

Effect of Nb, Mo, V Contents on Oxidation Resistance of Ti₃Al Based Alloys

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Abstract. In the present paper, the effect of the contents of Nb, Mo, V on the oxidation properties (700°C, in air) of Ti₃Al based alloys has been studied. It has been shown that the alloys were oxidized rapidly as exposed at 700°C in the air. After 100 h exposure, oxygen-affected alloy surface layer of about 10 μm thickness has been formed on account of the poor protection of the oxide film. An addition of (11–13%)¹ Nb enhanced the oxidation resistance. The addition of Mo and V in the Ti₃Al-Nb system alloy reduced the oxidation resistance significantly.

Keywords: intermetallic compound, oxidation resistance, Ti₃Al

1. Introduction

In recent years, considerable attention has been drawn to the development of Ti₃Al based alloys due to their low density and better high temperature strength, stiffness, oxidation resistance, and combustion resistance than conventional titanium alloy. Most of the Ti₃Al based alloys developed are of Ti-Al-Nb system, and four most typical alloys are: Ti-24Al-11Nb, Ti-25Al-10Nb-3V-1Mo, Ti-24Al-17Nb and Ti-23.5Al-24Nb, among which Ti-25Al-10Nb-3V-1Mo is probably going to be the first titanium aluminide to find application in the aerospace industry.

Ti₃Al based alloys possess incomparable high oxidation resistance to conventional titanium alloys, even to Alloy β-21s which is to be applied as the matrix material of the composites of 600–800°C. However, oxidation resistance is still limiting factor to the application at temperature 650–700°C or higher. Generally, the oxidation limit temperature of Ti₃Al alloys is about 650°C [2].

The effect of the contents of Nb, Mo, V on the oxidation behavior in the air of 700°C has been studied basing on the tests of the oxidation behavior of 24 different alloys. A guidance effect may be get from the study to further experiments and modification of composition for a higher oxidation resistance.

2. Experimental

The chemical compositions of the alloys used in the present work are shown in Table 1. All the material was ingots of approximately 60 g by non-consumable electrode arc melting under an argon atmosphere. The specimens (with 10 × 10 × 2 mm³ in size) for oxidation tests were cut from the ingots using an electrical discharge wire cutting machine and polished by No. 800 every paper. All the specimens were cleaned in acetone and ethanol before the test.

Table 1. Composition of the investigated alloys.

Alloy		Alloy		Alloy	
1	Ti-24Al-11Nb	9	Ti-25Al-11Nb-6Mo	17	Ti-24Al-9Nb-1Mo
2	Ti-25Al-10Nb-3V-1Mo	10	Ti-24Al-10.5Nb-1.5V-0.5Mo	18	Ti-24Al-11Nb-1Mo
3	Ti-24Al-17Nb	11	Ti-25Al-10Nb-3V-0.5Mo	19	Ti-24Al-13Nb-1Mo
4	Ti-23.5Al-24Nb	12	Ti-24Al-1Mo	20	Ti-24Al-15Nb-1Mo
5	Ti-25Al-13Nb-1Mo	13	Ti-24Al-1Nb-1Mo	21	Ti-24Al-17Nb-1Mo
6	Ti-25Al-15Nb-1Mo	14	Ti-24Al-3Nb-1Mo	22	Ti-24Al-19Nb-1Mo
7	Ti-25Al-11Nb-2Mo	15	Ti-24Al-5Nb-1Mo	23	Ti-24Al-21Nb-1Mo
8	Ti-25Al-11Nb-4Mo	16	Ti-24Al-7Nb-1Mo	24	Ti-24Al-23Nb-1Mo

The effect of the contents variation were evaluated by discontinuous cyclic oxidation tests in a static air atmosphere at 700°C for 5, 10, 25, 50, 75 and 100 hours. The mass gain of the specimens in each oxidation cycle was measured at room temperature. To verify the accuracy of discontinuous method, continuous method of assessment of reaction kinetics was also applied for 3 alloys: Ti-25Al-(13, 15, 17)Nb-1Mo, at a Cahn System 113 instrument with a automatic recording balance and a data center, also in air atmosphere at 700°C for 50 hours.

The oxide layer formed on the surface was also examined by an optical microscope, a scanning electron microscope (SEM), an X-ray diffractometer and an X-ray photoelectron spectroscopy (XPS or ESCA).

3. Results

Oxide structure of Ti₃Al based alloys

Figure 1 shows a cross-section microstructure of the oxide layer formed on a Ti₃Al based alloy specimen (Ti-24Al-11Nb). The oxide layer reaches a thickness of approximately 2 μm during the oxidation at 700°C air atmosphere for 100 hours. A 10 μm thick oxygen-affected region of the alloy surface was observed obviously in the substrate below the oxide layer. As determined by the EDAX on the SEM, the concentration of oxygen reaches the level of the matrix at a depth of approximately 20 μm. The oxide layer of the alloys was identified to be composed of Al₂O₃ and TiO₂ by X-ray diffraction analysis. Only when the content of Nb reaches or is more than 17%, the niobium oxide (Nb₂O₅ and NbO₂) peaks with extremely weak intensity was detected.

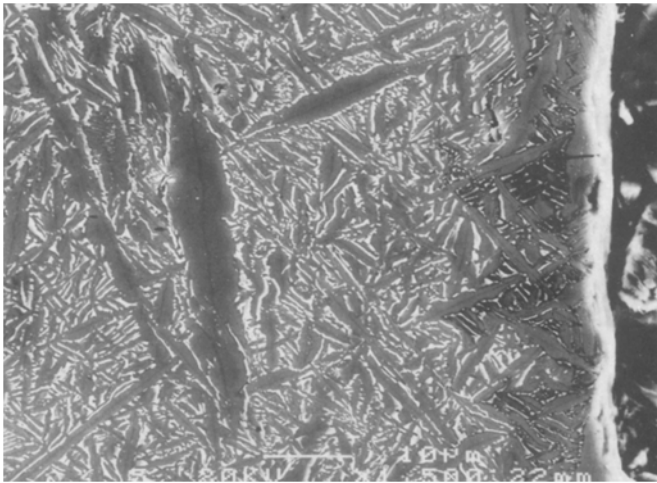
XPS method was also used to investigate the oxide layer of Ti-24Al-(0, 3, 11, 21)Nb-1Mo alloys. After sputtering for 5 minutes, the composition and the combining state of the elements at the utmost layers (<10 nm) was shown with high sensitivity by the experimental data and theoretical analysis (Table 2). The results show that the contents of Al and Nb oxides increase with the increasing Nb content in the alloy, while that of Ti oxide decreases.

Oxidation kinetics

Weight gain curves for the four most typical Ti₃Al based alloys are shown in Fig. 2. The results in Fig. 2 show that Ti-24Al-11Nb possesses the best oxidation resistance, and the

Table 2. XPS analysis result of the composition of the oxide film on alloys with various Nb content.

Alloy	Atomic concentration (%)			
	Ti	Al	Nb	O
Ti-24Al-1Mo	26.23	9.30	—	63.53
Ti-24Al-3Nb-1Mo	22.74	12.73	0.01	64.32
Ti-24Al-11Nb-1Mo	9.13	27.91	0.28	62.47
Ti-24Al-21Nb-1Mo	3.63	33.00	1.53	61.76

Figure 1. Oxide film and the surface of substrate of a Ti_3Al based alloy after 100 h of exposure at 700°C.

worst one is Ti-23.5Al-24Nb. As Mo content varies from 0 to 6%, the oxidation resistance of the alloys will decrease evidently as shown in Fig. 3. When the content of Mo is partly substituted by V, the alloy will have a poorer oxidation resistance (Fig. 4).

During the first period of the experiment, weight gain curves of five alloys with various Nb content have been obtained by discontinuous method (Fig. 5A). Unexpectedly, the oxidation resistance decreases with increasing Nb content. Continuous method is thus applied to verify the accuracy of the results from discontinuous tests (Fig. 5B). These two results show quite the same tendency, although discrepancy in experimental data exists between these two testing methods.

To confirm the influence regularity of Nb content on oxidation resistance more comprehensively, oxidation resistance of the alloys with wide variation of Nb content was tested (Fig. 6). It has been found that, from an oxidation resistance point of view, the best addition of Nb in Ti_3Al alloy is 11–13%. The oxidation resistance increases with increasing Nb addition until the Nb content reaches 11–13%, and then decreases with the further increase of Nb content.

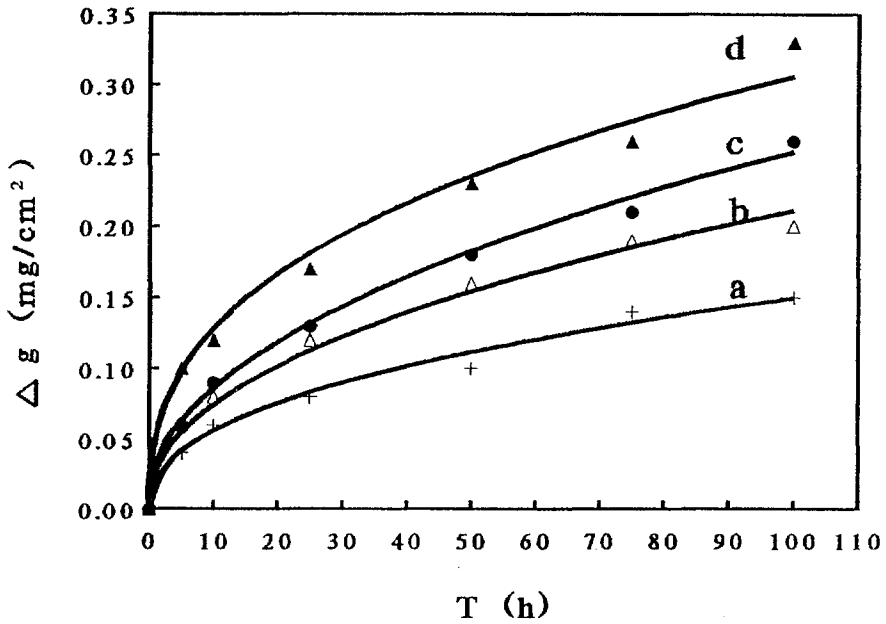


Figure 2. The oxidation properties of four typical Ti₃Al based alloys at 700°C: (a) Ti-24Al-11Nb, (b) Ti-25Al-10Nb-3V-1Mo, (c) Ti-25Al-17Nb-1Mo, (d) Ti-23.5Al-24Nb.

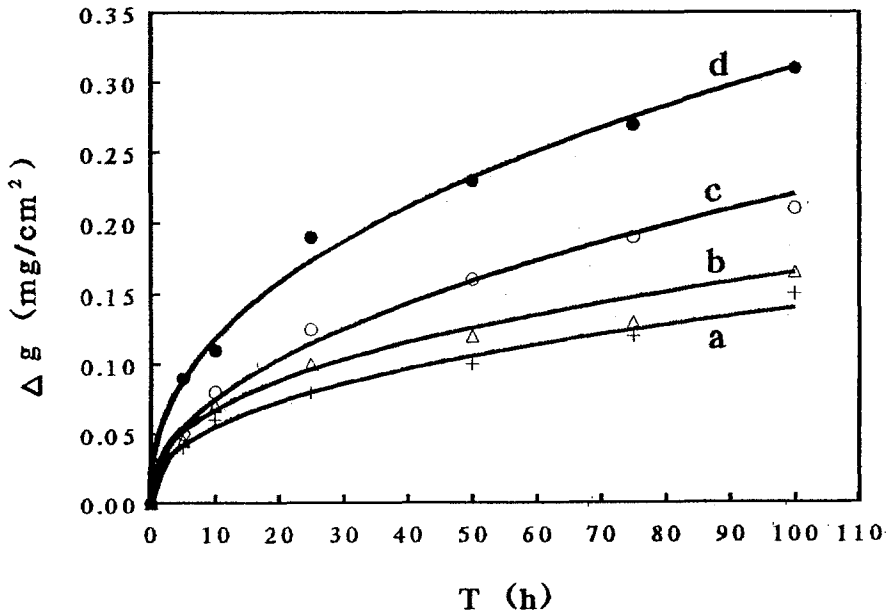


Figure 3. The effect of Mo contents on the oxidation properties of Ti₃Al based alloys at 700°C: (a) Ti-24Al-11Nb, (b) Ti-24Al-11Nb-2Mo, (c) Ti-24Al-11Nb-4Mo, (d) Ti-24Al-11Nb-6Mo.

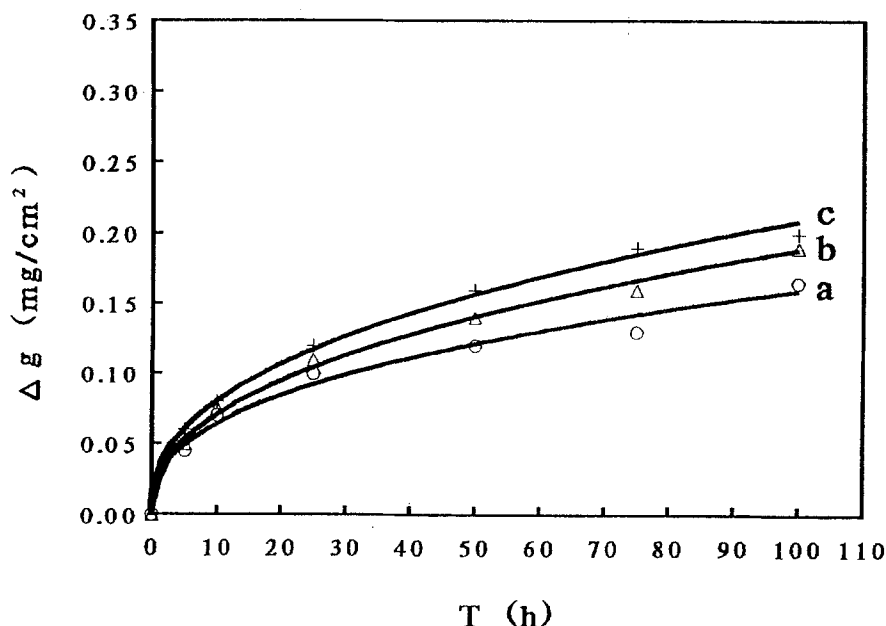


Figure 4. The effect of V contents on the oxidation properties of Ti_3Al based alloys at $700^\circ C$: (a) $Ti-24Al-11Nb-2Mo$, (b) $Ti-24Al-10.5Nb-1.5V-0.5Mo$, (c) $Ti-25Al-10Nb-3V-0.5Mo$.

4. Discussion

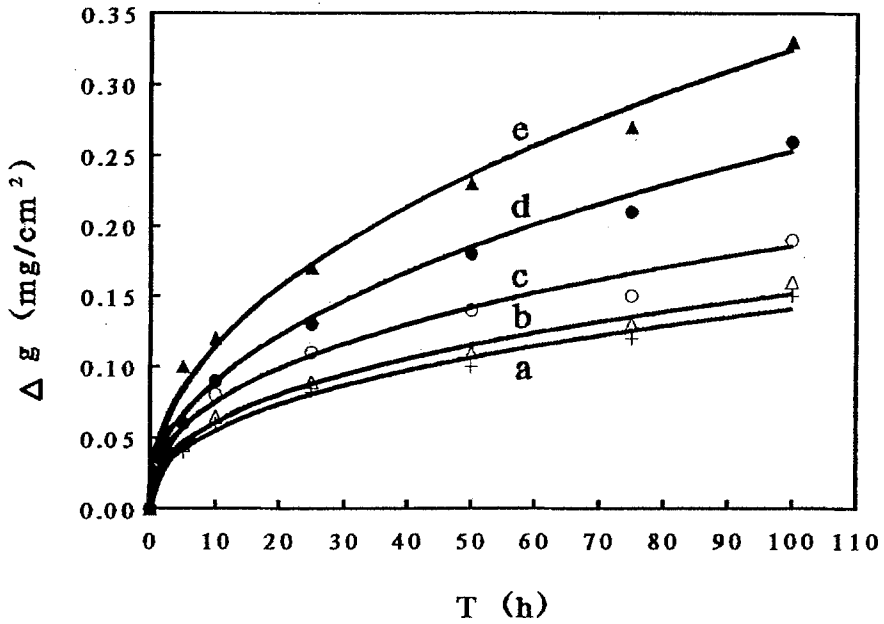
Oxidation mechanism of Ti_3Al based alloys

From the analysis above, the oxidation weight gain can be divided into two parts, that means oxygen have two kind of effects in Ti_3Al alloys. One is the formation of oxide layer on the surface. The other is the diffusion of oxygen into the metal and the formation of the oxygen-affected alloy surface layer because of the high affinity between titanium and oxygen and the high tendency of the formation of titanium oxide, and also because of the high diffusibility and solubility (can be 14.5%) of oxygen in titanium. Once the layer of titanium oxide, TiO_2 , loss its protection over the temperature of $650^\circ C$, oxygen can easily flux into the alloy and thus considerable contaminated region is formed.

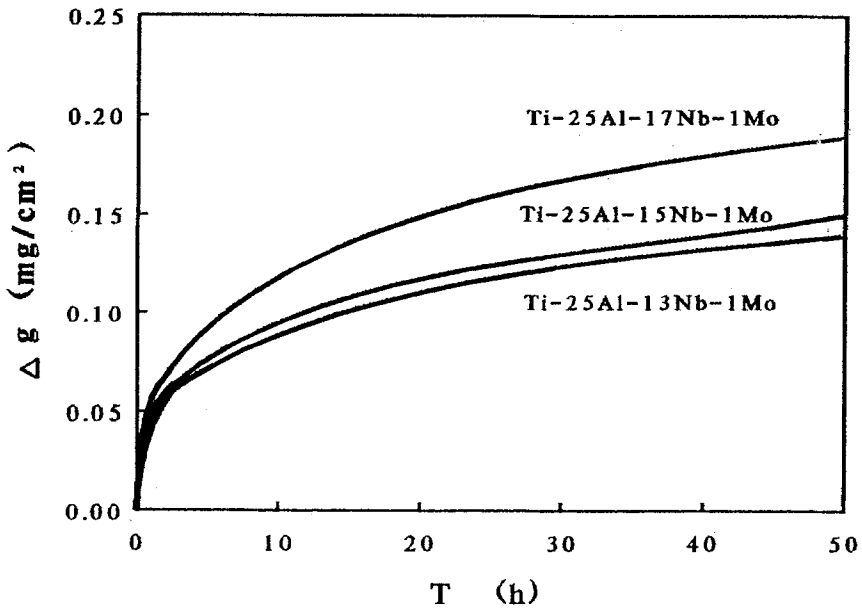
Al_2O_3 is known as the most protective material having a high stability and a smallest self diffusion coefficient of metallic ion. However, the continuous Al_2O_3 layer can be formed only when the content of Al is high enough for external oxidation. N_{Al}^* , the critical Al content necessary to form an external alumina scale, rather than internal oxide precipitates, on a Ti-Al binary alloy may be estimated by the approach of Wagner [3] as

$$N_{Al}^* = (\pi g^* N_O D_O V_M / 3 D_{Al} V_{OX})^{1/2}$$

Here $N_O D_O$ is the oxygen permeability in alloy, D_{Al} is the aluminum diffusivity, g^* is a factor determined by the volume fraction of oxide required for the transition (often near 0.3), and V_M and V_{OX} are the molar volumes of the alloy and oxide, respectively. It has been observed that N_{Al}^* increases with the solubility and diffusivity of oxygen and decrease with an increase in the aluminum diffusivity in the alloy.



(A)



(B)

Figure 5. The effect of Nb contents on the oxidation properties of Ti_3Al based alloys at 700°C : (A) Properties tested in discontinuous process; (a) Ti-24Al-11Nb, (b) Ti-25Al-13Nb-1Mo, (c) Ti-25Al-15Nb-1Mo, (d) Ti-25Al-17Nb-1Mo, (e) Ti-23.5Al-24Nb; (B) properties tested in continuous process.

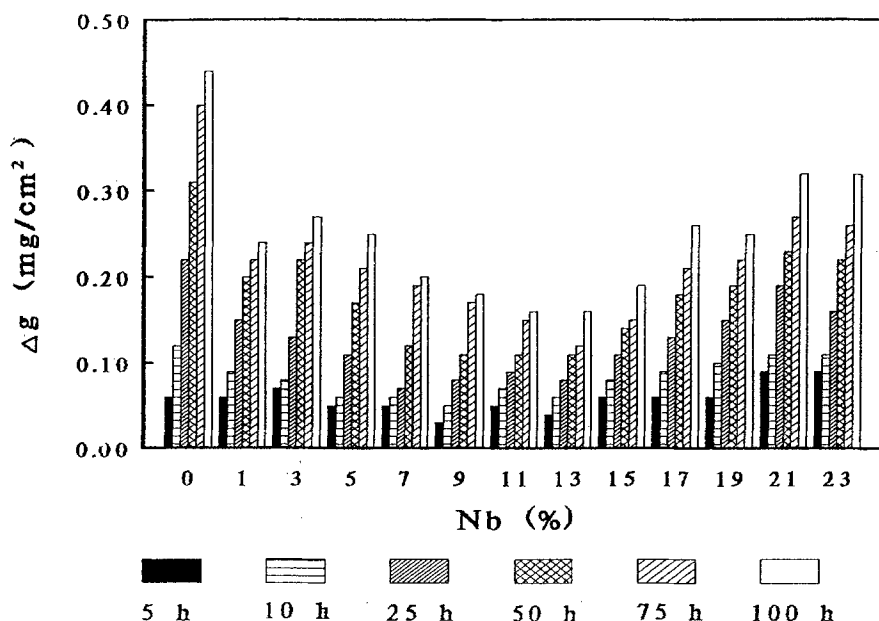


Figure 6. The influence of Nb content with a wide variation on the oxidation resistance of Ti_3Al based alloys at $700^\circ C$.

As determined by experiments earlier [4], the only Ti-Al binary alloys in the concentration range 16 to 50 wt% Al capable of exclusively forming alumina scales in air are those which occupy a small envelope on the diagram at temperatures from 1100 to $1300^\circ C$ and compositions in the Al-rich portion of the TiAl (γ) field. The experimental results in the present study showed that for the Ti_3Al based alloys, continuous alumina films are not formed, while the oxide layer is a mixture of titanium and aluminum oxide, although aluminum can be enriched at the surface by the modification of alloy composition.

Effect of Nb contents on oxidation resistance

As it has been reported by a number of investigations [2, 4, 5], the addition of Nb in Ti_3Al based alloy exhibited benefits to oxidation resistance. But all these reports were based on the alloys with Nb contents less than 11%. In the present investigation, the same behavior has also been observed as the addition of Nb is less than 11%. The benefits of adequate addition of Nb can be divided into two aspects. First, as it has been shown by the XPS analysis above, the volume fraction of alumina in the oxide film increases with the increasing Nb contents, while that of titanium oxide decreases with it. Obviously, the enhancement of alumina content in the oxide film will improve the protection. The second aspect of the benefits may be attributed to the changes in the defects structure of the oxide by Nb^{+5} cations. Since the Wagner mechanism applies in the range of temperature studied, and rutile and alumina are both electron-excess semiconductor, improvement can be expected by the addition of elements of higher valency than four.

When excessive Nb ($>13\%$) is added to Ti_3Al based alloy, oxidation resistance will decrease with the increasing Nb content, in contrast with the behavior of the alloy with

Nb less than 11%. It has been reported [6] that in Nb₂O₅ film formed above 500°C, small blister-like cracks start to form and increase in number with time until their density of the small cracks is quite high. Thus, the decrease of oxidation resistance can be first on account of the enhancement of niobium oxide fraction in oxide film, which is of poor protection. Secondly, the phenomenon can also be attributed to the improvement of diffusivities of oxygen in metal with the increasing β volume fraction. Alloying with niobium will stabilize a certain volume fraction of β phase to room temperature. A drawback of β phase alloy is internal oxidation in the oxygen-affected alloy surface layer. Since the diffusivity of elements is generally higher in β phase than in α_2 , regions of internal aluminum oxidation penetrate deeper along β lamellae, and again provide paths for crack propagation.

As the addition of V and Mo is of a small quantity, oxides of these two elements have not been detected even by XPS analysis. Besides, it is thought that the combined effect and interactions between these alloying addition would be complex. So the mechanism of the effect of V and Mo content is not discussed here.

5. Conclusions

1. Ti₃Al based alloys oxidize rapidly as exposed in the air at 700°C. Approximately 2 μ m thick oxide film and 20 μ m oxygen-affected alloy surface layer form after the exposure of 100 hours.
2. The oxide film is composed of titanium, aluminum and niobium oxide, and the increasing Nb concentration of the alloy increases the volume fraction of Al and Nb oxide, and decreases that of Ti oxide in the oxide film.
3. The oxidation resistance is influenced evidently by the variation of alloy composition. The oxidation resistance increases with increasing Nb content when Nb% is less than 11%. Excessive addition of Nb (>13%) concentration accelerate the oxidation rate.
4. The addition of Mo, V in alloy decrease the oxidation resistance of Ti₃Al based alloy.

Note

1. All the compositions presented are in atom present if not annotated.

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