Effect of Niobium Addition on the Oxidation Behavior of a Ti₃Al Alloy

R. G. Reddy^{*1}, Y. Li⁺ and D. Mantha⁺⁺

**ACIPCO Professor, ⁺Graduate Student, and ⁺⁺Research Associate
Department of Metallurgical and Materials Engineering
The University of Alabama, Tuscaloosa, AL 35487-0202, USA*

(Received July 8, 2003)

ABSTRACT

The effect of niobium on the oxidation behavior of a Ti₃Al alloy was studied in pure oxygen in the temperature range of 1123–1373 K. The experiments were carried out using Thermogravimetric Analysis (TGA) apparatus. The oxidation curves for the alloy followed parabolic law. Effective activation energy of 284 kJ/mol was deduced for the oxidation of Ti₃Al-Nb alloy. The oxidation products were analyzed using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) techniques. The oxidation products were mainly the mixture of TiO₂ (rutile), TiO, and Al₂O₃ (alumina) with small amount of niobium oxide. Oxidation resistance of Ti₃Al was found to have been improved by the addition of niobium. Layered structure comprising of a mixture of rutile and alumina was observed on the oxide scale of the Ti₃Al-Nb alloy at temperatures higher than 1273 K.

1. INTRODUCTION

Intermetallic compounds in the Ti-Al system have received great attention due to their unique properties of low density, good creep resistance and high temperature strength [1-4]. However, lack of sufficient resistance to oxidation at elevated temperatures is a major concern in

the applicability of these materials for various high temperature applications. Several investigations [5-10] have been carried out to study the oxidation behavior of the Ti-Al based intermetallics (Ti₃Al, TiAl and TiAl₃) both in air and in pure dry oxygen. Oxidation kinetics of TiAl₃ and Ti₃Al and subsequently the diffusion characteristics of the species present in the system have been studied [11-12].

Oxidation resistance of any alloy is based on the criterion that it forms a stable oxide layer, which protects the underlying alloy from further oxidation. There are several requirements that an oxide scale should meet so that it can be protective on the alloy. A continuous external oxide layer on an alloy must have (i) high thermodynamic stability, (ii) slow growth rate, (iii) adherence to the alloy and (iv) ease of formation/reformation. Al₂O₃ and SiO₂ oxides are stable and protective at high temperatures [13]. It was also reported in the literature [11] that a protective alumina layer could be formed on a TiAl₃ alloy when oxidized in a pure oxygen environment. In the case of Ti-Al alloys, the base metal oxide (TiO₂) has similar thermodynamic stability as that of Al₂O₃, and hence during the oxidation of these alloys, a protective layer of alumina exclusively may not be formed. 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

¹ Corresponding Author

Ti-Al alloys could improve the oxidation resistance significantly so as to enable their use up to about 1073 K /15/.

There have also been several studies on the effect of alloying additions such as Nb, Si on the oxidation resistance of Ti-Al based alloys /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/ also reported that alloying with niobium improves oxidation resistance of Ti-Al based alloys. Mixed scales consisting mainly of TiO₂ and Al₂O₃ along with small amounts of Nb oxides were observed in the oxidized scales of the Ti-Al based alloys with Nb additions. Sun *et al.* /21/ have studied the oxidation behavior of Ti₃Al 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.

The oxidation behavior of titanium aluminides with high niobium contents was reported in the literature /22/. They found that the oxidation resistance of titanium alloys did not improve with higher additions of niobium. They attributed the poor resistance of these alloys to formation of Nb₂O₅ in the oxide scale, which led to spallation of the scale. The study on the effect of addition of small amount of niobium to Ti₃Al alloy has been briefly mentioned by the author /23/. Interesting results were obtained at temperatures higher than 1273 K. This paper presents a detailed description of the influence of niobium addition on the oxidation resistance of Ti₃Al alloy in pure oxygen atmosphere.

II. EXPERIMENTAL PROCEDURE

A. Materials and Sample Preparation

Titanium wires of 99.9 pct purity, niobium and aluminum rods of 99.999 pct purity were used in this study. Ti₃Al-Nb alloy samples were prepared by repeatedly melting in a copper hearth using tungsten electrodes in purified argon. Aluminum was added to these melts in the form of rods. This was done to prevent the evaporation losses of the low melting aluminum at high temperatures. The chemical analysis of the alloy ingot is given in Table 1. The alloy will henceforth be referred to as Ti₃Al-Nb alloy in the

Table 1
Compositions of the Alloy Studied

<i>Alloy</i>	<i>Ti</i>	<i>Al</i>	<i>Nb</i>	<i>O</i>
Ti ₃ Al-Nb	67.47	29.65	2.68	0.20

remainder of the text. The Ti₃Al-Nb alloy ingot weighing about 50 g was homogenized at 1273 K for 100 hours in argon atmosphere. The homogenized ingot was cut into experimental coupons of approximately 10 mm diameter and 1.5 mm thickness using low-speed diamond saw. The coupons were polished using 600 grit emery papers and ultrasonically cleaned in acetone before being introduced into the furnace.

B. Oxidation Studies

Isothermal oxidation experiments were conducted using a Thermogravimetric (TGA) setup. The details of the setup and operation have been described elsewhere /24/. Each alloy coupon was suspended into a Kanthal-wound resistance furnace by means of a platinum wire from a continuously recording Cahn Model electro-balance. The electro-balance has a sensitivity of 1 µg and a capacity of 10 g. The specimens were suspended into the constant temperature zone of the furnace. The samples were heated under argon atmosphere at each temperature of measurement for 5 minutes after which pure dry oxygen was introduced into the furnace. The size of the sample enabled it to attain the furnace temperature in 2 minutes. The temperature was measured with an S-type thermocouple that was placed just beneath the specimen. The temperature difference between the ends of the specimen was ± 0.5 K.

The weight gain of the samples was measured via the electrobalance in the form of weight gain vs time and was recorded continuously by an X-Y recorder. Oxidation was assumed to have come to a completion when no further weight gain was observed. Samples were furnace cooled in argon atmosphere. Microstructure of oxidized region on the specimen surface was examined by Phillips XL30 Scanning Electron Microscope (SEM) equipped with Energy-Dispersive X-ray analysis (EDX). The oxidation products were characterized by Siemens D500 X-ray Diffractometer.

III. RESULTS AND DISCUSSION

A. Oxidation Kinetics

The experimental data obtained for the $\text{Ti}_3\text{Al-Nb}$ alloy samples can be expressed by the following parabolic rate equation:

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

where $\left(\frac{\Delta W}{S}\right)$ is the weight gain per unit surface area of the sample, k_p is the parabolic rate constant and t is the oxidation time. The temperature dependence of k_p is given by:

$$k_p = k_o e^{\left(-\frac{Q}{RT}\right)} \quad (2)$$

where k_o is a constant and Q is the effective activation energy for oxidation. Figure 1 shows the weight gained per unit surface area as a function of time for the $\text{Ti}_3\text{Al-Nb}$ alloy oxidized in pure oxygen at different temperatures. It can be seen that there is slight improvement in the oxidation resistance of the $\text{Ti}_3\text{Al-Nb}$ alloy over the binary Ti-32Al (Ti_3Al) alloy due to the addition of niobium. The curves exhibit a transition in the oxidation behavior from parabolic to linear. The parabolic rate constant estimated from the parabolic portion of the weight gain curve at various temperatures is plotted in Figure 2. Effective activation energy of 284 kJ/mol was deduced from this plot. Table 2 lists the effective activation energies for oxidation obtained of the present alloy along with those of the Ti-Al binary alloys obtained from the literature [9,12,27] for the sake of comparison. The improved oxidation resistance of Ti_3Al alloy with the addition of niobium may be due to

Fig. 1: Weight gain vs. time for $\text{Ti}_3\text{Al-Nb}$ alloy oxidized in pure dry oxygen at different temperatures. Data for the binary Ti-32Al alloy [12] are also plotted for the sake of comparison.

an increase in the e/a ratio that decreases oxygen solubility in the alloy. Doping of niobium into the TiO₂ lattice reduces the oxygen vacancy concentration thereby decreasing the diffusivity of oxygen through the oxide film.

Fig. 2: $\ln(k_p)$ vs $1/T$ for Ti₃Al-Nb alloy oxidized in pure dry oxygen.

Table 2

Comparison of effective activation energies of oxidation of Ti₃Al-Nb ternary alloy with some Ti-Al binary alloys

Alloy	Reference	$Q_{eff}, kJ/mol$
Ti-25Al	Roy <i>et al.</i> /27/	289
Ti-26Al	Welsch and Kahveci /9/	255
Ti ₃ Al-Nb	This work	284
Ti-32Al	Reddy <i>et al.</i> /12/	295
Ti-34Al	Welsch and Kahveci /9/	299

B. Phase and Microstructure Analysis

The Ti₃Al-Nb alloy specimen was characterized with the aid of Scanning Electron Microscope (SEM),

Energy Dispersive X-ray (EDX) and X-ray Diffraction (XRD) techniques. XRD technique was used to identify the various phases present in the oxide scale. After XRD analysis, the samples were brittle fractured into two pieces and polished before examining the oxide morphology under the SEM. EDX spectra revealed the amounts of various elements present at different locations of the oxide scales on the oxidized samples. The products of oxidation were mainly TiO₂ (rutile), TiO, and Al₂O₃ (alumina). In the present investigation oxides of niobium were not identified in the oxide scales by XRD technique. This could probably mean that either oxides of niobium did not form during oxidation or the content was too small for detection. However, EDX spectra showed the presence of elemental niobium in the oxide scale.

Figure 3 shows SEM micrograph of fractured cross section of the Ti₃Al-Nb alloy oxidized in pure dry oxygen at 1123 K for 24 hours. The interface region between the oxide scale and the alloy sample is demarked by a white line on the SEM micrograph. EDX spectrum of interface region on the oxidized sample is also shown in Figure 3. The oxide scale was about 15 μm and spalled a little after the cool down period. Composition of the interface region as obtained from EDX analysis showed 66 at. pct of oxygen, 32.5 at. pct of titanium, 0.7 at. pct of aluminum and 0.8 at. pct of niobium, indicating that the interface was mostly composed of rutile. The outermost regions of the oxide scale consisted of rutile and alumina while the rest of the scale was almost rutile.

Oxidation of the Ti₃Al-Nb alloy at 1223 K for 24 hours in pure oxygen produced an oxide scale, which was more than 100 μm thick. Figure 4 shows the SEM micrograph of fractured cross-section of the oxidized sample through the alloy/oxide interface. EDX spectrum of the interface region on the sample depicted as a white line on the micrograph is also shown in Figure 4. A small part of the scale spalled after the cooling period. Composition of the interface as analyzed by EDX shows 79 at. pct of oxygen, 16 at. pct of titanium, 4.5 at. pct of aluminum and 0.5 at. pct of niobium.

The interface region consisted of mainly rutile and a small amount of alumina. No niobium oxide was detected by XRD in the oxide scale, although niobium could have been present as a solid solution in the oxide

Fig. 3: SEM micrograph showing fractured cross-section of the $\text{Ti}_3\text{Al-Nb}$ alloy oxidized in pure oxygen at 850°C for 24 hours. EDX spectrum of the alloy/oxide interface region (white line on the micrograph) is also shown.

Fig. 4: SEM micrograph showing fracture cross-section of the Ti_3Al -Nb alloy oxidized in pure oxygen at 950°C for 24 hours. EDX spectrum at the alloy/oxide scale interface region represented by the white line on the micrograph is also shown.

Fig. 5: SEM micrograph of magnified portion of the oxide scale shown in Fig. 4 indicating a clear mixture of rutile and alumina.

mixture. The oxide scale appeared as a sintered compact of rutile and alumina with a uniform porosity along the direction perpendicular to the growth axis. The oxide scale on the $\text{Ti}_3\text{Al-Nb}$ alloy was thicker and adherent to the alloy matrix beneath. Figure 5 depicts an SEM micrograph of magnified portion of the oxide scale shown in Figure 4. The micrograph clearly indicates that the oxide scale was composed of a homogeneous mixture of large rutile particles (dark) and small alumina particles (white). The micrograph contains large amounts of rutile particles (dark) with small alumina particles (white) well dispersed in the mixture.

Figure 6 shows SEM micrograph of fractured cross section of the $\text{Ti}_3\text{Al-Nb}$ alloy oxidized in pure oxygen at 1273 K for 24 hours. An interesting oxide scale was observed on the alloy surface. A layered pattern of the oxide scale can be clearly seen. The oxide layer was more than 100 μm thick. The oxygen-affected alloy surface layer was about 100 μm . The large thickness of oxygen-affected area on the alloy surface could be due to the stabilization of the β -Ti phase resulting from niobium addition to the alloy. EDX spectrum of the alloy/oxide interface region depicted as white line on the micrograph is also shown. The interface consisted

mostly of rutile with very small amounts of alumina and niobium. Some of the oxide scale spalled after the cool down period in the form of several large pieces. The remnant oxide scale on the $\text{Ti}_3\text{Al-Nb}$ alloy was thick (> 100 μm) and layered in nature with a mixture of rutile and alumina. The overall oxide scale was comprised of layers of varying thickness (< 40 μm). Each layer was composed of a mixture of rutile and alumina.

Figure 7 depicts SEM micrograph of magnified portion of one of the interfaces in the oxide layer structure shown in Figure 6. It can be clearly seen that the oxide layer was composed of large faceted particles interspersed with small particles. The large faceted particles (3 to 4 μm) were found to be rutile and the small particles (average 1 μm) were found to be alumina. There can be seen some alumina particles which are in the submicron size range (500 nm – 800 nm). It is clear from Figure 7 that nanoscale alumina particles could be seen interspersed between the rutile particles in the interface region. The interface itself was a mixture of rutile and alumina and the immediate following layer was mainly comprised of rutile.

The interesting feature of oxide scale on the $\text{Ti}_3\text{Al-Nb}$ alloy oxidized at 1273 K was the layered structure

Fig. 6: SEM micrograph showing fractured cross-section of the Ti_3Al -Nb alloy oxidized in pure oxygen at 1000°C for 24 hours. EDX spectrum at the interface region represented by the white line on the micrograph is also shown.

Fig. 7: SEM micrograph of magnified portion of one of the interfaces in the layered oxide structure showing clearly the large faceted rutile intermixed with small nanoscale alumina particles.

Fig. 8: SEM micrograph showing fractured cross-section of the Ti₃Al-Nb alloy oxidized in pure oxygen at 1100°C for 24 hours.

forming alternate layers of rutile and alumina with small amounts of niobium. The white layers composed of a mixture of rutile and alumina are typically 30 μm thick followed by 5 to 6 μm thick dark layer of rutile, which appeared like smoothed rocks. The white layers were a mixture of rutile and alumina particles (smaller in size compared to that of rutile) with rutile being the major oxide. The layered oxide structure was formed due to the difference in the diffusion rates of aluminum and titanium in rutile. Additionally, the structure of rutile facilitates easy diffusion paths for the transport of oxygen. Rutile structure has channels parallel to the c-axis, which can constitute the faster diffusion paths for oxygen. Since diffusion rate is temperature dependent, the formation of layered oxide structure was distinct on the alloys oxidized at temperatures higher than 1000°C but was not obvious at lower temperatures.

Figure 8 shows SEM micrograph of fractured cross-section of the Ti₃Al-Nb alloy oxidized at 1373 K in pure dry oxygen for 24 hours. The oxide scale was more than 200 μm thick and outermost layers spalled after the cool down period. The layered structure of the oxide scale observed at this temperature was even more pronounced than that observed at 1273 K for the same alloy. The characteristics of oxide strata on the alloy oxidized at 1373 K were different from those observed on the alloy oxidized at 1273 K. Individual layer thickness on the oxide scale was smaller than that in the case of 1273 K and more number of layers were formed than those observed at 1273 K for the same alloy. A magnified SEM micrograph of the oxide structure is shown in Figure 9 along with the EDX spectrum of the interface region marked by the rectangular box on the micrograph. The dark layered region was made up of large rutile particles and less than 10 μm thick. The white layered region was made up of small particles, which were predominantly of alumina with small amounts of niobium and was less than 5 μm in thickness. Individual particles in the white layered region were of the order of 500-1000 nm. The number of such alternate layers increased from that observed at 1273 K while the layer thickness decreased considerably. The formation of multiple-layer oxide scale on the Ti₃Al-Nb alloy can be attributed to differences in the diffusivities of the various species (aluminum, titanium and oxygen ions) in the oxide

layers involved in the system.

Addition of a small amount of niobium to the Ti₃Al alloy did not result in a compact, dense and continuous layer of alumina during oxidation. It is expected that the oxide scale, though a mixture of rutile and alumina, would render effective protection from further oxidation of the alloy if there were large amounts of alumina in the overall scale. These layers consist of rutile as the major oxide with very little alumina. The presence of alumina layer on the surface protects the alloy from further oxidation and thereby prevents deterioration of mechanical properties of the alloy in service. In the Ti₃Al-Nb alloy, instead of a continuous impervious alumina layer, layers of oxides mixture were formed on the surface of the alloy containing small amounts of alumina. Hence, long term protection of the alloy cannot be guaranteed. Due to the doping effect of niobium in the rutile structure, a slight improvement in oxidation resistance of the Ti₃Al-Nb alloy over the base Ti₃Al intermetallic alloy was observed. Such a doping in the rutile structure results in a decrease in oxygen vacancy concentration, which is the primary mechanism for the oxide scale growth.

Figure 10 shows the schematic representation of the oxide scale structure on α_2 -Ti₃Al alloys with small additions of niobium. In general, the oxide scales were composed of a mixture of rutile and alumina in various proportions depending on the temperature of oxidation. In case of alloys containing niobium, a layered structure of a mixture of oxides was observed. The schematic diagram shows typically the oxide scale in the case of Ti₃Al-Nb alloy oxidized in pure oxygen atmosphere. The outermost layers consisted of a mixture of rutile and alumina with rutile as the major oxide. The layer beneath the outermost layer was mostly TiO₂ followed by a predominantly alumina rich layer. There exists an oxygen-affected alloy surface layer below the oxide scale where internal oxidation took place. As the temperature increased, the number of layers in the oxide scale also increased with a corresponding decrease in the individual layer thickness.

The effect of niobium addition to Ti₃Al alloy on the oxidation behavior and the subsequent formation of multilayered oxide scales could be understood from the chemistry of the oxide crystal lattice. Niobium has a valence of +5 in the fully oxidized state and with an

Fig. 9: SEM micrograph of magnified portion of the layered oxide scale on $\text{Ti}_3\text{Al-Nb}$ alloy oxidized in pure oxygen at 1100°C for 24 hours. EDX spectrum of the interface region marked by the rectangular box on the micrograph is also shown.

Fig. 10: Schematic representation of oxide scale structure on Ti_3Al -Nb alloys oxidized in pure dry oxygen at temperatures higher than 1273 K.

ionic radius of 0.64 Å [25]. Doping of a higher valent element such as Nb to TiO_2 (rutile) influences the defect structure of the oxide layer by reducing the oxygen vacancy concentration in the following manner:

Oxygen diffusion has been proposed to occur via vacancy migration [26]. Since oxide layer grows essentially by the diffusion of oxygen in the oxide scale, a decrease in the oxygen vacancy concentration leads to an improved oxidation resistance of the alloy. It was reported that the presence of Nb in TiO_2 as a solid solution improves the oxidation resistance of the base Ti_3Al alloy [27]. 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 [28]. 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.

The relative diffusivities of titanium and aluminum ions in the oxide scale consisting of both rutile and alumina were believed to be responsible for this kind of a multi-layered structure. It is extremely difficult at this stage to elucidate the exact mechanism for such a multi-layered oxide scale formation on the Ti_3Al -Nb alloy during oxidation. However, further investigation is warranted to understand the mechanism of a multi-

layered oxide scale formation on a Ti_3Al -Nb alloy containing small amount of niobium.

IV. CONCLUSIONS

1. Oxidation kinetics of Ti_3Al -Nb alloy exhibited a transition from parabolic to linear in the weight gain curve and the effective activation energy of 284 kJ/mol was deduced from parabolic portion of the oxidation curve.
2. Niobium addition showed only a slight improvement in the oxidation resistance of the Ti_3Al alloy at all the temperatures of study.
3. The oxidation products identified in the scales consisted of mainly TiO_2 (rutile), TiO and Al_2O_3 (alumina) in the temperature range of 1123 to 1373 K.
4. Ti_3Al -Nb alloy showed layered structure of oxide scale on the surface when oxidized in pure oxygen environment. The layered oxide scale consisted of alternate layers of TiO_2 and a mixture of TiO_2 and Al_2O_3 above 1273 K. The number of layers increased with temperature with a corresponding decrease in the individual layer thickness.
5. There was slight improvement in the oxidation resistance of the α_2 - Ti_3Al alloy with the addition of niobium, but an adherent protective layer of alumina could not be formed in the temperature range of the present investigation.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the financial support for this research by National Science Foundation, Grant No. DMR-9696112 and DMR-0312172.

REFERENCES

1. S. G. Kumar and R. G. Reddy: *Metall. Mater. Trans. A*, **27A**, 1121-1126 (1996).
2. S. G. Kumar, R. G. Reddy, J. Wu, and J. Holthus: *J. Mater. Engg. Performance*, **4** (1), 63-69 (1995).
3. S. G. Kumar, R. G. Reddy and L. Brewer: *J. Phase Equilibria*, **15** (3), 279-284 (1994).
4. S. G. Kumar and R. G. Reddy: *Proc. Intl. Symp. on Synthesis/Processing of Lightweight Metallic Materials*, TMS, Warrendale, PA, 1995; pp. 129-139.
5. N. Birks, G. H. Meier, and F. S. Pettit: *JOM*, **46** (12), 42-46 (1994).
6. J. Subrahmanyam: *J. Mater. Sci.*, **23**, 1906-1910 (1989).
7. J. L. Smialek: *Corr. Sci.*, **35** (5-8), 1199-1208 (1993).
8. X. Wen and R. G. Reddy: *Processing and Fabrication of Advanced Materials*, TMS, Warrendale, PA, 1996; pp. 379-389.
9. G. Welsch and A. I. Kahveci: *Oxidation of High-Temperature Intermetallics*, T. Grobstein and J. Doychak (Eds.), TMS, Cleveland, Ohio, September, 1988; pp. 207-218.
10. G. H. Meier, D. Appalonia, R. A. Perkins, and K. T. Chiang: *Oxidation of High-Temperature Intermetallics*, T. Grobstein and J. Doychak (Eds.), TMS, Cleveland, Ohio, September, 1988; pp. 185-193.
11. R. G. Reddy, X. Wen and I. C. I. Okafor: *Metall. Mater. Trans. A*, **31A**, 3023-3028 (2000).
12. R. G. Reddy, X. Wen and I. C. I. Okafor: *Metall. Mater. Trans. A*, **32A**, 491-495 (2001).
13. A. Rahmel and P. J. Spencer: *Oxid. Met.*, **35** (1/2), 53-68 (1991).
14. Y. Umakoshi, M. Yamaguchi, T. Sakagami and T. Yamane: *J. Mater. Sci.*, **24**, 1599-1603 (1989).
15. Y. Shida and H. Anada: *Oxid. Met.*, **45**, 197 (1996).
16. T. A. Wallace, R. K. Clark and K. E. Weidemann: *Oxid. Met.*, **42** (5/6), 451-464 (1994).
17. G. Chen, Z. Sun and X. Zhou: *Corrosion*, **48** (11), 939-946 (1992).
18. J. S. Wu, L. T. Zhang, F. Wang, K. Jiang and G. H. Qiu: *Intermetallics*, **8**, 19-28 (2000).
19. S. K. Jha, A. S. Khanna and C. S. Harendranath: *Mater. Sci. Forum*, **251-254**, 203-210 (1997).
20. K. Hauffe: *Oxidation of Metals*, Plenum Press, NY, 1965; pp. 217-223.
21. Y. Sun, C. Cao and M. Yan: *Advanced Performance of Materials*, **2**, 281-288 (1995).
22. M. N. Mungole, R. Balasubramaniam, and A. Ghosh: *Intermetallics*, **8**, 717-720 (2000).
23. R. G. Reddy: *JOM*, **54** (2), 65-67 (2002).
24. R. G. Reddy and R. B. Inturi: *Minerals and Metall. Trans.*, **16** (20), 46-50 (1999).
25. K. Kitayama: *J. Solid. State Chem.*, **83**, 37-44 (1989).
26. R. Haul and G. Dumbgen: *J. Phys. Chem. Solids.*, **26**, 1-10 (1965).
27. T. K. Roy, R. Balasubramaniam, and A. Ghosh: *Metall. Mater. Trans. A*, **27A**, 3993-4002 (1996).
28. R. G. Reddy, Y. Li, and M. F. Arenas: *High Temp. Mater. Process.*, **21** (4), 195-205 (2002).

10
2000-10-10

1000-10-10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10