Effect of Nitrogen on the Oxidation Behavior of Ti₃Al-Based Intermetallic Alloys

T.K. ROY, R. BALASUBRAMANIAM, and A. GHOSH

The effect of nitrogen on the oxidation behavior of Ti-25Al, T-24Al-15Nb, and Ti-25Al-11Nb (at. pct) has been examined in this study. The gases employed were nitrogen and oxygen-nitrogen and oxygen-argon mixtures in various proportions at a total pressure of 1 atmosphere. The experiments were carried out in the temperature range of 1100 to 1300 K by thermogravimetry. The suitability of employing the parabolic rate law as the basis of interpretation of weight gain *vs* time data has been discussed. Oxidation resistance of Nb-containing alloys was superior to that of binary Ti-25Al, irrespective of the gas composition employed. The nitridation rates of alloys, with or without Nb, were more than an order of magnitude lower than those for oxidation. The scales were characterized by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray (EDX) analysis. The scales formed in all the conditions mostly consisted of TiO_2 and Al_2O_3. However, TiN was observed in scales of Nb-containing alloys in all nitrogen bearing gases and seemed to primarily account for improved oxidation resistance of the preceding in comparison to alloys without Nb. Nitrogen pretreatment was provided for some samples before oxidation for further elucidation of the role of nitrogen.

I. INTRODUCTION

THE oxidation behavior of intermetallic Ti₃Al, with and without the addition of niobium, has been the subject of many earlier studies.[1–6] Ti₃Al suffers from poor oxidation resistance, because the scale does not consist of protective Al_2O_3 but rather TiO_2 or a mixture of TiO_2 and Al_2O_3. In general, addition of Nb improves the room-temperature ductility[7] and also increases the oxidation resistance of Ti₃Al.[2–5]

The effect of gas composition on the oxidation behavior of titanium aluminides is significant with regard to rates, reaction product composition, and morphology. Choudhury *et al.*[8] concluded that the faster oxidation of TiAl in air as compared to that in oxygen is due to the presence of nitrogen in air. Meier *et al.*[9] observed that protective alumina scales formed on TiAl upon exposure in oxygen up to 1000 °C, while the same exposure in air resulted in the formation of titania-rich scale exhibiting faster growth rates. Even trace amounts of N_2 influenced the oxide morphology. Meier *et al.* suggested that the presence of nitrogen caused a nitride layer to form which prevented the development of a continuous alumina scale. In a recent study on oxidation of TiAl in air, Rakowski *et al.*[10] reported the formation of intermixed TiN and Al_2O_3 rather than a layered scale. This prevented development of a continuous alumina layer leading to accelerated rates in air. Moreover, higher rates were maintained in the presence of a continuous supply of nitrogen. According to Rakowski *et al.*, this indicated that the mixed oxide layers were permeable to nitrogen.

Several studies have demonstrated the positive role of niobium in improving the oxidation resistance of Ti₃Al, in oxygen as well as in air.[2,3,4] However, the role of nitrogen has not yet been adequately studied. It is interesting to note that unlike in TiAl,[8,9,10] nitrogen has a beneficial effect on the oxidation of Ti₃Al-based alloys.[2] Qiu *et al.*[11] has attributed the improved resistance to oxidation of Ti₃Al, with 11 at. pct Nb or 5 at. pct Si or combined addition of both, to the formation of TiN and reduction of porosity in the oxide scale, rather than to continuous alumina layer formation.

A detailed study of the oxidation of Ti₃Al-based intermetallic alloys has been recently conducted over a wide range of temperatures and gas compositions.[12] The oxidation behavior of these alloys in dry oxygen[13] and the role of carbon dioxide[14] have been presented elsewhere. The present article focuses on the effect of nitrogen on the oxidation behavior of three Ti₃Al-based alloys.

II. EXPERIMENTAL

Three alloys with compositions Ti-25Al, Ti-24Al-15Nb, and Ti-25Al-11Nb were studied in the present investigation. Alloy compositions are in atomic percent unless mentioned otherwise. Specimens were exposed isothermally in the temperature range of 1100 to 1300 K, mostly for 14.4 ks (4 hours) to 21.6 ks (6 hours). Gas compositions employed were nitrogen, nitrogen-oxygen mixtures (20/80, 50/50, and 80/20 vol pct), and oxygen-argon mixtures (20/80, 50/50, and 80/20 vol pct) at a total pressure of 1 atmosphere. Gases and gas mixtures were purified from probable impurities and dried using a gas train. Weight gain was recorded continuously by a Cahn 1000 electrobalance. The experimental setup and procedure have been presented in detail elsewhere.[13] A few samples were pretreated either in dry oxygen or nitrogen for 1 hour and then were exposed in oxygen or oxygen-nitrogen mixture (20/80). The scales were initially observed by unaided eye or by

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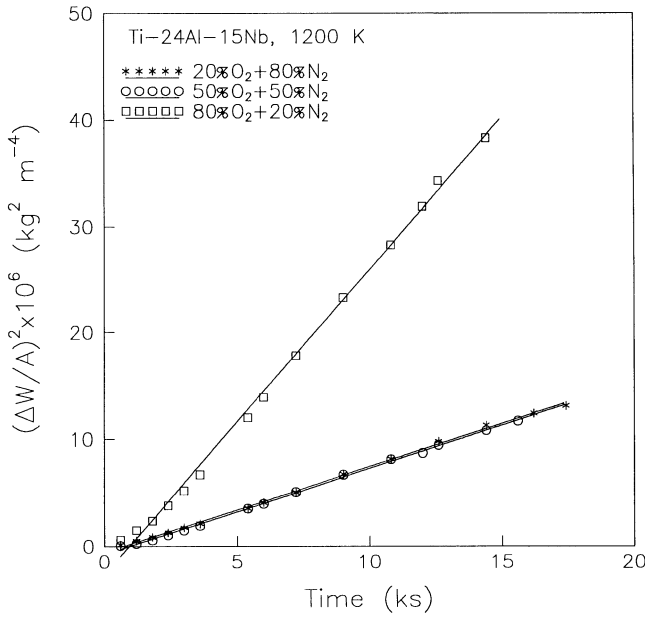Manuscript submitted March 6, 1996.

Fig. 1—Parabolic plots of sample weight gain for oxidation of Ti-24Al-15Nb in O_2-N_2 mixtures at 1200 K.
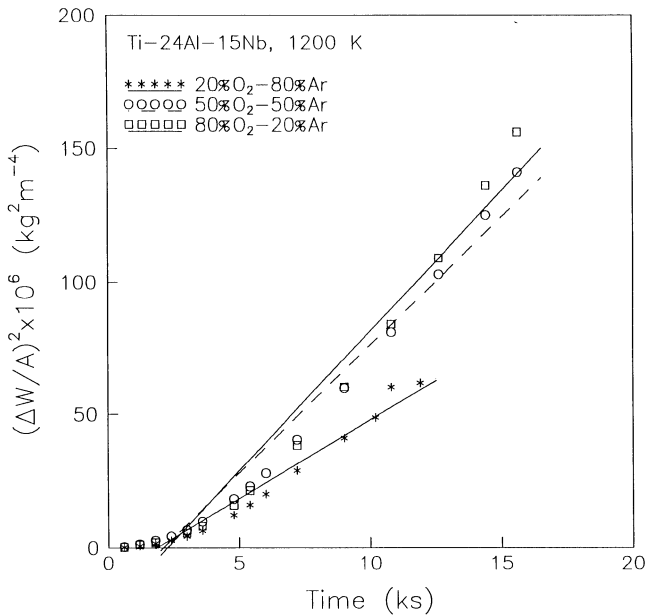

Fig. 2—Parabolic plots of sample weight gain for oxidation of Ti-24Al-15Nb in O_2-Ar mixtures at 1200 K.

low magnification portable microscope after each sample was taken out of the furnace. An ISO DEBYEFLEX* 2002

*DEBYEFLEX is a trademark of Rich-Seifert and Co., Ahrensburg, Germany.

X-ray diffractometer with monochromatic Cu K_α radiation was employed to obtain X-ray diffraction (XRD) patterns from the surface oxides in order to identify the phases in the scales of the oxidized specimens. The XRD patterns of the polished, unoxidized alloys were also recorded for comparison. A scanning electron microscope (SEM) (JEOL**

**JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

JSM 840A) was employed for morphological observation of the scales. Elemental analyses along scale cross sections were performed using the energy dispersive X-ray (EDX) analysis facility attached to the SEM.

III. RESULTS AND DISCUSSIONS

A. *Data Processing and Rate Laws*

A review of earlier investigations revealed that the parabolic rate law has been, in general, the basis of interpretation of the weight gain *vs* time data, although oxidation of titanium aluminides did not exhibit a singular rate law. Hence, the parabolic rate law was considered as the basis of data processing and interpretation of results. The methods of processing weight gain *vs* time data have been fully presented and discussed elsewhere.[13] However, they will be briefly discussed subsequently for the sake of completeness.

The parabolic rate constant (k_p) is related to weight gain per unit surface area of specimen $\left(\dfrac{\Delta W}{A}\right)$ and exposure time (t) by

$$(\frac{\Delta W}{A})^2 = k_p t \qquad [1]$$

where k_p was obtained from the slope of the linear regression-fitted line of $\left(\dfrac{\Delta W}{A}\right)^2$ *vs* t data. In general, experimental data exhibited some systematic deviations from linearity. Figures 1 and 2 present $\left(\dfrac{\Delta W}{A}\right)^2$ *vs* t data for oxidation of Ti-24Al-15Nb in O_2-N_2 and O_2-Ar gas mixtures, respectively, at 1200 K. It may be noted that experimental data approximately agreed with the regression-fitted straight lines. However, some systematic trends of departure from linearity also may be observed.

The parabolic rate law is theoretically valid under certain ideal conditions.[15] If these conditions remain valid throughout the duration of an experiment, then the instantaneous rate constant, $k_i \left(= \dfrac{d\left[\left(\frac{\Delta W}{A}\right)^2\right]}{dt} \right)$, is independent of time. The k_i value was obtained from the regression-fitted slopes of fourth-order polynomial curves of $\left(\dfrac{\Delta W}{A}\right)^2$ *vs* t data. As discussed elsewhere,[13] k_i was found to vary significantly with time for most of the experiments.

Attempts were also made to fit the data with power law as follows:

$$(\frac{\Delta W}{A})^m = k_m t \qquad [2]$$

The rate constant k_m and exponent m were evaluated from linear regression fitting of $\log \left(\dfrac{\Delta W}{A}\right)$ *vs* $\log t$ data. The values of m were between 1 to 1.86. Therefore, as a gen-
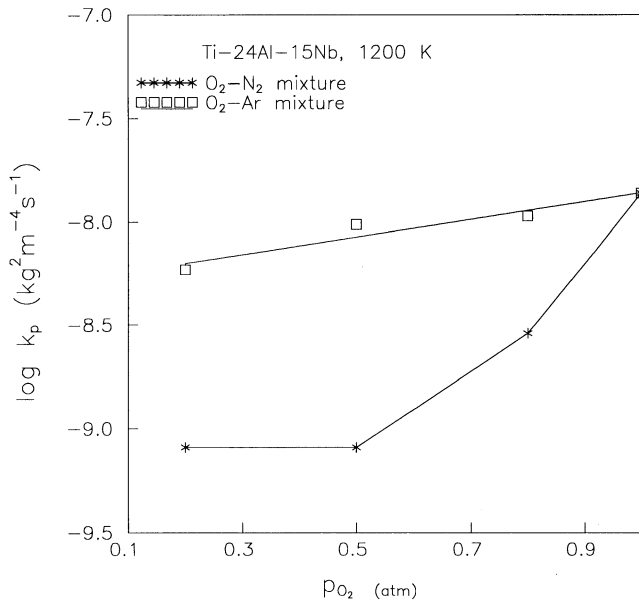
Fig. 3—log k_p vs p_{O_2} plots in O_2-Ar and O_2-N_2 mixtures for Ti-24Al-15Nb at 1200 K.

eralization, the oxidation behavior of the alloys in the present study may be stated as "paralinear."

The departures from the parabolic law can be ascribed to the variation in uniformity and/or nature and composition of scale with progress of oxidation, such as changes in scale porousness, adherence, nature of defects, cracking, etc. However, reproducibility of $\left(\dfrac{\Delta W}{A}\right)$ and t data was fairly good, and k_p values for duplicate sets were observed to be similar. On the other hand, the difference between k_m values for duplicate sets was large. The values of m also exhibited a lot of scatter and significant irreproducibility. Moreover, no trend could be observed with variation of temperature. Hence, the large scatter in m can be attributed to a large extent to the empirical nature of Eq. [2].

The preceding findings show that agreement of data with the parabolic rate law was approximate. However, they also confirmed that evaluation of the rate constant on the basis of parabolic law (Eq. [1]) was more reliable as compared to the use of the empirical Eq. [2]. Moreover, it may also be noted that (1) the parabolic rate constant (k_p) has a theoretical basis and (2) the earlier investigators employed it; hence, it can be used for comparison with the literature. Therefore, k_p shall be employed for further discussion of results.

B. Oxidation Behavior in O_2-N_2 and O_2-Ar Mixtures

Values of k_p were obtained as the slopes of regression-fitted straight lines of $\left(\dfrac{\Delta W}{A}\right)^2$ vs t data, such as those presented in Figures 1 and 2 for Ti-24Al-15Nb alloy. Figure 3 is a plot of log k_p vs p_{O_2}, illustrating the dependence of p_{O_2} on the oxidation rate of Ti-24Al-15Nb at 1200 K. It may be noted that k_p decreased approximately by an order of magnitude when p_{O_2} was lowered in O_2-N_2 mixtures from 1 to 0.5 atm, and then became almost independent of p_{O_2}. This is in contrast to the behavior in O_2-Ar gas mixtures,

where the change was less significant. It is important to note that Ti-25Al did not exhibit such a behavior. At a given temperature, values of k_p of Ti-25Al in O_2-N_2 and O_2-Ar mixtures were approximately equal to that in pure oxygen (Table I). Becker et al.[16] also reported that the influence of oxygen pressure (in the range of 0.01 to 1 bar O_2) on the oxidation of TiAl in the N_2-free atmosphere was negligible.

Several experiments were carried out in $20O_2 + 80N_2$ mixtures at different temperatures, since the composition is close to that of air. Figure 4 shows the plots of log k_p vs $1/T$ for Ti-25Al and Ti-24Al-15Nb in $20O_2 + 80N_2$. The plots for Ti-25Al and Ti-24Al-15Nb in oxygen are also included in the figure for comparison. In Ti-24Al-15Nb, values of k_p were approximately an order of magnitude lower in the preceding gas mixture at all temperatures in the range of 1100 to 1300 K, as compared to those in O_2. A similar observation was made for Ti-25Al-11Nb, which was exposed only at 1300 K. On the other hand, the values of k_p were similar in magnitude for Ti-25Al both in O_2 and in the $20O_2 + 80N_2$ mixture at a given temperature, as recorded in Table I.

It may also be noted from Figure 4 that Nb-containing alloys showed improved oxidation resistance in oxygen at all the temperatures, as compared to Ti-25Al. The effective activation energies (Q_{eff}) of oxidation in the $20O_2 + 80N_2$ mixture were 351 and 274 kJ/mole for Ti-25Al and Ti-24Al-15Nb, respectively, whereas in oxygen, these were 289 and 329 kJ/mole, respectively.[13] Wallace et al.[3] obtained activation energy of 248 kJ/mole for oxidation of Ti-25Al-10Nb-3V-1Mo in air. Figure 4 includes the data obtained by Sankaran et al.[17] for oxidation of Ti-25Al-11Nb in air. Their data lie between those of Ti-25Al and Ti-24Al-15Nb of the present investigation. As already stated, the addition of niobium enhanced the oxidation resistance of Ti$_3$Al-based alloys in oxygen. Further enhancement of resistance in the $20O_2 + 80N_2$ gas mixture (Figure 4) can be attributed to the presence of nitrogen in the atmosphere.

C. Nitriding Behavior

In order to obtain more information on the behavior in nitrogen, further experiments were carried out on all three alloys in purified nitrogen, freed from O_2, CO_2, and moisture by a purifying gas train. As recorded in Table I, values of k_p in nitrogen were approximately 15 to 25 times lower than those in pure oxygen. However, XRD studies of the scales showed that, in addition to nitridation, significant oxidation also occurred. This is because the oxygen level in nitrogen gas could not be kept low enough by the BTS*

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*BTS is a trademark of BASF, Ludwigshafen am Rhein, Germany.

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catalyst (fine copper dispersed in ceramic pellets) used for the purification purpose, to avoid the formation of stable oxides of aluminum and titanium.

Hence, further experiments were performed where nitrogen was passed, after usual purification, through a getter column placed inside the reaction chamber in order to obtain very low p_{O_2} in gas. Zirconium drillings were employed for gettering, since thermodynamic considerations revealed that they possessed the capacity to reduce oxygen to an

Table I. Experimental Conditions and Salient Results of Some Experiments in N_2, O_2-N_2, and O_2-Ar Mixtures

Alloy	Gas Composition	Temperature (K)	$\left(\dfrac{k_p}{k_{p,\,O_2}}\right)^*$	X-ray Diffraction	
				Major Phase	Minor Phase
Ti25Al	N_2	1300	0.04	TiO_2	Al_2O_3, TiN
Ti25Al	N_2 (with getter)	1200	0.015	TiN	TiO_2
Ti25Al	N_2 (with getter)	1300	0.008	TiO_2, TiN	Al_2O_3
Ti25Al	$20O_2 + 80N_2$	1200	1.06	—	—
Ti25Al	$20O_2 + 80N_2$	1300	1.36	TiO_2	Al_2O_3
Ti25Al	$20O_2 + 80Ar$	1200	1.10	—	—
Ti24Al15Nb	N_2	1300	0.05	TiO_2	Al_2O_3, TiN
Ti24Al15Nb	N_2 (with getter)	1200	0.002	TiN	TiO_2
Ti24Al15Nb	N_2 (with getter)	1300	0.02	TiO_2, TiN	—
Ti24Al15Nb	$20O_2 + 80N_2$	1200	0.06	TiO_2	TiN, Al_2O_3
Ti24Al15Nb	$20O_2 + 80N_2$	1300	0.05	TiO_2	Al_2O_3, TiN
Ti24Al15Nb	$20O_2 + 80Ar$	1200	0.43	TiO_2	Al_2O_3
Ti25Al11Nb	N_2	1300	0.06	TiO_2	Al_2O_3, TiN
Ti25Al11Nb	$20O_2 + 80N_2$	1300	0.11	TiO_2	Al_2O_3, TiN

$^*k_p$ is a parabolic rate constant for the given experiment, and $k_{p,\,O_2}$ is k_p for the same alloy at the same temperature in oxygen.
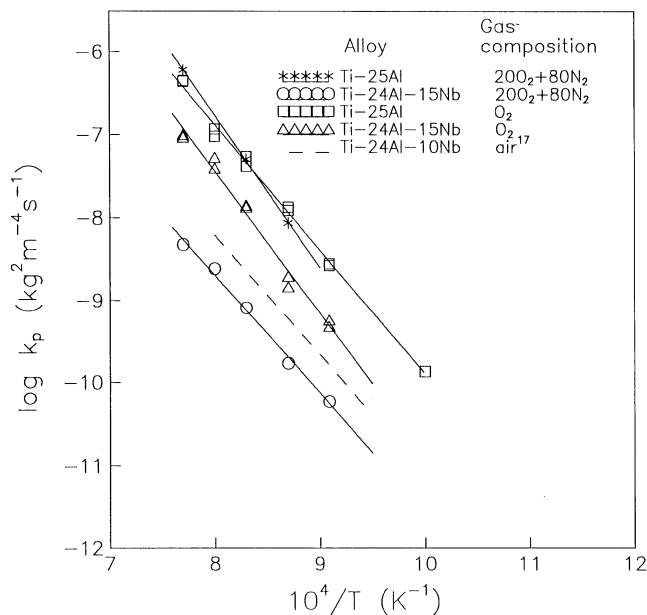

Fig. 4—log k_p vs $1/T$ plots for oxidation of Ti-25Al, and Ti-24Al-15Nb in the 20 pct O_2 + 80 pct N_2 mixture and in O_2.

extremely low level. These experiments were conducted for Ti-25Al and Ti-24Al-15Nb at 1200 and 1300 K. Table I also presents rate constants (k_p) and the analysis of scales of these experiments. It was observed that the use of getter lowered the rates only 3 to 5 times as compared to those without getter for both Ti-25Al and Ti-24Al-15Nb at 1300 K. The presence of TiO_2 in the scale for both alloys reveals that in addition to nitridation, oxidation also occurred even after the use of getter. This indicates that gettering could not be made as effective as expected. In order to understand whether the presence of nitrogen hindered gettering action by zirconium, a few experiments were conducted at 1200 K in argon using a getter column. Even in these cases some weight gains were recorded. The experiments confirmed that the getter element could not remove oxygen impurity present in argon efficiently to prevent oxidation in the present experimental setup.

As Table I shows, the experimental data and observations in nitrogen and in oxygen point out that the nitridation rate constants (k_p) for both Ti-25Al and Ti-24Al-15Nb were lower by one to two orders of magnitude as compared to those for oxidation. McDonald and Wallwork[18] also observed that the nitridation rates of pure titanium in the temperature range between 823 and 1273 K were much lower than the oxidation rates. Moreover, k_p in the $20O_2 + 80N_2$ mixture was 7 times lower than that in the $20O_2 + 80Ar$ mixture. This clearly demonstrates the significant retarding effect of nitrogen on the rate of oxidation for Nb-containing alloys.

D. Formation of TiN in the Scale

The XRD results revealed the presence of TiN in addition to TiO_2 and Al_2O_3 in the scales of Ti-24Al-15Nb and Ti-25Al-11Nb in the $20O_2 + 80N_2$ environment at all temperatures. Moreover, TiN was also detected in the scales of the Nb-containing alloys in all nitrogen-containing atmospheres. In contrast, TiN could not be detected in the scale of Ti-25Al for experiments in the $20O_2 + 80N_2$ mixture at high temperatures. Weak signals of TiN were detected at lower temperature (1150 K).

Figure 5 presents the SEM cross-sectional micrographs as well as elemental compositional line scans for Ti, Al, and Nb for the scales on Ti-25Al-11Nb in the $20O_2 + 80N_2$ mixture at 1300 K. It reveals that the outermost scale predominantly consisted of porous and poorly adhered TiO_2 layer followed by a porous mixture of TiO_2 and Al_2O_3. It was possibly doped with niobium, since no separate niobium oxide could be detected by XRD. The innermost layer was rich in titanium and niobium and tenaciously held, presumably a mixed nitride layer, although no niobium nitride was detected in the scale by XRD. A very thin layer on top of the nitride layer predominantly consisted of Al_2O_3. Aluminum enrichment could be distinctly observed at the scale/alloy interface (Figure 5). Becker et al.[16] found a buildup of Al concentration in the alloy beneath a Ti_2AlN layer and attributed this to the difficulty of diffusion of aluminum ions through the nitride layer.
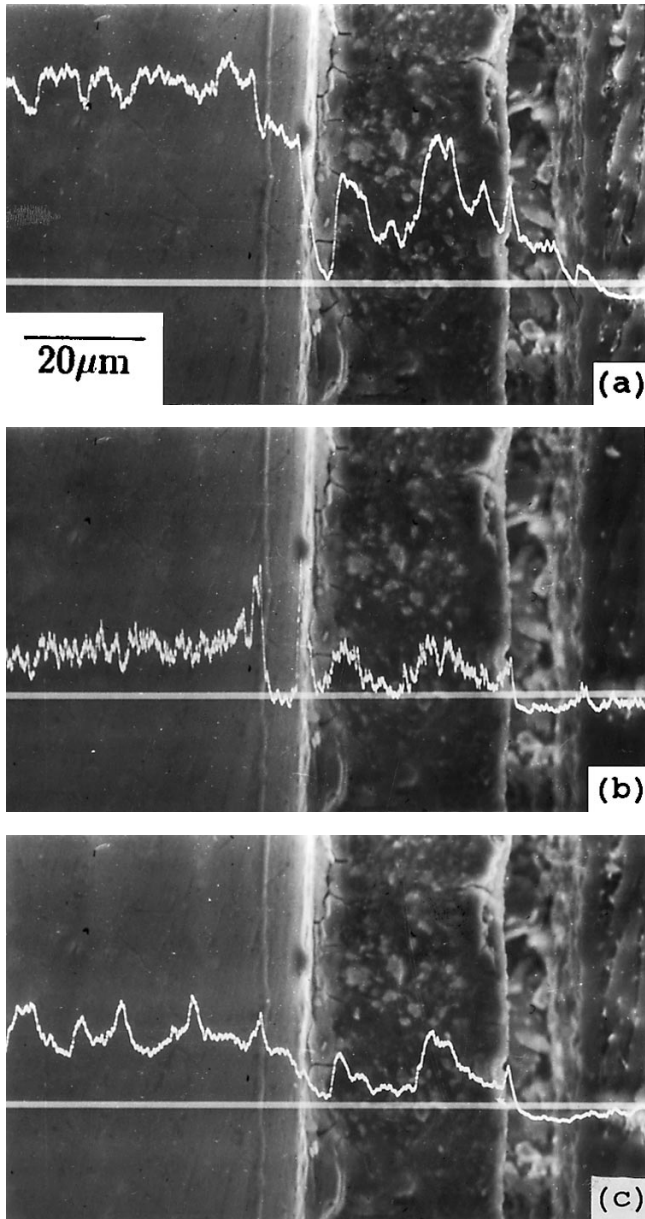
Fig. 5—SEM cross-sectional micrograph of Ti-25Al-11Nb exposed in 20 pct O_2 + 80 pct N_2 mixture at 1300 K with superimposed EDX compositional line analyses for (a) titanium, (b) aluminum, and (c) niobium.
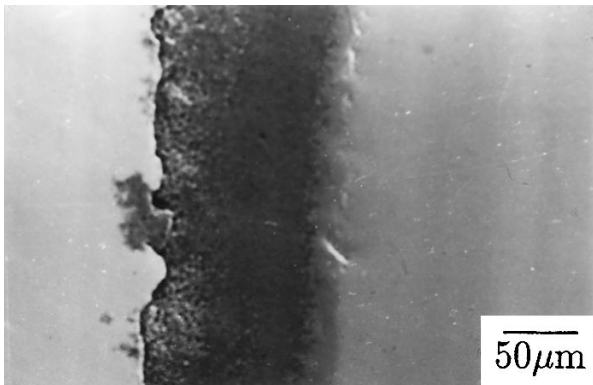

Fig. 6—SEM cross-sectional micrograph of Ti-25Al exposed in 20 pct O_2 + 80 pct N_2 mixture at 1300 K.

The outer scales on Ti-25Al formed in the $20O_2$ + $80N_2$ mixture were bluish white or yellow at all temperatures and spalled in most cases. The retained scales were compact and dark gray, except at 1300 K, in which case they were porous and white. Figure 6 presents a cross section of the retained scales for Ti-25Al formed in the preceding condition. As stated earlier, TiN could not be detected in the scale on Ti-25Al formed at 1300 K. Although the outer yellow scale had spalled, the retained scale was also thick (Figure 6). It is probable that X-rays could not penetrate the retained scale completely and generate signals for TiN layer which might have formed presumably at the alloy/scale interface.

Formation of nitrides or nitrogen-bearing phases in the scale upon oxidation of Ti-Al and Ti-Al-Nb alloys in air has been reported in the literature. Wiedemann et al.[2] detected TiN by XRD as the only nitride in the scale formed on Ti-25Al-11Nb in air at 1255 K. They also mentioned the possibility of the presence of niobium nitride. Wallace et al.[3] also detected a thin TiN layer near the scale/alloy interface of Ti-25Al-10Nb-3V-1Mo oxidized in air over a range of temperature between 973 to 1273 K. The outermost layer was Al_2O_3, while the middle layer (top of TiN) was TiO_2 doped with niobium. Two different nitride layers, viz. TiN and Ti_2AlN, were identified by Becker et al.[16] beneath the Al_2O_3 layer in the scale formed on TiAl in air. The innermost layer was TiN, outside that was Ti_2AlN, and a single Al_2O_3 layer was the outermost scale. Rawe and Rosa[19] also observed a very thin TiN layer in the innermost scale of Ti-4.32Nb (wt pct) alloy exposed to air.

1. Thermodynamic analysis

The values of $\Delta G°$ per mole O_2 of some oxides at 1300 K are as follows:[20] Al_2O_3: -840 kJ, TiO: -792 kJ, TiO_2: -638 kJ, and Nb_2O_5: -475 kJ. Al_2O_3 is the most stable oxide followed by TiO, TiO_2, and Nb_2O_5. However, the real criterion of stability is the chemical potential of oxygen in equilibrium with the alloy and the oxide, and it depends on activities of Ti, Al, and Nb in the alloy as well. Although TiO_2 is less stable compared to TiO, all investigations including the present study observed the formation of TiO_2 and not TiO. The $\Delta G°$ for the reaction

$$2TiO + O_2 = 2TiO_2 \qquad [3]$$
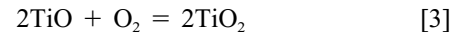
is highly negative, and this explains the presence of TiO_2 in the scale. The values of $\Delta G°$ for some nitrides per mole N_2 at 1300 K are as follows:[20] TiN: -407 kJ, AlN: -354 kJ, and NbN: -299 kJ. TiN is the most stable nitride followed by AlN and NbN. However, the real guide to stabilities of nitrides is chemical potential of nitrogen in equilibrium with the alloy and nitride, and it depends on the activities of Ti, Al, and Nb in the alloy. For the reaction

$$Al_2O_3 + 2TiN = 2AlN + TiO_2 + TiO \qquad [4]$$
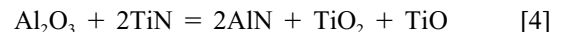
$\Delta G_4°$ is 279 kJ/mole. Therefore, TiN is stabler than AlN in contact with aluminum and titanium oxides. This is in conformity with the formation of TiN rather than AlN in experiments.

Relative stabilities of oxides and nitrides may be assessed considering the following reaction as an example:

$$2TiO\ (s) + N_2\ (g) = 2TiN\ (s) + O_2\ (g) \qquad [5]$$

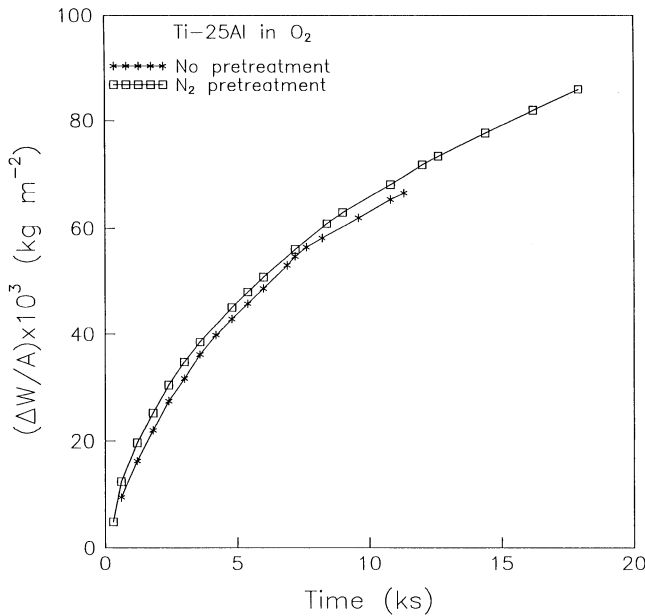At 1300 K, $\Delta G_5° = 385$ kJ/mole for Reaction [5]. Consid-

Fig. 7—Weight gain plots for oxidation of Ti-25Al in O_2 at 1300 K with and without N_2 pretreatment.
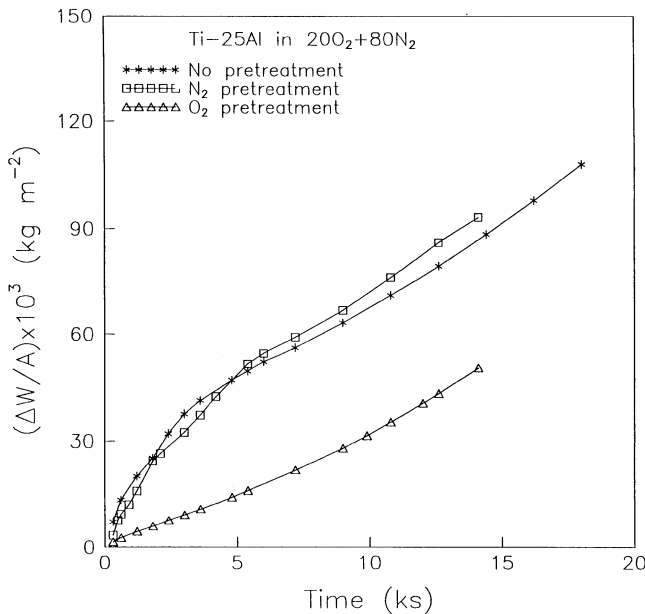

Fig. 8—Weight gain plots for oxidation of Ti-25Al in the 20 pct O_2 + 80 pct N_2 mixture at 1300 K after N_2 and O_2 pretreatment and without pretreatment.

ering TiO and TiN to be pure (a_{TiO} = 1 and a_{TiN} = 1), at 1300 K,

$$\left(\frac{p_{O_2}}{p_{N_2}}\right)_e = \exp\left(-\Delta G_5^\circ / RT\right) = 3.4 \times 10^{-16} \qquad [6]$$

where subscript e designates equilibrium.

Thus, thermodynamic analysis for Reaction [5] shows that TiO is much more stable as compared to TiN. For actual example, at 1300 K, $\left(\frac{p_{O_2}}{p_{N_2}}\right) < 3.4 \times 10^{-16}$ for formation of TiN in preference to TiO. Therefore, a principal question is how can TiN form at all? Obviously, it is a transient phenomenon, and as per literature reports, it forms as a thin layer adjacent to alloy surface. Attainment of such low $\left(\frac{p_{O_2}}{p_{N_2}}\right)$ ratio is possible if either oxygen diffusion through the scale is orders of magnitude lower compared to that of nitrogen, or both oxygen and nitrogen reach the surface from the gas phase at comparable rates but oxygen gets consumed primarily in dissolution in alloy and/or internal oxidation of Al to Al_2O_3. It seems from evidence available in the literature that the latter mechanism is more dominant. The diffusivity of oxygen[21] has been reported to be at least an order of magnitude larger compared to that of nitrogen[22] in α-Ti. The possibility of formation of the Al_2O_3 layer at or near the alloy surface may be attributed to aluminum enrichment at the scale/alloy interface in the presence of TiN, observed in the present study (Figure 5) and also reported in literature.[16]

2. Beneficial role of nitrogen in Nb-containing alloys

The scales were not protective in Ti-25Al as compared to those in Ti-24Al-15Nb and Ti-25Al-11Nb for the same experimental conditions. Niobium oxide could not be detected by XRD in the present investigation. However, the presence of niobium was noticed in the scale by EDX analyses (Figure 5). This may be taken as evidence that niobium ions were present as dissolved in TiO_2 rather than as a separate phase. As concluded earlier[13] and also reported in the literature,[23] the doping effect of niobium ion in TiO_2 slows down oxygen ion diffusion and hence promotes oxidation resistance.

Further enhancement of oxidation resistance of Nb-containing alloys in nitrogen-containing atmosphere seems to be due to the beneficial effect of the TiN layer. Rawe and Rosa[19] attributed the lowering of the rate for Ti-4.32Nb (wt pct) to the barrier qualities of the TiN layer. The development of a dense protective scale is possible only when the Pilling–Bedworth ratio (PBR) is sightly above 1. TiN satisfies this requirement, since the PBR is approximately 1.1.[22] Second, nitrides, in general and including TiN, are more metallic in nature and, therefore, would be able to accommodate more stresses before cracking. In principle, these factors indicate that TiN would be protective against oxidation. Münster and Schlamp[24] studied oxidation of TiN in the temperature range of 898 to 1348 K in oxygen and found the rates to be significantly lower than those for pure titanium. This indicates that TiN, once formed, is likely to resist its conversion to oxides by oxidation. Therefore, all these support the viewpoint that TiN would act as a barrier to oxidation.

E. Sequential Exposure to Different Gases

Some experiments were also performed at 1300 K in changing environments for further elucidation of the role of nitrogen. Accordingly, both Ti-25Al and Ti-24Al-15Nb were exposed in one type of gas for 1 hour (*i.e.*, pretreatment) and then switched over to another gas or gas mixture.

Figure 7 presents the weight gain data of Ti-25Al for oxidation in oxygen after nitrogen pretreatment, and Figure 8 shows the same for oxidation in the $20O_2 + 80N_2$ mixture after pretreatment either in nitrogen or oxygen. For comparison, the weight gain plots for oxidation in oxygen and in $20O_2 + 80N_2$ without pretreatment have been included
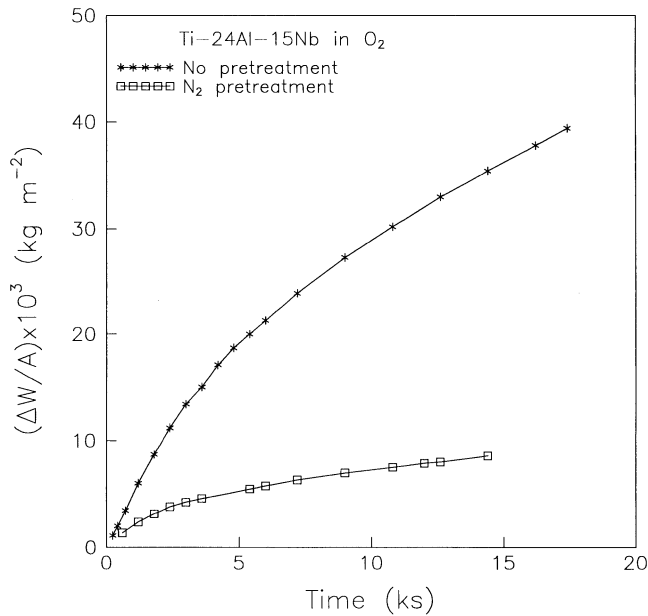
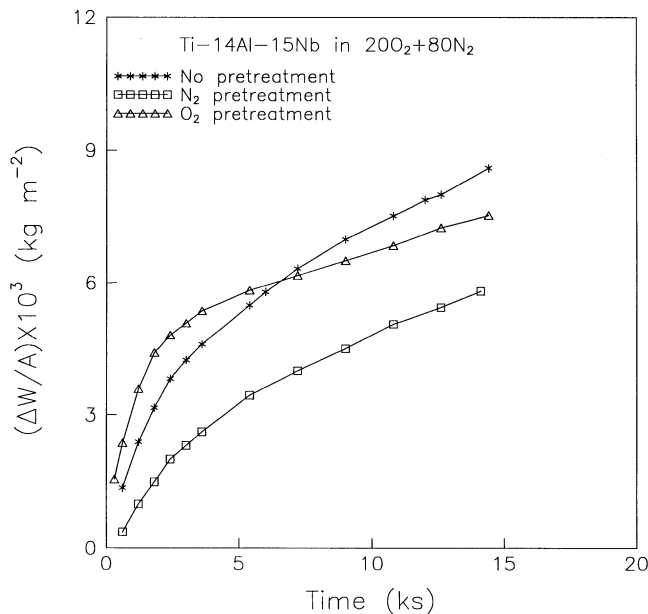Fig. 9—Weight gain plots for oxidation of Ti-24Al-15Nb in O_2 at 1300 K with and without N_2 pretreatment.

Fig. 10—Weight gain plots for oxidation of Ti-24Al-15Nb in the 20 pct O_2 + 80 pct N_2 mixture at 1300 K after N_2 and O_2 pretreatment and without pretreatment.

in Figures 7 and 8, respectively. It is clear from these figures that nitrogen pretreatment did not play a beneficial role for Ti-25Al in both the environments, whereas oxygen pretreatment lowered the oxidation rate in the $20O_2$ + $80N_2$ mixture. The scales for all the cases consisted of a nonadherent yellow outer layer with an adherent, noncompact grayish blue subscale. In the scales, TiO_2 was the major phase and Al_2O_3 was the minor phase. TiN could not be detected by XRD. Examination of scale by SEM did not provide any information about the mechanism. On the contrary, Choudhury et al.[8] observed nitrogen to be detrimental during exposure of oxygen pretreated Ti-36Al (wt pct) alloy either in N_2 or air at 1223 K. In their study, the preox-

idation time was 24 hours. The XRD analyses did not reveal the presence of nitrogen-containing phases in the oxidized sample.

Figure 9 shows the weight gain data for oxidation of Ti-24Al-15Nb in oxygen after nitrogen pretreatment, and Figure 10 shows the same for oxidation in the $20O_2$ + $80N_2$ mixture after pretreatment either in N_2 or O_2. The weight gain plots of oxidation of this alloy in O_2 and the $20O_2$ + $80N_2$ mixture without any pretreatment have been included in Figures 9 and 10, respectively, for comparison purposes. Nitrogen pretreatment proved to be beneficial for Ti-24Al-15Nb during subsequent oxidation either in O_2 or in the $20O_2$ + $80N_2$ mixture. The scales were mostly grayish blue, adherent, and compact. The XRD studies revealed the presence of TiN in the scales formed in the $20O_2$ + $80N_2$ mixture after pretreatment either in N_2 or O_2. However, TiN could not be detected in the specimen oxidized in oxygen after N_2 pretreatment. The beneficial effect of nitrogen on Ti-24Al-15Nb by retarding the oxidation rate has already been discussed. The additional beneficial effect in sequential exposure may be attributed to the initial nitride layer formed during N_2 pretreatment.

IV. CONCLUSIONS

1. Niobium-containing alloys showed superior oxidation resistance as compared to that without niobium, irrespective of the gas composition employed.
2. The effect of p_{O_2} on the parabolic rate constant, k_p, for Ti-24Al-15Nb was not significant in the range of 0.2 to 1 atmosphere in the O_2-Ar mixtures. However, in O_2-N_2 mixtures. k_p decreased approximately by an order of magnitude when p_{O_2} was lowered from 1 to 0.5 atmosphere, and then became almost independent of p_{O_2}. In contrast, for Ti-25Al, the k_p values were approximately equal in O_2-Ar and O_2-N_2 mixtures and in O_2.
3. For Ti-24Al-15Nb, the values of k_p were about an order of magnitude lower at all temperatures in the 20 pct O_2 + 80 pct N_2 mixture as compared to those in O_2. However, for Ti-25Al, k_p was similar in magnitude both in the O_2-N_2 mixture and in O_2. The effective activation energies (Q_{eff}) for oxidation in the $20O_2$ + $80N_2$ mixture were 274 and 351 kJ/mole for Ti-24Al-15Nb and Ti-25Al, respectively.
4. For Nb-containing alloys exposed to O_2-N_2 mixtures, TiN was detected in the scales in addition to TiO_2 and Al_2O_3. This nitride layer seems to have contributed significantly to further improving the oxidation resistance of Nb-containing alloys in O_2-N_2 mixtures in comparison to that in only O_2.
5. The k_p value in nitrogen for all three alloys was found to be 15 to 25 times lower than the k_p in oxygen at 1300 K.
6. Nitrogen pretreatment was observed to be beneficial for Ti-24Al-15Nb in lowering weight gain during oxidation in oxygen as well as in the O_2-N_2 mixture. Oxygen pretreatment was beneficial for Ti-25Al, while nitrogen pretreatment showed no effect.

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