aluminide layers formed on the alloy with lower oxygen content (Fig. 10b) after a high Al activity diffusion treatment. Under a lower Al activity treatment, however, Al_2O_3 scale was developed on both low and high oxygen concentration alloys. This result indicates that the formation behavior of Al_2O_3 scale strongly affected by oxygen content and activity of Al on diffusion treatment.

Figure 11 shows the sample appearance of an Nb-5at.%Al alloy, which was treated by the two-step diffusion process, after oxidation at 1200°C for 4h in air. Although the thickness of Al_2O_3 scale that developed after the two-step diffusion process was not homogeneous, it was developed continuously on the alloy surface. However, this Al_2O_3 scale was not able to provide good oxidation resistance. This is because the alloy with 5at.%Al did not have sufficient ability to re-form an Al_2O_3 scale if the preformed Al_2O_3 scale was cracked or spalled off. Further work is still required in order to provide good oxidation resistance on Nb-based low-Al alloys. However, the results obtained in this study suggest that using oxygen as an alloying element could be one of the methods to increase the stability of Al_2O_3 scales on Nb based alloys, and therefore assist in improving oxidation resistance.

Summary

A two-step diffusion treatment was investigated to develop exclusive Al_2O_3 scales on Nb based alloys. The results obtained may be summarized as follows.

1. Exclusive Al_2O_3 scale was able to be formed using a two-step diffusion process, with an initial oxygen diffusion step followed by aluminum diffusion.
2. With a higher Al activity diffusion process, the oxidation mode changed when the

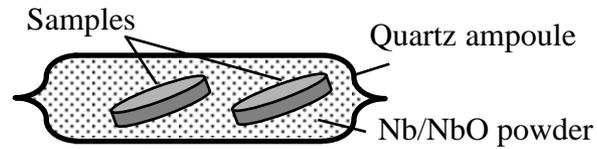
alloy oxygen content decreased, from exclusive Al_2O_3 scale formation -> internal oxide + inner Al_2O_3 layer formation -> internal oxidation -> aluminide precipitate formation. The transition from external to internal oxidation was found to occur at an oxygen content of about 2 at. %.

3. With a lower Al activity diffusion process, exclusive Al_2O_3 scale was developed on all alloys even though the alloy oxygen content was low.

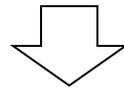
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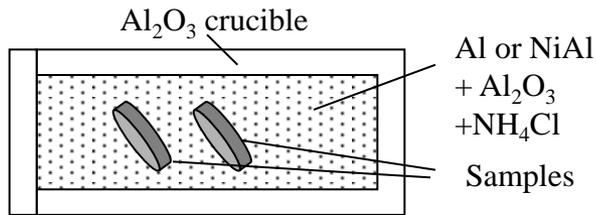
Oxygen diffusion treatment



P_{O_2} : Nb/NbO 2.0×10^{-22} atm
Temperature : 1100 ° C
Time : 100hr



Al diffusion treatment



Temperature : 1100 ° C
Time : 64hr
Atmosphere : vacuum

Figure 1 Illustration of the two-step diffusion process used in this study

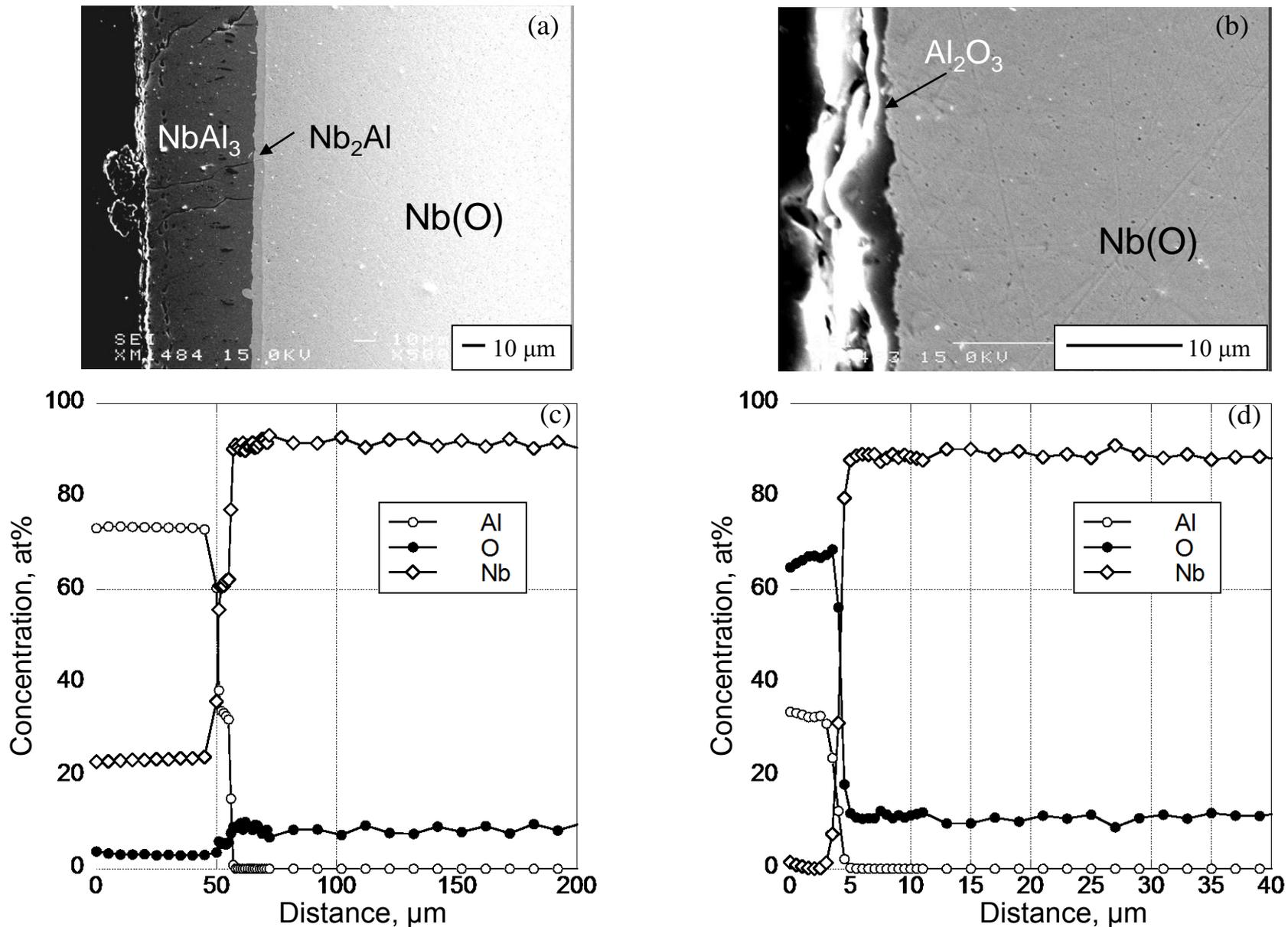


Figure 2 Cross-sections and concentration profiles of Nb after Al diffusion treatment with/without pre-oxygen diffusion treatment. (a) (c) without oxygen treatment, (b)(d) with oxygen treatment

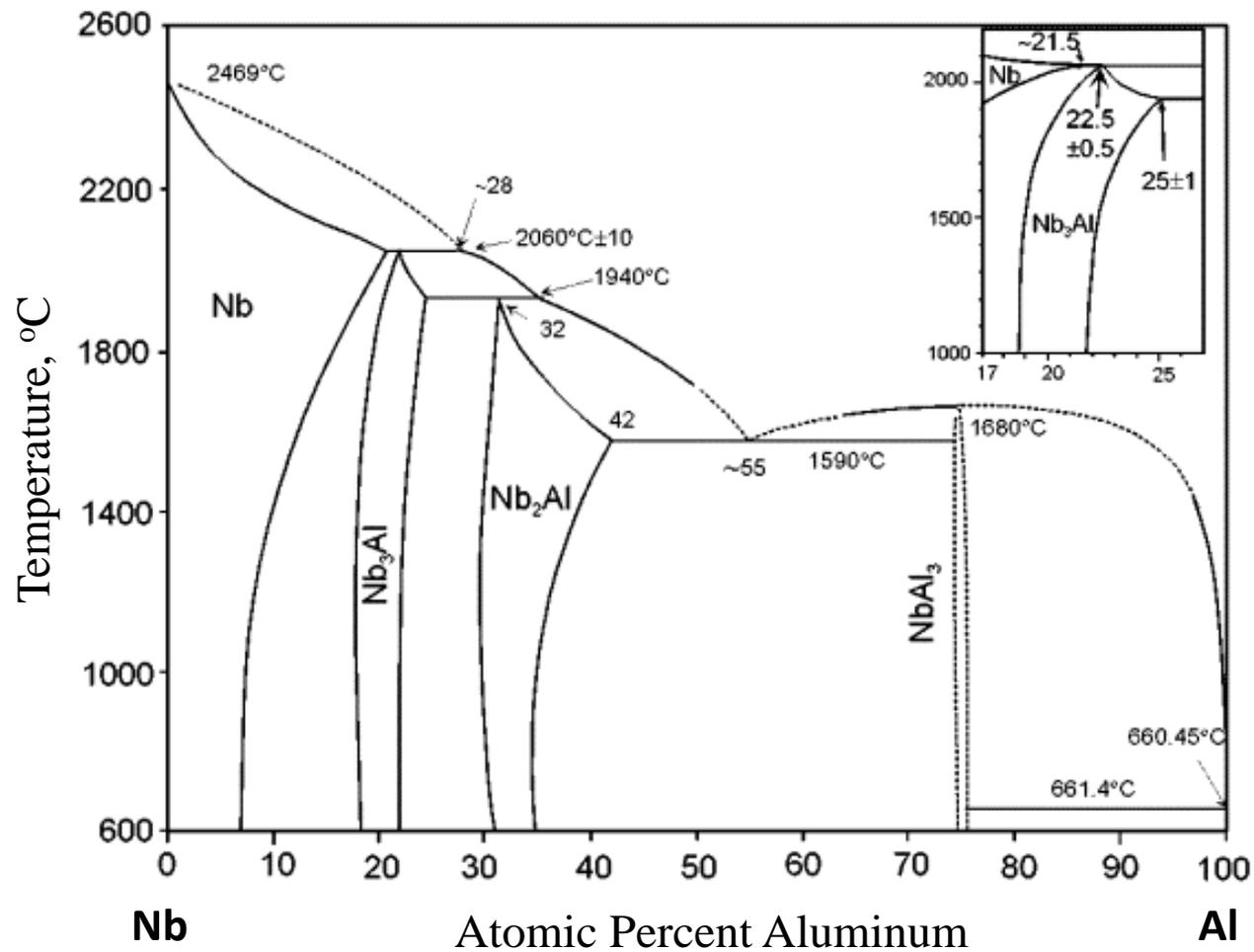


Figure 3 The binary Nb-Al phase diagram

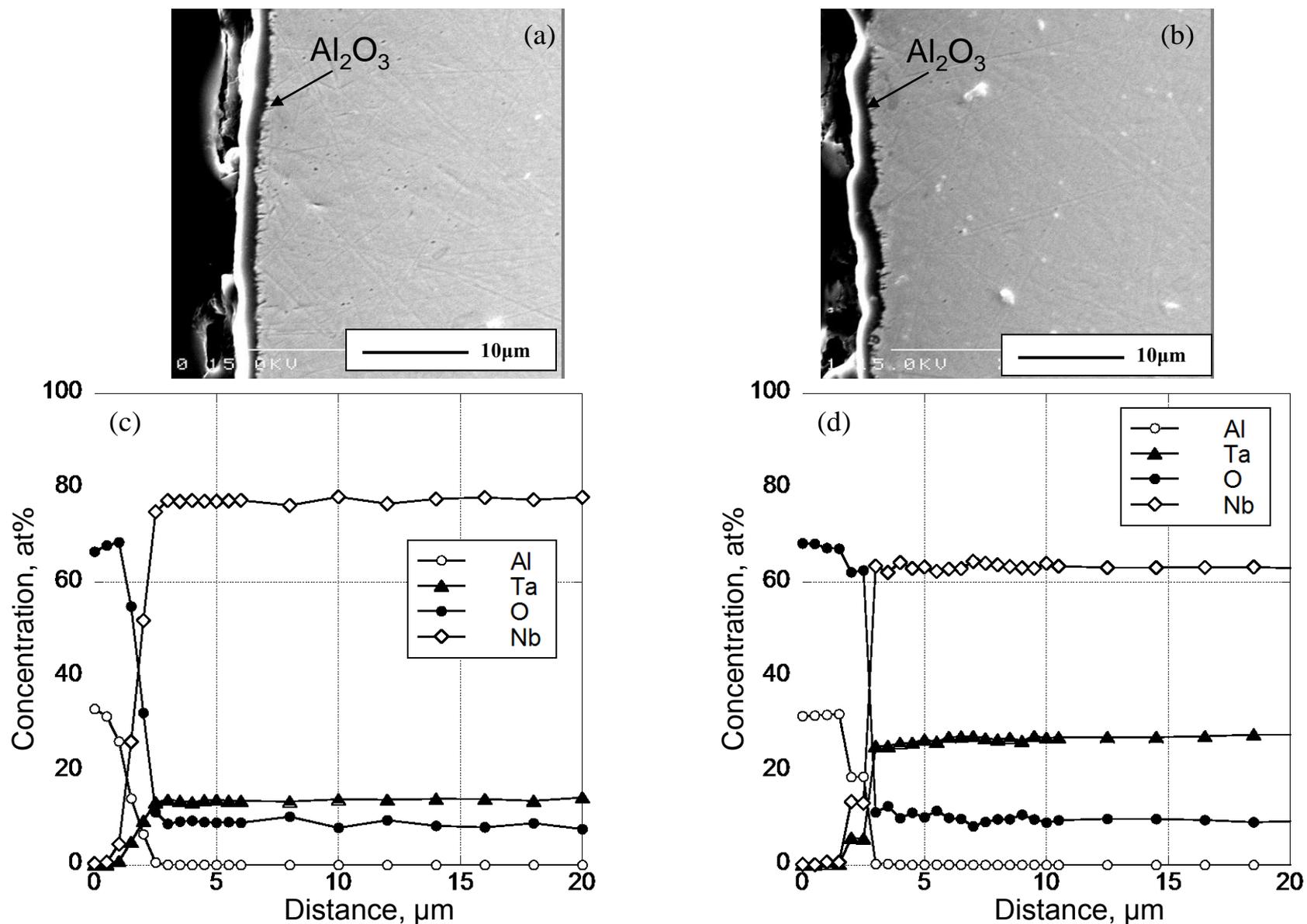


Figure 4 Cross-sections and concentration profiles of alloys after the two-step diffusion process. (a)(c) Nb-15Ta, and (b)(d) Nb-30Ta alloys

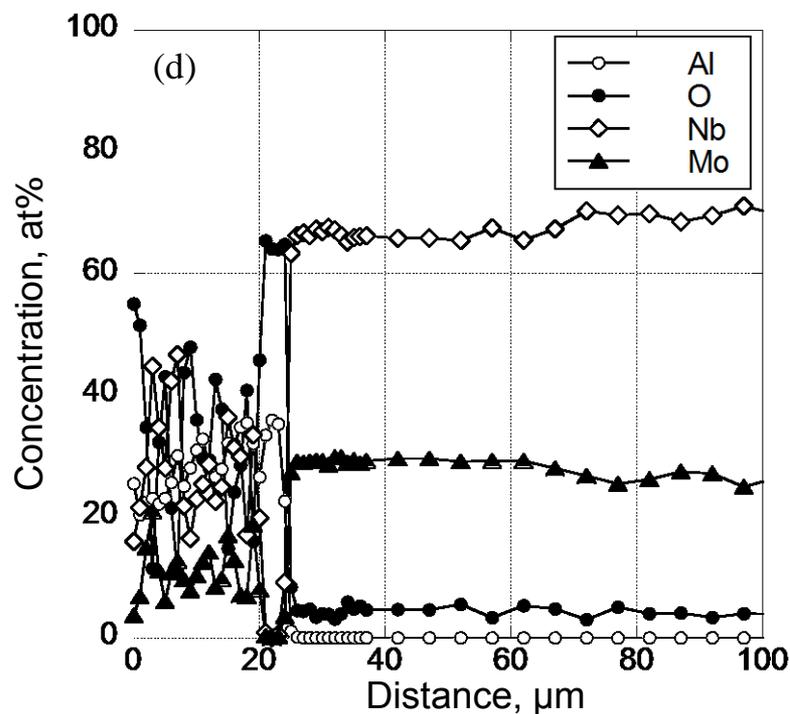
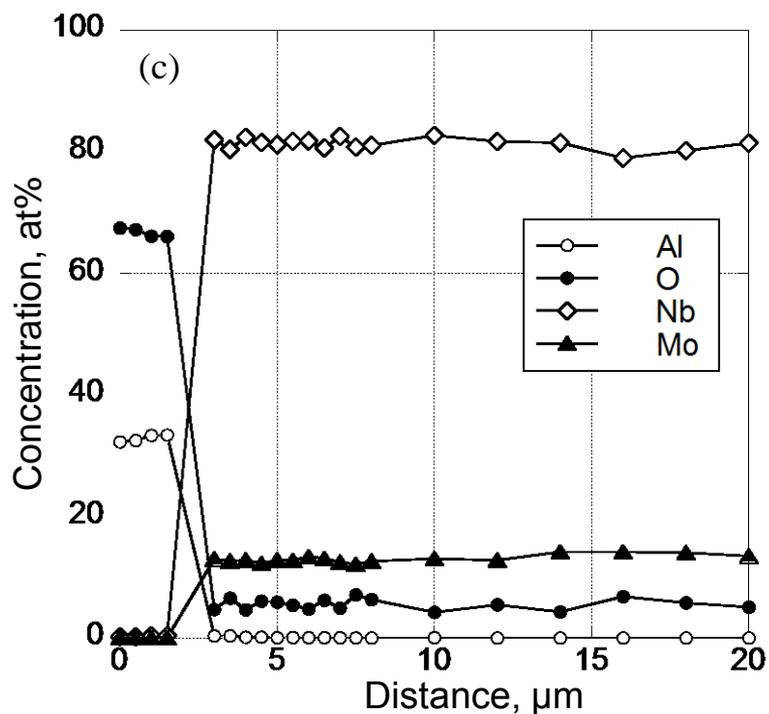
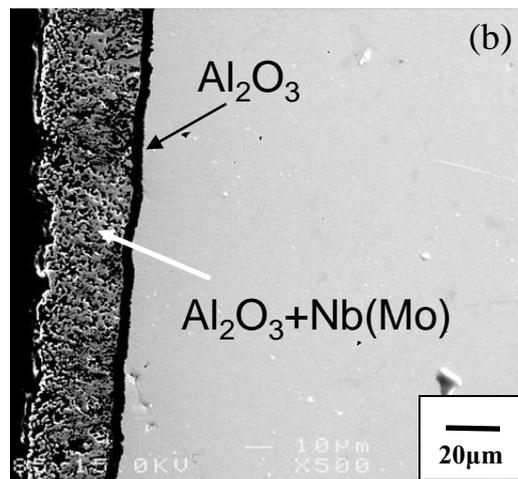
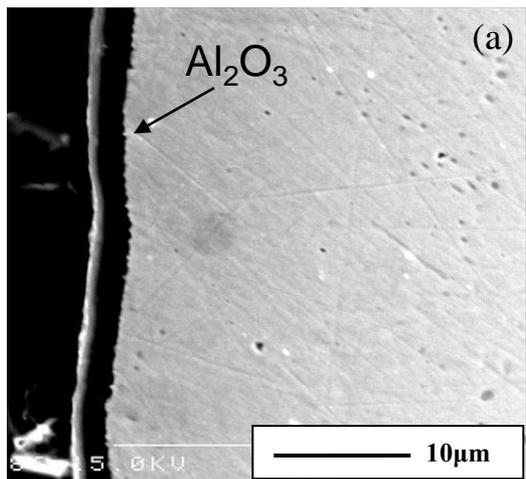


Figure 5 Cross-sections and concentration profiles of alloys after the two-step diffusion process. (a)(c) Nb-15Mo, and (b)(d) Nb-30Mo alloys

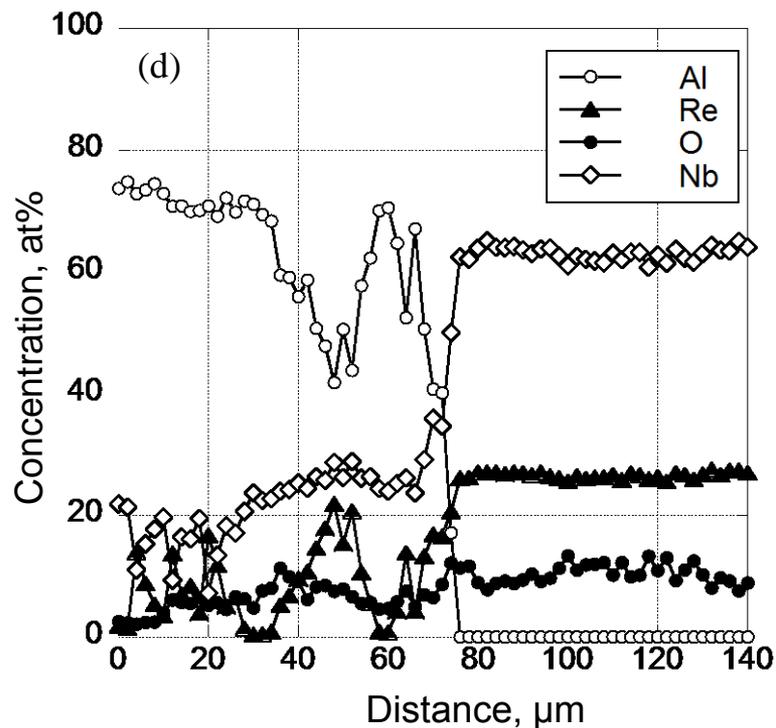
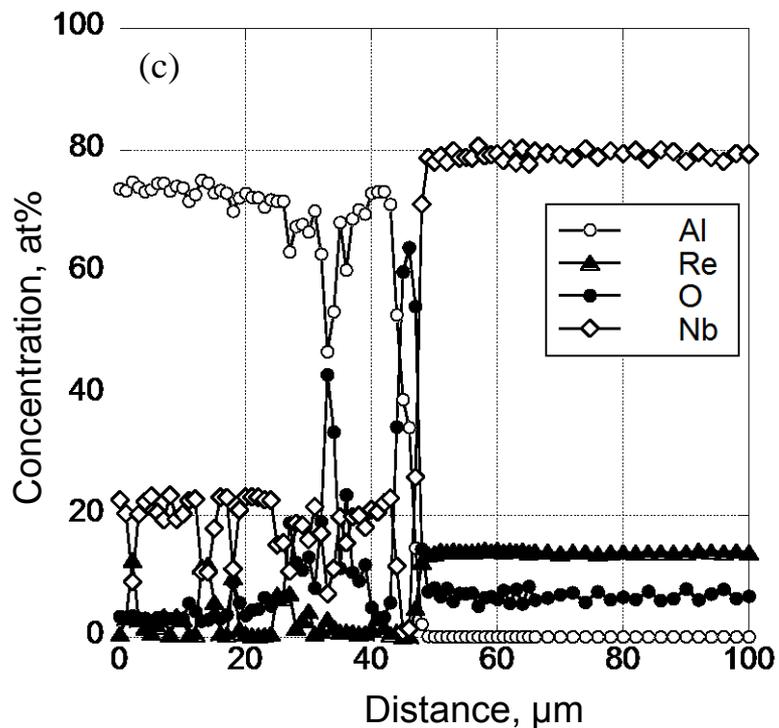
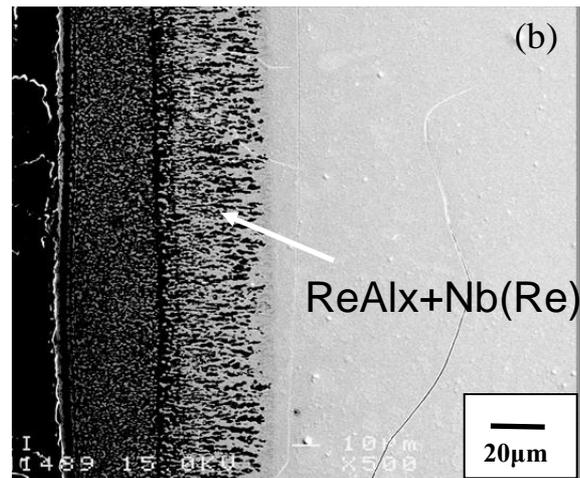
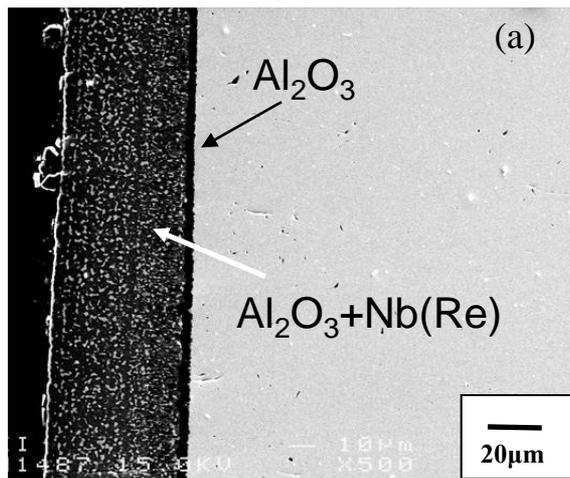


Figure 6 Cross-sections and concentration profiles of alloys after the two-step diffusion process. (a)(c) Nb-15Re, and (b)(d) Nb-30Re alloys

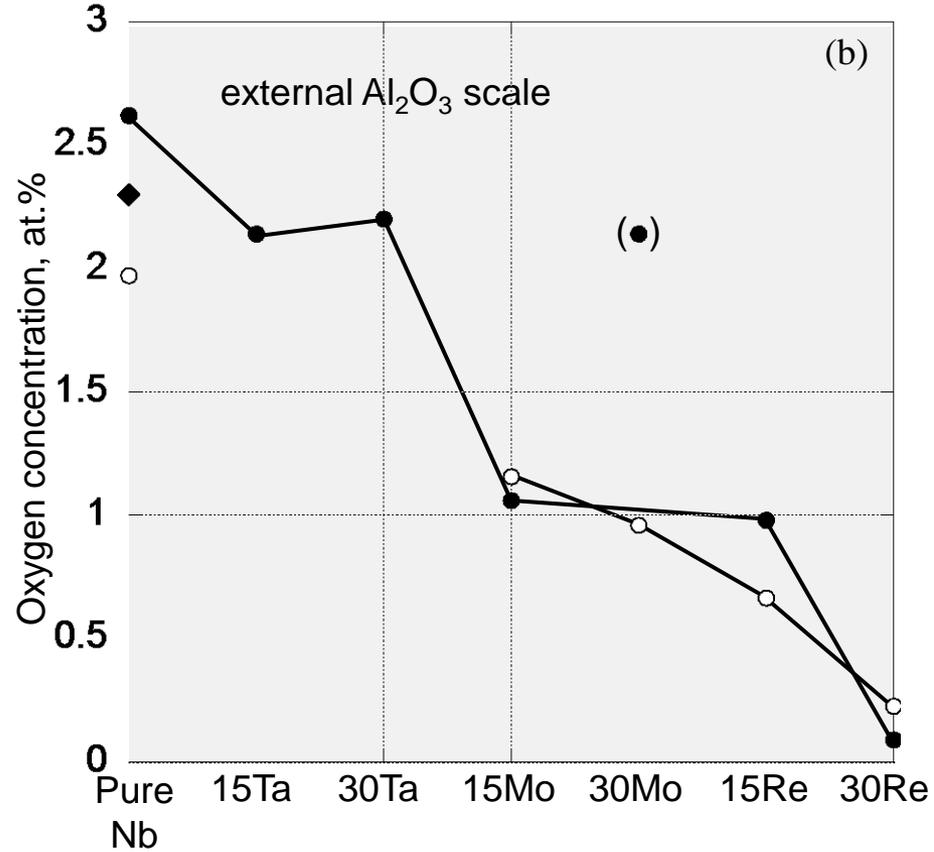
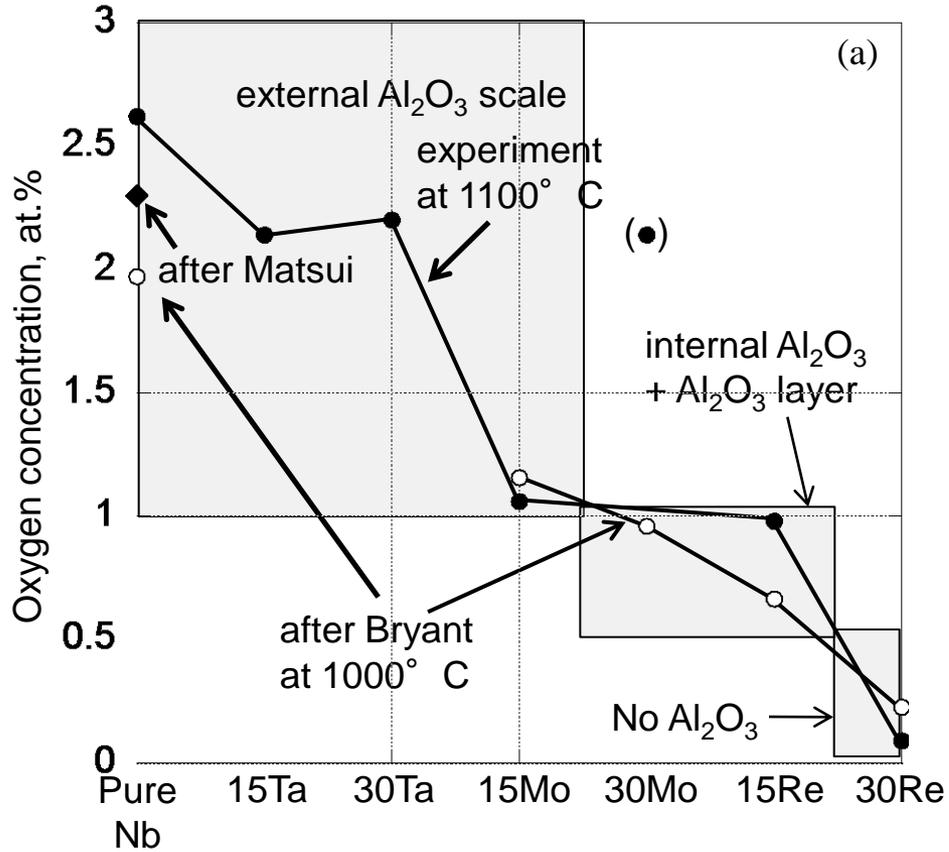


Figure 7 Oxide map as a function of oxygen content with different alloying elements and content.
 (a) High Al activity treatment, (b) low Al activity treatment

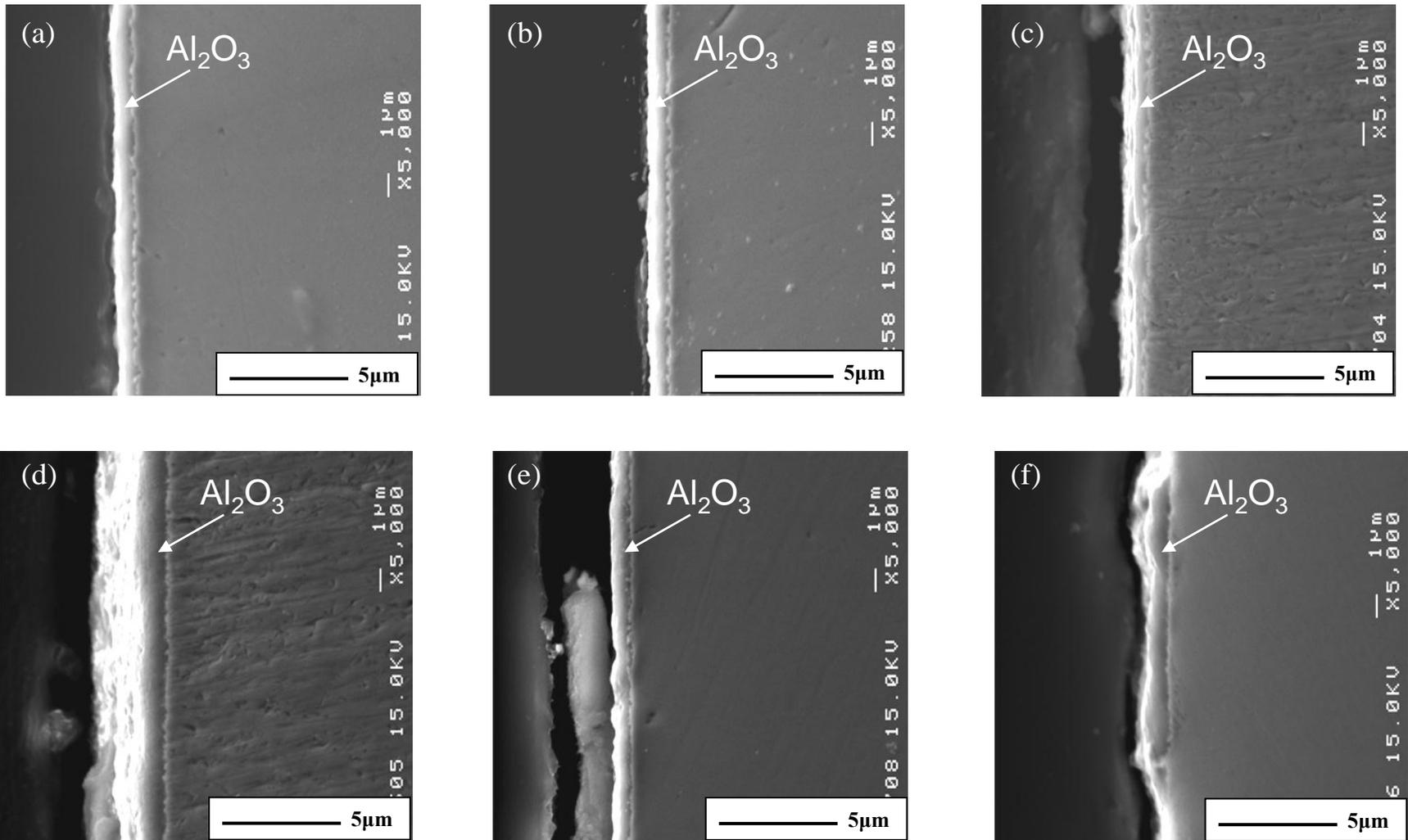


Figure 8 Cross-sections of alloys after the two-step diffusion process with low Al activity treatment. (a) Nb-15Ta, (b) -30Ta, (c) -15Mo, (d) -30Mo, (e) -15Re, and (f) -30Re alloys

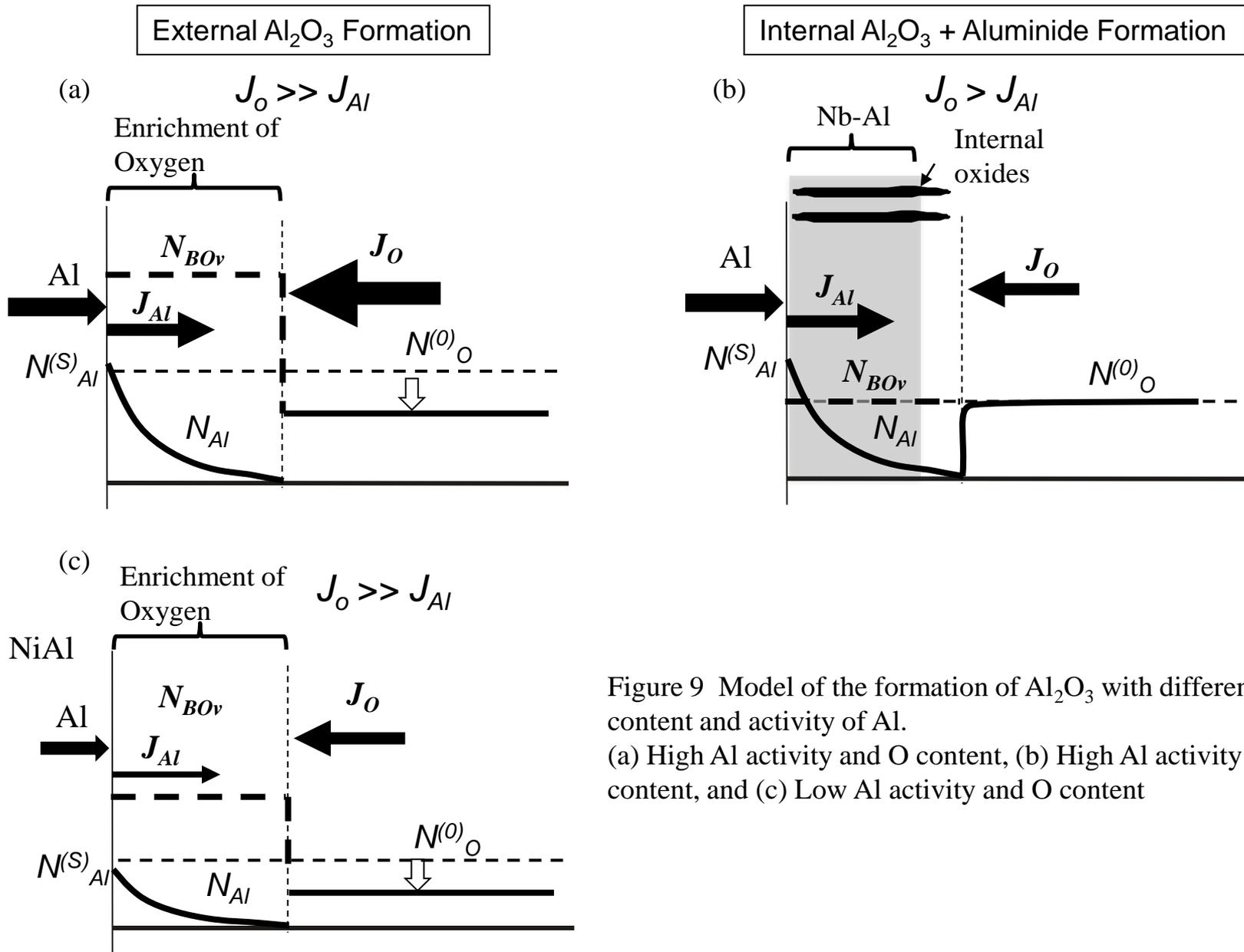


Figure 9 Model of the formation of Al_2O_3 with different oxygen content and activity of Al.
 (a) High Al activity and O content, (b) High Al activity and low O content, and (c) Low Al activity and O content

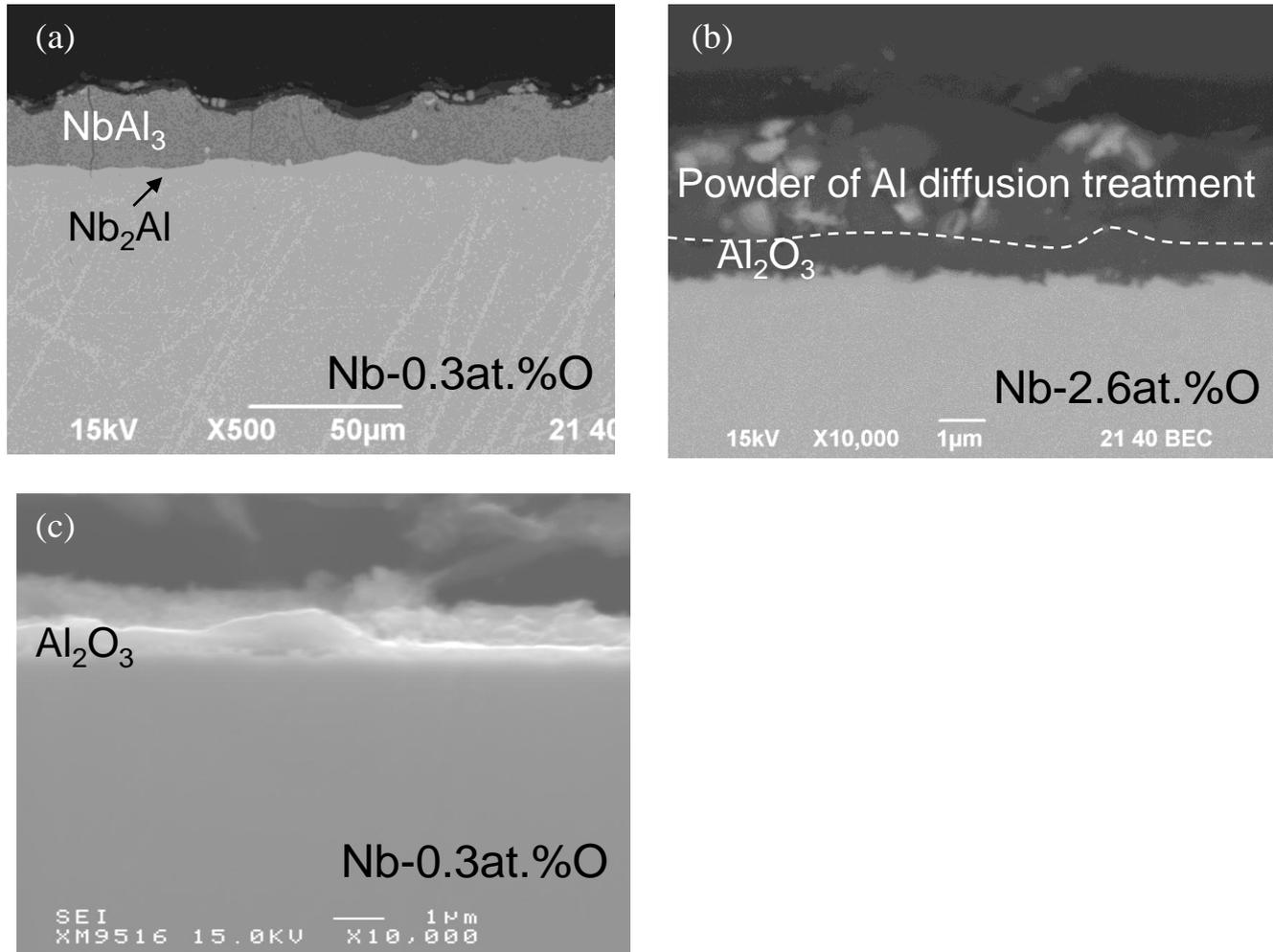


Figure 10 Cross-sections of alloys after the Al diffusion process with low or high Al activity treatment. (a) (c) Nb-0.3at.%O, (b) Nb-2.6at.%O, (a)(b) are treated by higher Al activity, and (c) is treated by lower Al activity diffusion process.

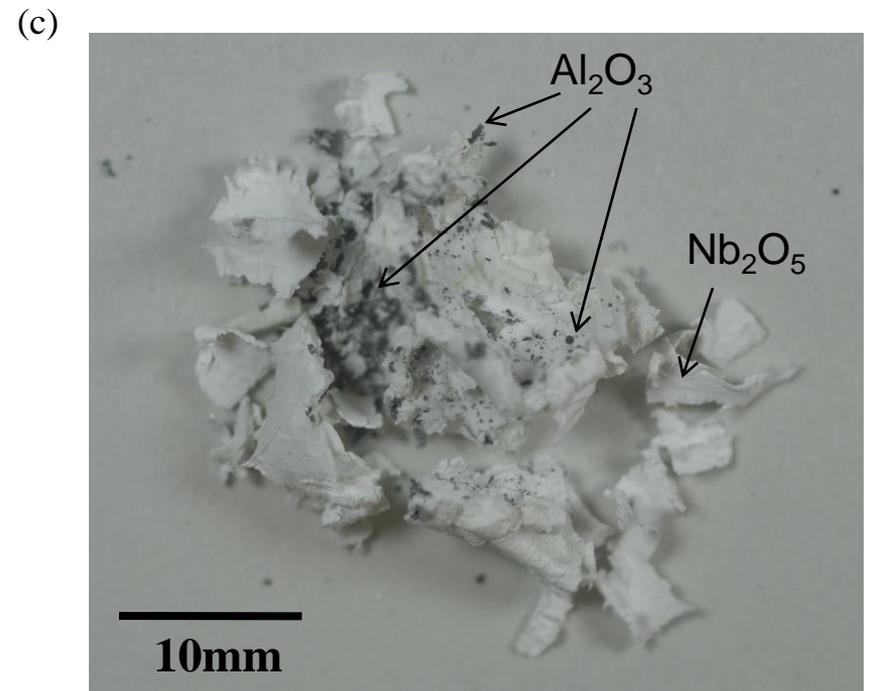
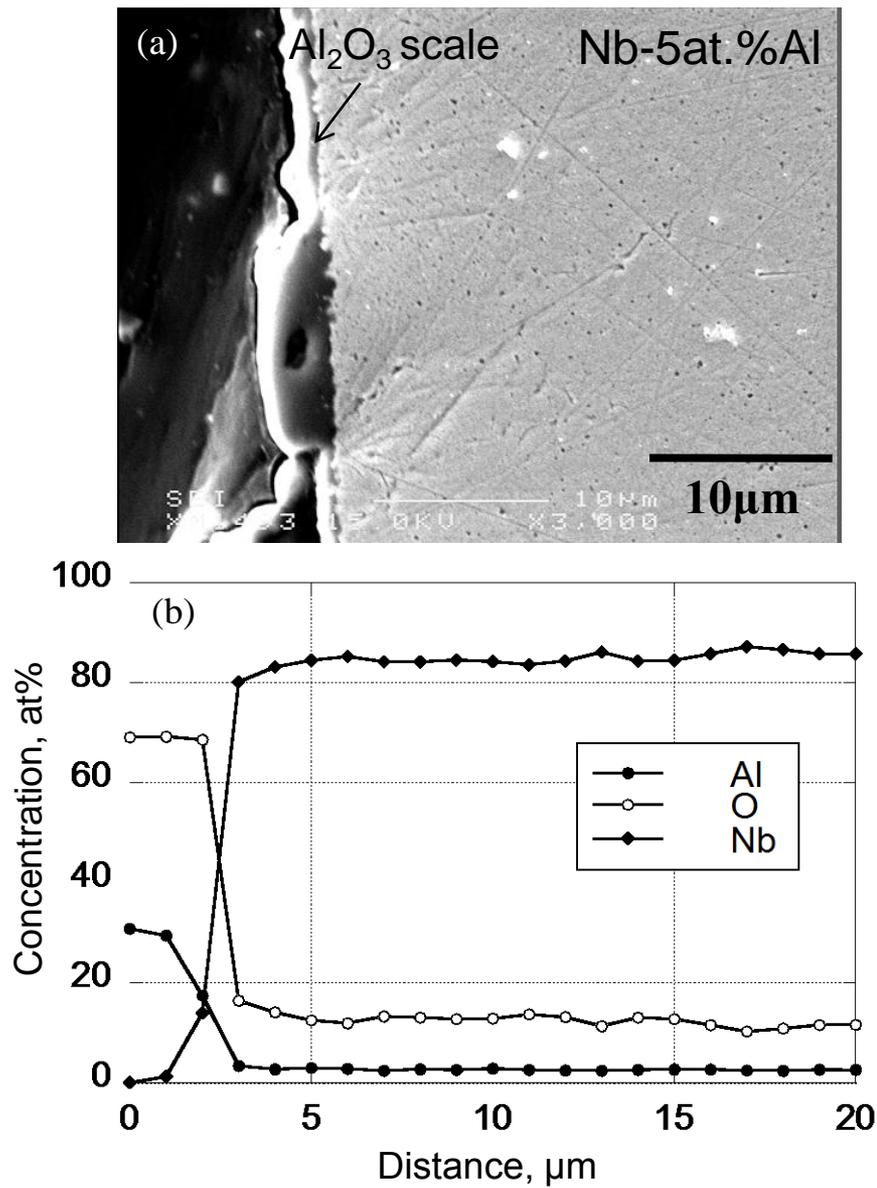


Figure 11 Oxidation performance of oxygen saturated Nb-5Al-O alloy at 1200 ° C for 4h in air. (a)(b) before oxidation test, i.e., after Al diffusion treatment, thin Al_2O_3 scale was developed on the alloy surface, (c) appearance of alloy after oxidation test, white area is Nb_2O_5 and gray precipitates-like oxide is Al_2O_3