Oxidation Kinetics of Ti_3Al-2.63 at % Nb Alloy

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ABSTRACT

Oxidation kinetics of a Ti_3Al-2.63 at % Nb alloy in pure oxygen in the temperature range of 1073–1373 K. Experiments were conducted using a Thermo-gravimetric Analysis (TGA) apparatus with a data acquisition system. The oxidation curves for the alloy followed parabolic law at all temperatures studied. Effective activation energy of 193 kJ/mol was deduced for the oxidation of Ti_3Al-Nb alloy. The oxidation products were analyzed using X-ray Diffraction (XRD). The oxidation products were mainly the mixture of TiO_2 (rutile) and Al_2O_3 (alumina) and base alloy (Ti_3Al). Oxidation resistance of the present alloy (Ti_3Al-2.63 at % Nb) was found to be better than that observed in an earlier alloy.

I. INTRODUCTION

The Ti-Al binary phase diagram has very interesting features and intermetallic phases (Ti_3Al, TiAl, $TiAl_3$, etc.) present in the system have unique properties of low density, good creep resistance and high temperature strength /1-4/. Insufficient resistance to oxidation of the intermetallic phase (Ti_3Al) at the titanium-rich end of the phase diagram is well known. Several investigations /5-10/ have been carried out to study the oxidation behavior of the Ti-Al based intermetallics (Ti_3Al, TiAl and $TiAl_3$) both in air and in pure dry oxygen. Oxidation kinetics of $TiAl_3$ and Ti_3Al and subsequently the diffusion characteristics of the species present in the system have also been studied /11, 12/. High temperature oxidation of Ti_3Al alloy in Argon-5% SO_2 environment was studied by one of the authors /13/.

In the case of Ti_3Al alloys, the oxide of the major component (TiO_2) has similar thermodynamic stability to that of Al_2O_3, and hence during the oxidation of these alloys, a protective layer of alumina may not be formed throughout the alloy surface. Earlier studies confirmed that the oxidation resistance of Ti-Al alloys in pure oxygen improved with the increase in aluminum content of the alloy /14/. Addition of elements, such as Nb, Mo etc., to Ti-Al alloys could improve the oxidation resistance significantly so as to enable their use up to about 1073 K /15/.

Effects of alloying additions such as Nb, Si on the oxidation resistance of Ti-Al based alloys were studied /16-19/. These studies showed that addition of Nb improved the oxidation resistance but did not assist the formation of compact continuous alumina layer in the Ti-Al based alloys. Hauffe /20/ observed mixed scales consisting mainly of TiO_2 and Al_2O_3 along with small amounts of Nb oxides in the studies of the Ti-Al based alloys with Nb additions. Sun *et al.* /21/ have studied the oxidation behavior of Ti_3Al alloy with Nb additions at 973 K in air and found that the best resistance was observed when Nb addition was in the range of 11–13 at. pct.

High niobium additions up to 27 at% Nb to the Ti_3Al alloys have been studied for the oxidation resistance of the base alloy in the temperature range of 1125-1325 K /22/. Higher contents of niobium in the alloy did not improve resistance to oxidation due to the

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formation of Nb_2O_5 which led to spallation of scale. It was reported that presence of Nb in TiO_2 as a solid solution improves the oxidation resistance of the base Ti_3Al alloy /23/. The effect of tantalum addition on the oxidation behavior of α_2-Ti_3Al alloy in pure dry oxygen had been studied by the author /24/. Addition of tantalum improved the oxidation resistance of the Ti_3Al alloy by favoring the formation of Al_2O_3. However, adherent oxide scale on the alloy was not observed. Significant spallation of the oxide scale took place at temperatures higher than 1223 K. A study on the effect of addition of small amounts of niobium to Ti_3Al alloy was briefly mentioned by the author /25/. Interesting results were obtained at temperatures higher than 1273 K. An explanation in detail of the interesting formation of multi-layered microstructure on the Ti_3Al-Nb alloy oxidized in pure oxygen was presented in an earlier publication /26/. This paper presents a short term oxidation study on the Ti_3Al-2.63Nb alloy in pure oxygen atmosphere in the temperature range of 1073-1373 K.

II. EXPERIMENTAL PROCEDURE

A. Materials and Sample Preparation

Puratronic rods of titanium, 99.999 %, puratronic ingot of aluminum, 99.999 %, and puratronic rod of niobium, 99.99 % were used to prepare the Ti_3Al-Nb alloy samples. The samples were cut using a Sutter saw. The samples were placed inside an arc-melter and the current of the melter was adjusted to ensure melting. The samples were re-melted for a total of three times to enable a homogeneous mixture. The chemical analysis of the alloy ingot is: titanium: 67.73 at %, aluminum: 29.44 at %, niobium: 2.63 at %, and oxygen: 0.2 at %. The alloy will henceforth be referred to as Ti_3Al-2.63 at % Nb alloy in the remainder of the text.

After allowing the samples to cool, they were removed from the arc-melter and were ground using the grinder to remove any contaminants from the arc-melter tray. After grinding the alloy ingots, weighing about 100 g, they were wrapped in Zr foil and were sealed in a quartz tube under vacuum. The quartz capsules containing the samples were heat-treated at 1273 K for seven days. After heat treatment the samples were cut using an EDM wire cutting machine. Experimental specimens of the dimensions approximately equal to 5 mm × 5mm × 2 mm were cut from the alloy samples. The pieces were polished with #240 grit and #600 grit SiC papers and then cleaned ultrasonically in acetone before using for oxidation experiments.

B. Oxidation Experiments

Isothermal oxidation experiments were conducted using a Perkin Elmer® Thermogravimetric Analysis (TGA 7 HT) apparatus along with a dedicated data acquisition system called Pyris. TGA 7 HT apparatus can be used for oxidation/reduction/decomposition studies up to a temperature of 1473 K. The experimental sequence (heating/isothermal/cooling) fed into the Pyris data acquisition program. The polished alloy specimens were placed in a platinum pan provided in the apparatus. Ultra high pure oxygen (99.999 % purity) is used as the experimental gas for the experiment. The high temperature furnace is lowered and raised by pneumatic control. The procedure given for the apparatus is followed to start up the experimental sequence. After each experimental run the samples are carefully removed from the platinum pan and secured for further analysis. Experiments were carried out for at least 24 hours at all temperatures in the range of 1073 – 1373 K. The oxidation products were characterized by Philips X-ray Diffractometer.

III. RESULTS AND DISCUSSION

A. Oxidation Kinetics

Weight gain per unit surface area as a function of time for the Ti_3Al-2.63 at % Nb alloy oxidized in pure oxygen at different temperatures is plotted in Fig. 1. With increase in temperature the slope of weight gain *vs.* time curve also increases. At 1373 K the weight gain curve shows distinctly several slopes indicating the typical stages that are observed during the oxidation of Ti-Al based alloys containing third elements such as Nb, Mo, etc. It has been known that when a third element is added to the Ti-Al alloys, especially Ti_3Al and TiAl intermetallic phases, the oxidation curves at higher temperatures may consist of three stages /27/. At

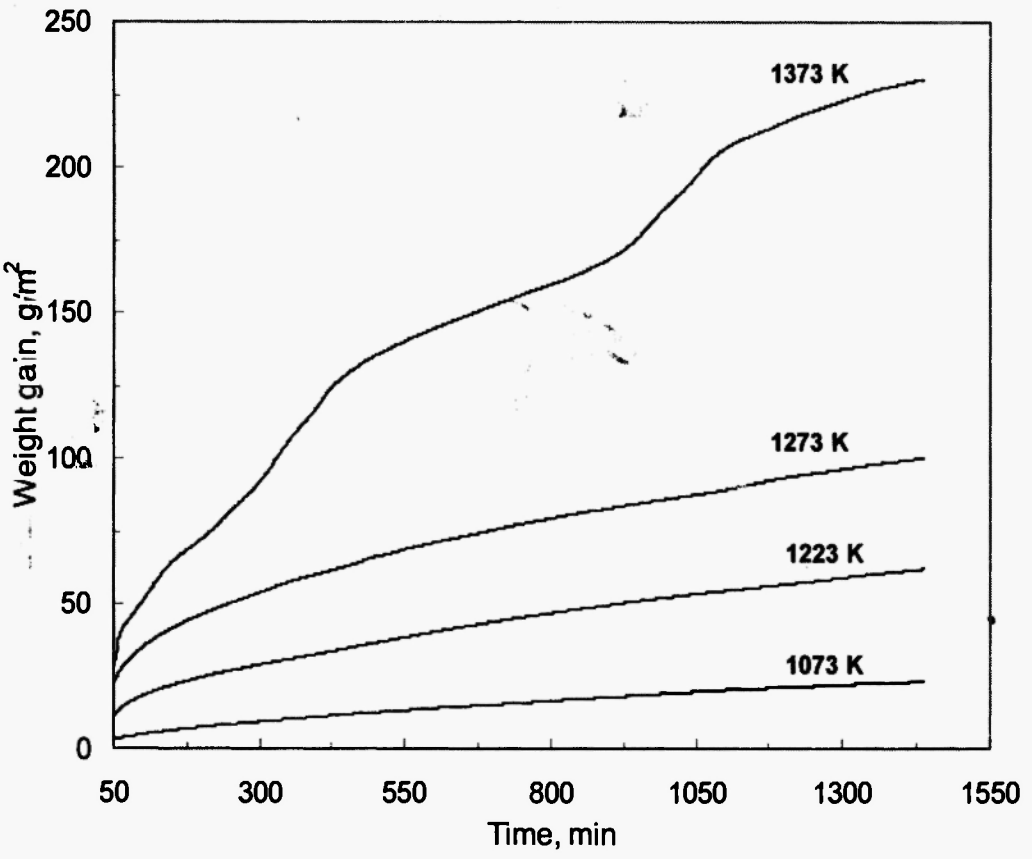

Fig. 1: Weight gain *vs.* time for Ti_3Al-2.63 at % Nb alloy oxidized in pure dry oxygen at different temperatures.

lower temperatures the monotonic weight gain with time is attributed to the formation of Al_2O_3 layer which grows very slowly. However, at high temperatures, the oxidation proceeds with the formation of oxides of both Al and Ti. The formation of TiO_2 beneath the Al_2O_3 layer leads to stresses due to the large volume increase of TiO_2 crystal growth yielding micro-cracks in the oxide scale. The growth of these micro-cracks can lead to partial breaking of the oxide scale which results in further increase in oxidation rate. In the present study a similar phenomena takes place at 1373 K which results in variations in weight gain as a function of time.

Figure 2 shows the comparison of oxidation curves between the present alloy and that of the binary Ti-32 at % Al alloy reported in an earlier study /12/. A marked improvement in the oxidation resistance of the present alloy over that of the Ti-32 at % Al alloy is seen due to the addition of small amounts of niobium.

The experimental data obtained during the oxidation of Ti_3Al-2.63 at % Nb alloy samples in pure oxygen can be expressed by the parabolic rate equation given by:

$$\left(\frac{dW}{S}\right)^2 = k_p\, t \qquad (1)$$

where k_p is called the parabolic rate constant, $\left(\frac{dW}{S}\right)$ is the weight gain per unit surface area of the specimen, and t is time. At each temperature of measurement, the square of weight gain per unit surface area is plotted as a function of time. This plot is a straight line for a perfect parabolic weight gain. At low temperatures, the above plot follows a straight line for the whole period of time. At high temperature, for example 1373 K, the weight gain square plot *vs.* time shows segments of straight line portions. We chose the initial period of oxidation to evaluate the parabolic rate constant. This

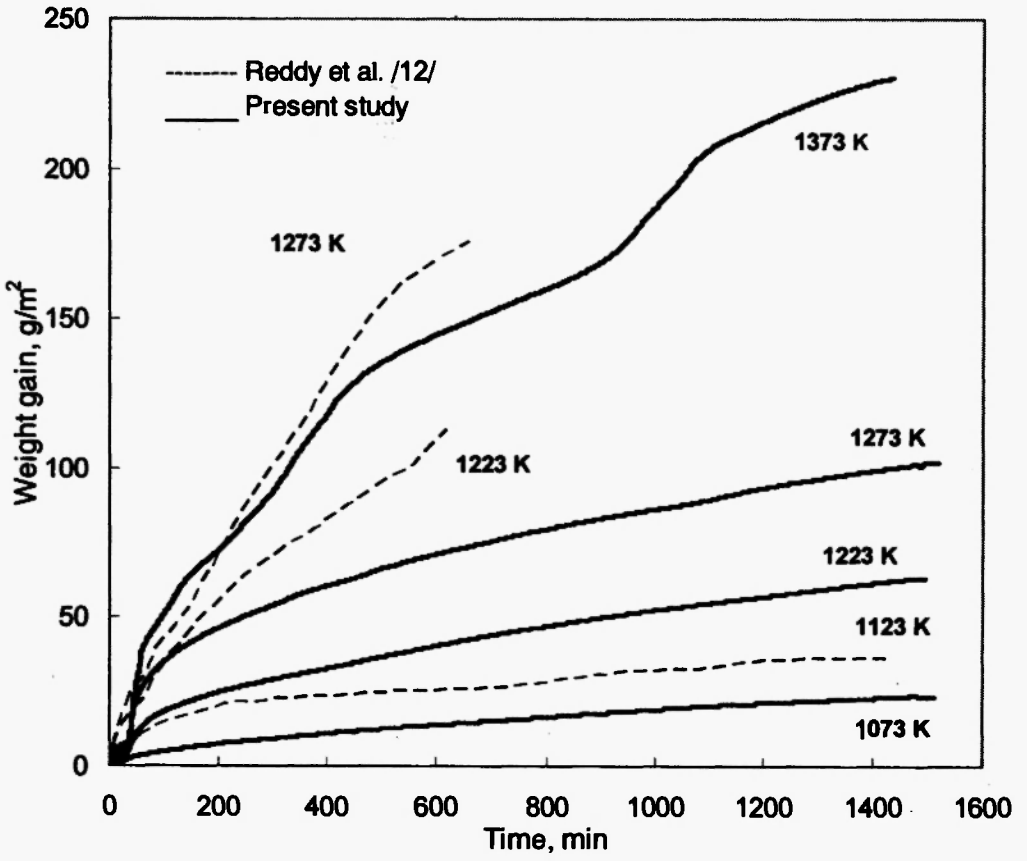

Fig. 2: Comparison of the oxidation data of Ti_3Al-2.63 at % Nb alloy and that of a previous study /12/ in pure oxygen at different temperatures.

procedure is followed in cases where the oxidation curve does not follow a straight line for the entire time of the experiment.

The error involved in the experimental oxidation curve at high temperature cannot be estimated since there are several parameters such as sample preparation, surface roughness, and fluctuation in gas flow rate during experiment, which influence the overall oxidation profile. To minimize these errors, at high temperatures we restrict our analysis to the initial portion of the oxidation profile curve where the curve follows the parabolic rate equation (1).

The slopes of the curves at different temperatures were plotted as a function of inverse of absolute temperature to determine the activation energy for oxidation. The parabolic rate constant estimated from the parabolic portion of the weight gain curve at various temperatures is plotted in Fig. 3. The effective activation energy of 193 kJ/mol was deduced from this plot. Table 1 lists the effective activation energies for oxidation obtained for the present alloy along with those of the Ti-Al binary alloys obtained from the literature /9,12,13,23/. A range of activation energies for the oxidation of binary Ti_3Al in oxygen, air and in SO_2 environments have been observed due to the activity of oxygen in the respective environments and several other factors such as alloy homogeneity and sample preparation.

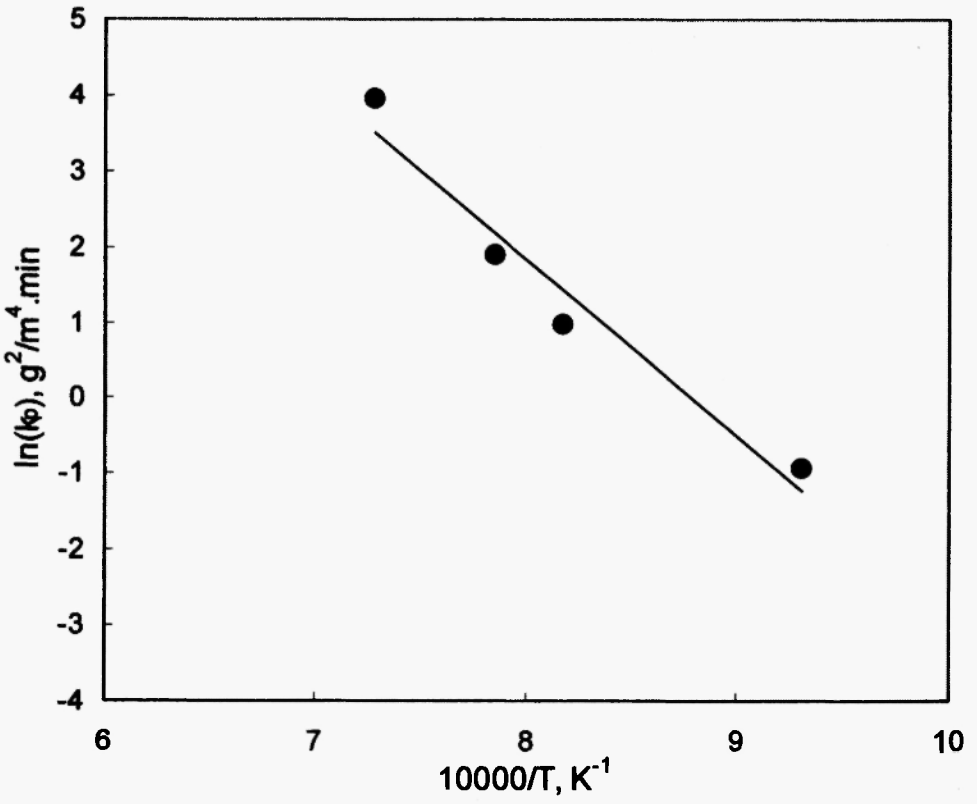

Fig. 3: ln (k_p) *vs.* 10^4/T for Ti_3Al-2.63 at % Nb alloy oxidized in pure dry oxygen.

Table 1

Comparison of effective activation energies of oxidation of Ti_3Al-Nb ternary alloy with some Ti-Al binary alloys

Alloy	*Reference*	Q_{eff}, *kJ/mol*
Ti-25at % Al	Roy *et al.* /23/	289
Ti-26 at % Al	Welsch and Kahveci /9/	255
Ti_3Al-2.63 at % Nb	This work	193
Ti-32 at % Al	Reddy *et al.* /12/	295
Ti-34 at % Al	Welsch and Kahveci /9/	299
Ti-32.3 at % Al	Mantha *et al.* /13/	313

B. Phase Analysis Using XRD Patterns

Figure 4 shows the XRD pattern of the Ti_3Al-2.63 at % Nb alloy oxidized at 1073 K for 24 hours in pure oxygen. Very little alumina was formed at this temperature of measurement after 24 hours and hence the pattern reveals only the presence of TiO_2 as the major oxide formed and some peaks of the base alloy (Ti_3Al). At 1223 K, the pattern is very similar to that obtained at 1073 K after 24 hours except that the intensity of peaks of TiO_2 was low as seen from Fig. 5.

Figure 6 shows the XRD pattern of the alloy oxidized in pure oxygen at 1273 K for 24 hours. Al_2O_3 peaks were visible in the oxide scales and the peaks of TiO_2 were lower in intensity. As the temperature increased from 1073 to 1273 K, the oxide scale consisted of a mixture of TiO_2 and Al_2O_3. Figure 7

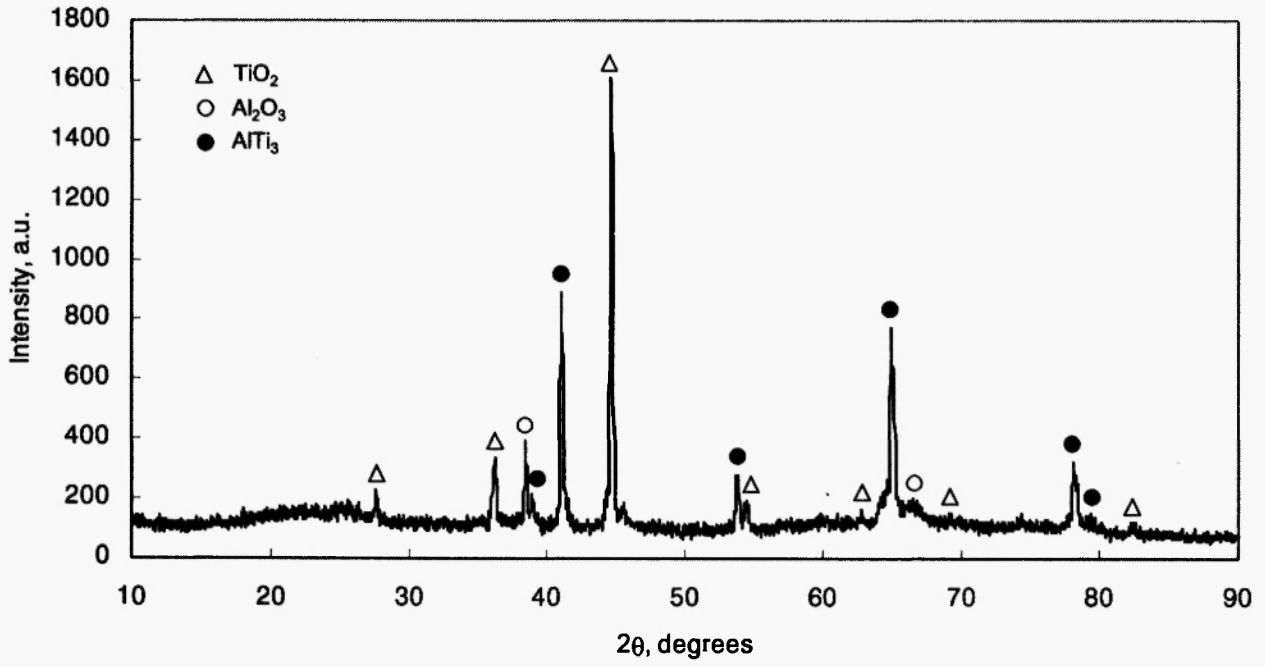

Fig. 4: XRD pattern of Ti_3Al-2.63 at % Nb alloy oxidized in pure oxygen at 1073 K for 24 hours.

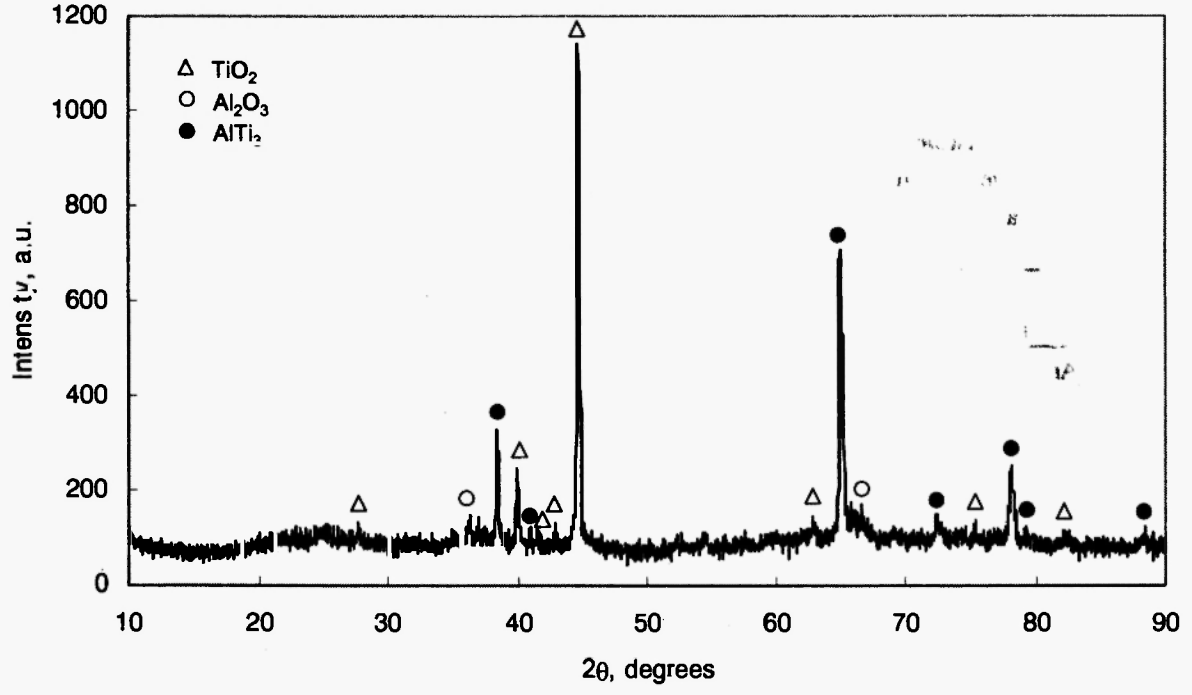

Fig. 5: XRD pattern of Ti_3Al-2.63 at % Nb alloy oxidized in pure oxygen at 1223 K for 24 hours.

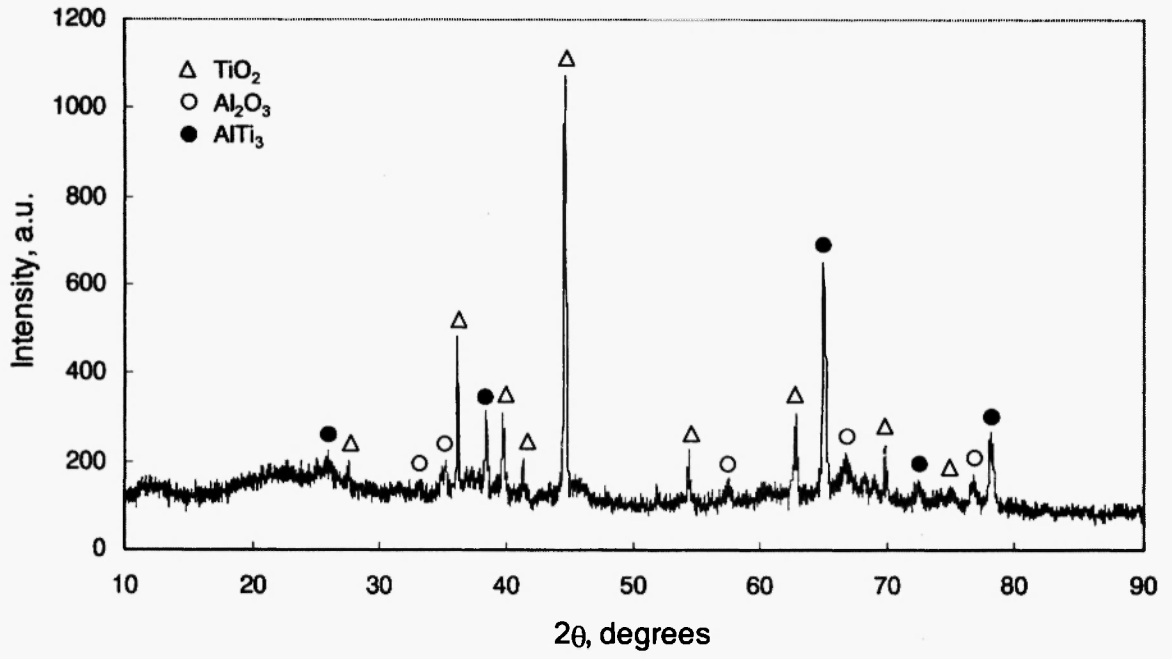

Fig. 6: XRD pattern of Ti_3Al-2.63 at % Nb alloy oxidized in pure oxygen at 1273 K for 24 hours.

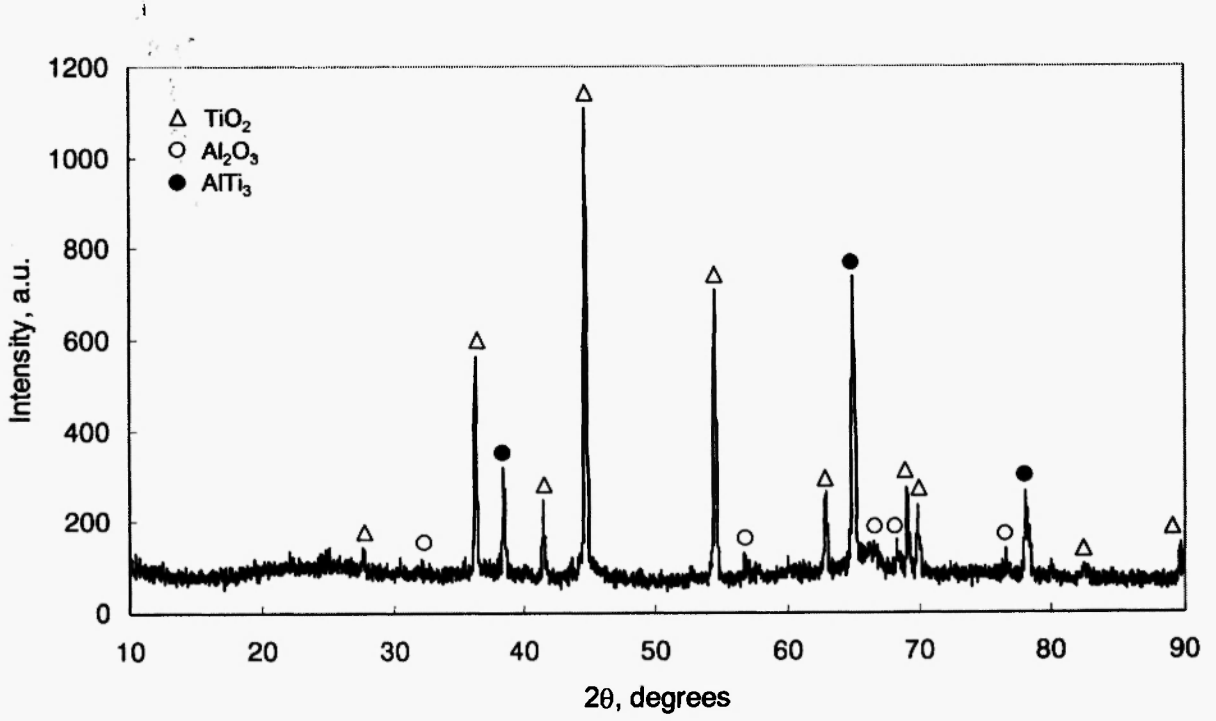

Fig. 7: XRD pattern of Ti_3Al-2.63 at % Nb alloy oxidized in pure oxygen at 1373 K for 24 hours.

shows the XRD pattern of the oxidized alloy at 1373 K for 24 hours in pure oxygen. An identical pattern was observed to that of Fig. 5 except for variation in the intensities. From the overall analysis of the oxidation study of Ti_3Al-2.63 at % Nb alloy in pure oxygen for 24 hours, it can be concluded that the oxide scale formed on the alloy was a mixture of TiO_2 and Al_2O_3 with variation in the amounts characterized by the variation in their intensities as observed from the XRD patterns. Ternary oxides or the oxides of Nb were not formed and so were not detected by the X-ray analysis.

IV. CONCLUSIONS

1. Oxidation kinetics of Ti_3Al-2.63 at % Nb alloy in pure oxygen exhibited improved resistance over the binary Ti_3Al alloy. Effective activation energy of 193 kJ/mol was deduced from weight gain data.
2. The oxidation products identified in the scales consisted of mainly TiO_2 (rutile) and Al_2O_3 (alumina) in the temperature range of 1073 to 1373 K.
3. XRD analysis revealed that the products of oxidation were TiO_2 and Al_3O_3. Base alloy (Ti_3Al) peaks were also visible in the patterns.
4. Addition of niobium improved the oxidation resistance of Ti_3Al alloy but did not provide adherent oxide scales as indicated by the XRD patterns at all temperatures of measurement.

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