Effect of Nb and Mo on the Oxidation Rates of Ti-Al Intermetallics

M Ramachandran¹ and R G Reddy^{2,1}

¹Graduate Student, ²ACIPCO Professor and Head
Department of Metallurgical and Materials Engineering
The University of Alabama, Tuscaloosa, AL 35487, USA

(Received December 16, 2008; final form January 9, 2009)

ABSTRACT

The use of Ti-Al intermetallics has increased in various practical applications due to its improved mechanical properties but for the oxidation resistance. Oxidation studies were carried out in pure oxygen by alloying niobium and molybdenum to Ti₃Al intermetallic. The composition of niobium was varied from 1.1 at.% to 4.0 at.% while the molybdenum's composition was varied between 1.0 at.% and 2.9 at.%. A thermodynamic analysis was carried out to determine the most stable oxide phases. It is seen that TiO₂ and Al₂O₃ are formed by using Ti₃Al and TiAl₃ respectively, while the effect of Nb- and Mo- addition increased the formation of mixed layers with TiO₂ and Al₂O₃, which is substantiated using XRD and SEM. Ti₃Al with 2.9 at.% Nb and 4.0 at.% Nb showed a formation of oxide scale rich in Al₂O₃. The activation energies of these oxidation reactions were determined to be 370.5 kJ/mol and 160 kJ/mol for Ti₃Al-4.0 at.% Nb and Ti₃Al-2.9 at.% Mo respectively.

intermetallics, TiAl₃ forms a continuous α -Al₂O₃ protective scale /1-4/ while Ti₃Al has the highest solubility of oxygen /5/, which also stabilizes the α_2 phase. Low density, high-temperature creep resistance and specific modulus of Ti₃Al has increased its interest and alloying studies with Cr, Mn, Nb, etc., have shown an increase in the oxidation resistance. The high temperature strength of these materials is through the protective oxide layer formation. Oxidation kinetics of the Ti-Al intermetallics has been investigated in various environments such as air, and pure oxygen /2-12/ while oxidation / sulfidation of metals and alloys have been tested in sulfur containing environments such as SO₂ /13-21/.

Numerous studies with the effect of alloying elements have been reported /22,23/ but the effect of alloying niobium and molybdenum in a wide composition range is reported here. Niobium varied from 1.1 at.% - 4.0 at.% and molybdenum varied from 1.0 at.% to 2.9 at.% in the Ti₃Al intermetallic compound. The thermodynamic stability of the titanium and aluminum oxides is compared with that of the oxides of the alloying elements.

1. INTRODUCTION

Titanium aluminide intermetallic compounds have numerous applications as high temperature materials which lead to a fundamental material-property relationship study. Of the compounds in the Ti-Al

2. EXPERIMENTAL

Ti₃Al micro-alloyed with either niobium or molybdenum was prepared from 99.999% pure titanium

¹ Corresponding Author. Tel.: +1 (205)348-4246; Fax: +1 (205)348-2164; E-mail address: rreddy@eng.ua.edu

rods, 99.99% pure aluminum ingots, 99.9% pure molybdenum rods or 99.999% pure niobium rods (Alfa Aesar, MA, USA) by arc melting stoichiometric quantities in a copper crucible under ultra-high purity argon atmosphere. The surface of the micro-alloyed Ti_3Al ingots were ground and were subsequently heat treated by wrapping in tantalum foil and encasing in quartz tubes at 1273 K under vacuum. The heat treated ingots were cut into 5mm $\times$ 5mm $\times$ 2mm tokens and were used in the oxidation studies. A thin piece from each of the sample ingots were sliced and used for X-Ray Diffraction (XRD) analysis. The intermetallic, Ti_3Al , was micro-alloyed with 1.1, 1.34, 2.63 and 4.0 at.% Nb and 1.0, 1.7, 2.2, and 2.9 at.% Mo.

3. RESULTS

3.1 Thermodynamics

The feasibility of oxidation depends on both the thermodynamics and the kinetics of the reaction. The formation of an oxide scale of a particular element depends on the Gibbs energy of its oxidation reaction. An analysis of Gibbs energy for the oxidation of various elements using a simulation software [24] is given in Table 1. A micro-alloying element or a component added to the intermetallic has to favor the formation of

the targeted protective oxide layer, while the quantity of the micro-alloying element should be maintained at a minimum so as to not form an oxide layer of its own. This can be done by a comparison of the Gibbs energies of formation of oxides from its elements.

3.2 Determination of reaction rates

The oxidation of Ti-Al intermetallics and those alloyed with Nb and Mo follow parabolic form of rate equation. The specific weight gain or the weight gain per unit area of all the samples are fitted to parabolic rate law using one of the following equations.

$$\left(\frac{\Delta W}{S}\right)^2 - k_p t \quad (1)$$

$$t = A + B\left(\frac{\Delta W}{S}\right) + C\left(\frac{\Delta W}{S}\right)^2 \quad (2)$$

$(\Delta W/S)$ represents the weight gain per unit area and t represents the time. A, B and C are constants, in which, the reciprocal of the constant C represents the inverse of the parabolic rate constant (k_p). Hence $C = (1/k_p)$.

A plot of $\ln(k_p)$ vs. $1/T$ is shown in Figures 1, 2 and 3 for various binary Ti-Al intermetallics and microalloyed Ti_3Al compounds. A comparison of the rate constants for the oxidation of Ti-Al intermetallics in pure oxygen and in an argon-5% SO_2 atmosphere is shown in Figure 1. TiAl_3 forms predominantly an oxide scale of Al_2O_3 , while Ti_3Al forms TiO_2 as the predominant oxide scale. When an argon atmosphere with 5% SO_2 was used to determine the oxidation resistance of Ti_3Al , the only product scales formed were TiO_2 and Al_2O_3 . No sulfur containing compounds were detected in the scales. As we know from the thermodynamic calculations, the formation of Al_2O_3 . TiO_2 will be inevitable due to the presence of equi-abundance of Al and Ti. The binary Ti-48.6Al alloy forms an oxide scale comprising various oxides such as TiO , TiO_2 , Ti_2O_3 and Al_2O_3 . The reaction rates, from Figure 1, for the oxidation of TiAl_3 and Ti_3Al are much lower compared to that of Ti-48.6Al and Ti_3Al in argon-5% SO_2 atmosphere, which could be attributed to various types of oxides that are formed. Ti_3Al , which

Table 1

Gibbs energy of reaction for the oxidation of elements

Compound	ΔG (kJ)			
	1023 K	1123 K	1223 K	1373 K
Al_2O_3	-1353.33	-1320.13	-1287.03	-1237.55
Nb_2O_5	-1452.81	-1411.18	-1369.84	-1308.32
NbO_2	-609.12	-592.23	-575.81	-551.49
NbO	-326.75	-318.04	-309.38	-296.49
Ti_2O_3	-1235.38	-1209.64	-1183.59	-1144.71
TiO_2	-758.60	-740.99	-723.17	-696.41
TiO	-444.23	-435.09	-425.77	-412.20
MoO_2	-403.58	-386.49	-369.58	-344.54
MoO_3	-487.66	-466.21	-447.48	-420.04
Mo_4O_{11}	-1736.08	-1616.81	-1495.60	-1310.41
Mo_9O_{26}	-3909.65	-3603.20	-3290.30	-2809.83
Al_2O_3 . TiO_2	-2108.09	-2058.30	-2008.39	-1933.73

has the lowest oxidation rate, was alloyed with other elements to determine the feasibility of formation of a protective and adherent Al_2O_3 scale. The rate constants of Nb- and Mo- alloyed Ti_3Al as a function of $1/T$ is shown in Figures 2 and 3 respectively.

Fig. 1: $\ln(k_p)$ vs. $1/T$ for various Ti-Al intermetallics in pure oxygen and Ar + 5% SO_2 mixture.

Fig. 2: $\ln(k_p)$ vs. $1/T$ for Nb-alloyed Ti-Al intermetallics.

Fig. 3: $\ln(k_p)$ vs. $1/T$ for Mo-alloyed Ti-Al intermetallics.

3.3 Phase analysis and morphology

The phase analysis was done using X-Ray Diffraction (XRD). The micro-alloyed TiAl intermetallic was tested for proper phase formation, while the oxidized product was tested to determine the oxide phase formed. Figures 4 – 9 show a variation of the oxide phase formed with the increase in temperature for the $\text{Ti}_3\text{Al-2.9Mo}$ sample. The base metal alloy Ti_3Al is seen in a pronounced quantity in the sample oxidized at 1023 K. It also has a trace of TiO_2 as can be seen in Figure 4. As the temperature is increased to 1073, 1123, and 1173 K, the formation of Al_2O_3 is predominant (Figures 5, 6, and 7) with trace amounts of TiO_2 and Ti_3Al . Figure 8 shows the XRD pattern obtained from the sample oxidized at 1223 K. It shows an increased formation of TiO_2 with Al_2O_3 being the major phase. Above 1223 K, the formation of TiO_2 is favored which can be seen from the increased TiO_2 peaks in the XRD spectra in Figure 9. Hence, the formation of Al_2O_3 is favorable at temperatures at or below 1223 K while TiO_2 is the major oxidation product above 1223 K.

The morphology of the oxide layer formed helps in the determination of the type of oxide layer formed. Al_2O_3 forms a dense fine-grained protective layer over Ti-Al intermetallics while TiO_2 forms coarser or platelet like structures. Figures 4 – 9 show the morphology of oxide layers formed along with the XRD spectra for every temperature of interest in this study. The

morphological results obtained from SEM corresponds to the phase analysis obtained from XRD. The formation of Al_2O_3 particles of 200 – 500 nm in size is observed at 1023 K with finely interdispersed TiO_2 . The oxidation product at 1073, 1123, and 1173 K is Al_2O_3 with increasing particle size (1-5 μm) and a formation of a continuous protective scale (Figures 5, 6 and 7). Figure 8 shows the formation of platelet like TiO_2 as the oxidation product at 1223 K while Figure 9, the oxidation product at 1373 K shows TiO_2 particles ranging from 2 – 6 μm with a porous microstructure. These platelet like or large grained structure of TiO_2 forms an easier diffusion path for the transfer of oxygen, leading to a faster oxidation kinetics.

Fig. 4: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1023 K.

Fig. 5: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1073 K.

Fig. 6: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1123 K.

Fig. 8: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1223 K.

Fig. 7: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1173 K.

Fig. 9: XRD pattern and corresponding SEM micrograph of $\text{Ti}_3\text{Al-2.9Mo}$ alloy oxidized at 1373 K.

4. DISCUSSION

The Gibbs energy for the formation of the oxides from individual elements shows that Mo_9O_{26} and Mo_4O_{11} have extremely low values in the temperature range of interest in this study, but require 9 and 4 moles of Mo respectively. Hence, formation of these oxides is not favorable in any of the Mo compositions studied (1.0 to 2.9 at.%). Even though the formation of MoO_2 and MoO_3 is possible at low Mo concentrations and the presence of excess oxygen, the Gibbs energies of formation are relatively higher compared to that of Al_2O_3 and TiO_2 making them thermodynamically unfavorable. Niobium oxides, Nb_2O_5 , NbO_2 and NbO , also have Gibbs energies of oxidation higher than that of Al_2O_3 and TiO_2 in the temperature range of this study and hence is not favorable thermodynamically. The formation of one or more of the following oxides, TiO_2 , Al_2O_3 , $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$, is more favorable due to the presence of excess molar quantities of Ti and/or Al. Thus the analysis using the concept of minimization of Gibbs energy of the system helps in determining oxides that are thermodynamically stable in the temperature range of 1023 - 1373 K.

Based on the results obtained from the thermodynamic analysis of the oxidation of elements, Ti_3Al was alloyed with varying percentages of niobium.

The amount of niobium addition to the intermetallic was kept to a minimum, to ensure no presence of Nb_2O_5 , which is thermodynamically stable. As can be seen from Figure 2, no specific trend in the variation of the oxidation rates with the percentage of alloy addition was observed. The compositions $\text{Ti}_3\text{Al-1.1Nb}$ and $\text{Ti}_3\text{Al-1.34Nb}$ had both TiO_2 and Al_2O_3 present in them, while TiO_2 was observed predominantly in the composition $\text{Ti}_3\text{Al-2.63Nb}$, with small amounts of Al_2O_3 . In the case of $\text{Ti}_3\text{Al-4.0Nb}$, temperature plays a major role in the composition of the oxide layers formed. Al_2O_3 was observed predominantly in the temperature range of 1073 – 1173 K and above 1173 K, TiO_2 was observed predominantly in the oxide scale. This can also be observed in the $\ln(k_p)$ vs. $1/T$ curve for $\text{Ti}_3\text{Al-4.0Nb}$, which shows lines with varying slopes above and below 1173 K. The $\text{Ti}_3\text{Al-4.0Nb}$ composition also has the lowest oxidation rates compared to its counter parts.

Figure 3 shows the effect of Mo-addition to Ti_3Al on its oxidation rates. Similar to that of Nb addition, no specific dependance was observed on the oxidation rates with increasing amounts of Mo in the alloy. The composition of the product oxide layer formed, on the other hand, does follow a trend with the amount of Mo addition. In the case of $\text{Ti}_3\text{Al-1.0Mo}$, the surface oxide layer formed was TiO_2 while an interdispersed phase of Al_2O_3 and TiO_2 was observed in between the surface oxide scale and the base Ti_3Al . The compositions $\text{Ti}_3\text{Al-1.7Mo}$ and $\text{Ti}_3\text{Al-2.2Mo}$ show a presence of both TiO_2 and Al_2O_3 on the oxide scale. As in the case of $\text{Ti}_3\text{Al-4.0Nb}$ alloy, the $\text{Ti}_3\text{Al-2.9Mo}$ alloy also shows a temperature dependence on the predominance of the oxide formed. Temperatures of 1173 K and below show the formation of small grained alumina, while temperatures above 1173 K forms a large grained rutile.

$$\ln(k_p) = \ln(k_0) - \left(\frac{Q}{R}\right)\left(\frac{1}{T}\right) \quad (3)$$

The oxidation of Ti-Al based intermetallics follows an Arrhenius form of relationship for the dependance of its reaction rates on temperature. This is represented in its linearized form in equation (3). k_p , in equation (3), is the parabolic rate constant, Q , the activation energy, R , the gas constant, T , the temperature, and k_0 , a constant. The activation energies of the oxidation processes were calculated from the slopes of the $\ln(k_p)$ vs. $1/T$ plots

shown in Figures 1 – 3. A tabulation of the activation energies along with the experimental temperature ranges is shown in Tables 2, 3, and 4.

Table 2

Activation energies of oxidation for Ti-Al intermetallics

Material	Activation Energy (Q), kJ/mol	Temperature Range (K)	Reference
TiAl ₃	64.7	1123 – 1273	/6/
Ti ₃ Al	292.2	1023 – 1273	/7/
Ti-48.6Al	404.0	1123 – 1273	/8/
Ti ₃ Al (in Ar – 5%SO ₂)	313.0	1123 – 1273	/13/

Table 3

Activation energies of oxidation for Ti-Al intermetallics with Nb addition

Material	Activation Energy (Q), kJ/mol	Temperature Range (K)	Reference
Ti ₃ Al-1.1Nb	297.0	1023 – 1223	/25/
Ti ₃ Al-1.34Nb	288.0	1073 – 1373	/26/
Ti ₃ Al-2.63Nb	193.0	1073 – 1373	/27/
Ti ₃ Al-4.0Nb	370.5	1023 – 1173	/28/
	97.9	1173 – 1373	

Table 4

Activation energies of oxidation for Ti-Al intermetallics with Mo addition

Material	Activation Energy (Q), kJ/mol	Temperature Range (K)	Reference
Ti ₃ Al-1.0Mo	290.0	1023 – 1173	/25/
Ti ₃ Al-1.7Mo	234.8	1073 – 1373	/29/
Ti ₃ Al-2.2Mo	154.9	1073 – 1373	/29/
Ti ₃ Al-2.9Mo	160.0	1023 – 1173	/25/
	371.0	1173 – 1373	

The activation energies for the oxidation process in Ti-Al intermetallics are relatively higher for oxide scales with TiO₂ in them. The activation energy for the oxidation of Ti₃Al in an argon-5%SO₂ atmosphere is slightly higher than that of pure oxygen. This substantiates the relative increase in the activation energy with the formation of TiO₂ in the product scale for Ti-Al intermetallics. On the contrary, the activation energy decreased with increased TiO₂ content in the oxide scale for Nb-alloyed Ti₃Al compositions. It is difficult to generalize the trend of activation energy in the case of Ti₃Al-Mo compositions due to the formation of interdispersed Al₂O₃ and TiO₂ in the oxide layer and the distinct TiO₂ layer formation in the Ti₃Al-1.0Mo composition. Although, the Ti₃Al-2.9Mo shows an increase in the activation energy when the formation of TiO₂ is predominant. This anomaly could possibly be explained in terms of the solid state diffusion of oxygen in the oxide layer and the microstructure of the formed scales.

5. CONCLUSIONS

Niobium and molybdenum were tested as alloying elements in Ti₃Al, a Ti-Al intermetallic compound. Ti₃Al-4.0Nb and Ti₃Al-2.9Mo both show a predominant formation of alumina (Al₂O₃) protective oxide scale at temperatures of 1173 K and below. The corresponding activation energies of the oxidation reactions were 370.5 kJ/mol and 160 kJ/mol for Ti₃Al-4.0Nb and Ti₃Al-2.9Mo respectively. The oxidation resistance of Ti₃Al intermetallic has improved due to the addition of the Nb and Mo alloying agents. The formation of the oxides (Al₂O₃ and TiO₂) was substantiated using XRD and SEM. Ti₃Al-2.9Mo shows improved oxidation resistance with lower activation energy and the formation of Al₂O₃ protective layer.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the financial support for this research by National Science Foundation, Grant Nos. DMR-0312172 and DMR-

9696112, and The University of Alabama. The authors would also like to acknowledge Dr. Divakar Mantha, Mr. Chris Williams and Ms. Dusti Livingston for their contribution to this study.

REFERENCES

1. R. G. Reddy, *Journal of Metals (JOM)*, **54** (2), 65-67 (2002).
2. J. Subrahmanyam, *J. Mater. Sci.*, **23**, 1906-1910 (1989).
3. N. Birks, G. H. Meier, and F. S. Pettit, *JOM*, **12**, 42-46 (1994).
4. J. L. Smialek, *Scripta Metall. Mater.*, **26**, 1763-1768 (1992).
5. R. E. Schafrik, *Metall. Trans. B*, **7B**, 713-716 (1976).
6. R. G. Reddy, X. Wen and C. I. Okafor, *Metall. Trans. A*, **31A**, 3023-3028 (2000).
7. R. G. Reddy, X. Wen and I. C. Okafor, *Metall. Trans. A*, **32A**, 491-495 (2001).
8. R. G. Reddy, X. Wen and M. Divakar, *Metall. Trans. A*, **32A**, 2357-2361 (2001).
9. J. L. Smialek, *Corr. Sci.*, **35** (5-8), 1199-1208 (1993).
10. X. Wen and R. G. Reddy, *Processing and Fabrication of Advanced Materials*, TMS (The Minerals, Metals & Materials Society), Warrendale, PA, (1996) p.379-389.
11. G. Welsch and A. I. Kahveci, *Oxidation of High-Temperature Intermetallics*, edited by T. Grobstein, J. Doychak, TMS, Cleveland, OH, (1988), p. 207-218.
12. G. H. Meier, D. Appalonia, R. A. Perkins, and K. T. Chiang, *Oxidation of High-Temperature Intermetallics*, edited by T. Grobstein, J. Doychak, TMS, Cleveland, OH (1988), p. 185-193.
13. D. Mantha, X. Wen and R. G. Reddy, *High Temp. Mater. Process*, **23** (2), 93-101 (2004).
14. K. N. Strafford, *Metall. Rev. (Review 138)*, **14**, 153-174 (1969).
15. K. N. Strafford and P. K. Datta, *Mater. Sci. and Tech.*, **5**, 765-779 (1989).
16. S. Mrowec, *High Temp. Mater. Process*, **22** (1), 1-24 (2003).
17. H. Mitsui, H. Habazaki, K. Hashimoto, and S. Mrowec, *Corr. Sci.*, **39** (1), 59-76 (1997).
18. H. Mitsui, H. Habazaki, K. Hashimoto, and S. Mrowec, *Corr. Sci.*, **39** (1), 9-26 (1997).
19. H. Mitsui, H. Habazaki, K. Hashimoto, and S. Mrowec, *Corr. Sci.*, **39** (9), 1571-1583 (1997).
20. H. Mitsui, H. Habazaki, K. Asami, K. Hashimoto, and S. Mrowec, *Corr. Sci.*, **38** (9), 1431-1447 (1996).
21. H. Habazaki, H. Mitsui, K. Ito, K. Asami, K. Hashimoto, and S. Mrowec, *Corr. Sci.*, **44**, 285-301 (2002).
22. R. G. Reddy, Y. Li and M. F. Arenas, *High Temp. Mater. Process*, **21** (4), 195-205 (2002).
23. R. G. Reddy, X. Wen, and D. Mantha, *High Temp. Mater. Process*, **22** (2), 73-85 (2003).
24. Ronie, A, *HSC Chemistry 5.11*, Outokumpu Research Oy, Pori, Finland.
25. C. Williams, M.S. Thesis, The University of Alabama, Tuscaloosa, AL, 2008.
26. D. Livingston, D. Mantha, and R. G. Reddy, *High Temp. Mater. Process*, **25** (3), 121-128 (2006).
27. D. Livingston, D. Mantha, and R. G. Reddy, *High Temp. Mater. Process*, **24** (4), 259-267 (2005).
28. C. Williams, D. Mantha, and R. G. Reddy, *Innovations in Titanium Technology: Microstructure and Properties II*, edited by M. N. Gungor, M. A. Imam, F. H. Froes, TMS, Warrendale, PA, (2007), p. 235-244.
29. D. Livingston, D. Mantha and R. G. Reddy, *Titanium Alloys for High Temperature Applications – A Symposium Dedicated to the Memory of Dr. Martin Blackburn*, edited by M. Peretti, D. Eylon, U. Habel, and G. C. Keijzers, TMS, Warrendale, PA, (2006), p. 113-122.