

Protective Coating of Gamma Titanium Aluminide at High Temperatures Using Niobium Disilicide

Saleh B. Abu Sulik¹, Masayuki Ohshima¹, Toshimitsu Tetsui², Kazuhiro Hasezaki¹

¹Department of Materials Science, Shimane University, Nishikawatsu-cho 1060, Matsue, Shimane 690-8504, Japan
Fax: +81-852-32-6402, email: s059705@matsu.shimane-u.ac.jp, saleh156@hotmail.com

²Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
Fax: +81-22-215-3465, email: tetsui@imr.tohoku.ac.jp

Niobium disilicide (NbSi₂) layers were applied on γ -TiAl specimens to enhance their oxidation resistance at 1050 °C. The NbSi₂ layers were prepared by joining thin Nb foils to γ -TiAl surfaces, and siliconizing the Nb/ γ -TiAl using molten salts. The coatings and their oxidation behavior were characterized using X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy techniques. Isothermal oxidation tests showed that oxidation resistance of the uncoated γ -TiAl at 1050 °C in air was inadequate for prolonged exposure and scale spallation occurred, causing severe oxidation of γ -TiAl at high temperature. NbSi₂ coatings were formed and adhered firmly to the underlying γ -TiAl. Oxidation of the NbSi₂-coated γ -TiAl (NbSi₂/Nb/ γ -TiAl) at 1050 °C in air showed improved oxidation resistance at exposure time of 10 h. The NbSi₂ coatings provided good intrinsic oxidation resistance at 1050 °C in air for prolonged oxidation exposure, and showed potential use in protecting γ -TiAl at high-temperature applications.

Key words: γ -TiAl, NbSi₂, Protective coatings, Oxidation, Ecomaterials.

1. INTRODUCTION

Gamma titanium aluminides (γ -TiAl) have an attractive combination of properties including low density, high specific yield strength, high specific stiffness, and favorable creep properties at elevated temperatures [1-3]. These properties make γ -TiAl suitable for applications such as turbocharger turbine wheels and engine exhaust valves [2,4]. Based on the resource productivity concept [5], γ -TiAl compounds are considered to be ecomaterials due to their role in reducing emission levels and enhancing performance of automotive engines. Accordingly, EURO-IV emission standards have necessitated reducing engine emissions and enhancing engine performance, which can be achieved by raising combustion gas temperature and reducing weights of rotating parts [1]. These needs can be met using γ -TiAl. However, the oxidation resistance of γ -TiAl in air is insufficient above 800-900 °C [3,6].

Two approaches have been adopted to improve oxidation resistance of γ -TiAl. The first approach involves alloying the γ -TiAl with various elements [7]. However, a disadvantage of this approach is that excessive addition of alloying elements may negatively affect the original properties of γ -TiAl. The second approach employs surface engineering modifications by providing protective coatings made of oxides [8], silicides [9], or other types of coatings [10]. The surface engineering approach has yet to show satisfactory results, especially at temperatures above 1000 °C.

Niobium disilicide (NbSi₂) has outstanding properties [11], and can be a candidate protective coating to improve the oxidation resistance of γ -TiAl at elevated temperatures, thus extending the potential of γ -TiAl as

ecomaterials in high-temperature applications.

The objectives of this study are to prepare NbSi₂ layers on γ -TiAl as protective coatings; to evaluate the oxidation resistance of NbSi₂-coated γ -TiAl at 1050 °C in air; and to investigate the intrinsic oxidation of NbSi₂ coatings at prolonged oxidation exposure. In this work, Nb foils were joined to γ -TiAl using spark plasma sintering (SPS) and siliconized using molten salts. Oxidation behavior of the NbSi₂-coated γ -TiAl prepared was isothermally examined at 1050 °C in air. Furthermore, to study the intrinsic oxidation resistance of NbSi₂ coatings at extended oxidation times, Nb specimens were siliconized (fully covered with NbSi₂ coatings) and then oxidized at 1050 °C for up to 400 h.

2. EXPERIMENTAL DETAILS

The specimens used in this study were γ -TiAl (Ti-46Al-7Nb at.%) [12], with minimum level of impurities and defects [4]. Tabular specimens 12×10×2 mm³ in dimension were cut for oxidation tests. Likewise, cylindrical coupons of 10 mm in diameter and 2 mm thick were prepared for joining with Nb foils. All specimens were ground and polished using SiC emery paper down to 1500#, and then ultrasonically cleaned using acetone, methanol, and deionized water for 5 minutes in turn. High purity Nb foils (75 μ m) were joined to the γ -TiAl specimens using SPS in a 10 mm diameter graphite chamber. The SPS parameters were pressure of 50 MPa and temperature of 1100 °C for 5 minutes. The Nb/ γ -TiAl specimens were then siliconized using molten salts [13]. This process allows siliconizing the specimen surfaces using a mixture of 29.2 wt.% NaCl, 37.3 wt.% KCl, 12.5 wt.% NaF, 12.6 wt.%

Na_2SiF_6 , and 8.4 wt.% silicon powder (150 μm). Siliconizing was made by dipping the specimens in the mixture before heating in a mullite crucible at 900 °C for 10 h in air.

The oxidation behavior of $\gamma\text{-TiAl}$ was examined isothermally at 1050 °C for 10-400 h in static air (at atmospheric pressure). Similarly, isothermal oxidation tests of the siliconized specimens ($\text{NbSi}_2/\text{Nb}/\gamma\text{-TiAl}$) were made in air at 1050 °C for 10 h with heating and cooling rates of 100 °C/h. Moreover, oxidation behavior of NbSi_2 -coated $\gamma\text{-TiAl}$ at prolonged times could not be investigated due to oxygen penetration from the uncoated sides of the specimens. To study the intrinsic oxidation behavior of NbSi_2 coatings at extended exposure, Nb specimens (19 mm in diameter and 2 mm thick) were siliconized using the molten salts and the NbSi_2 -coated Nb were oxidized at 1050 °C for 10-400 h.

Characterization of the prepared coatings and their oxidation was made using X-ray diffraction (XRD) (RIGAKU $\text{CuK}\alpha$, RINT 2500 PC), scanning electron microscopy (SEM) (JOEL JSM-5310 and Hitachi S-3500H at 10-15 kV), and energy dispersive X-ray spectroscopy (EDX) with secondary electron mapping.

3. RESULTS AND DISCUSSION

3.1. Oxidation behavior of uncoated $\gamma\text{-TiAl}$

SEM cross-sectional micrographs (Fig. 1) of the oxidized surfaces produced at 1050 °C for 10 and 100 h confirmed development of porous scales at prolonged oxidation (Fig. 1b). The oxide scales consisted of a mixture of TiO_2 and Al_2O_3 . Scale spallation was observed with cracks developed in the interface between the $\gamma\text{-TiAl}$ and the $\text{TiO}_2\text{-Al}_2\text{O}_3$ layer (Fig. 1b). Spallation of the oxide scales enhanced oxygen penetration and led to severe oxidation. Observation showed that the Al_2O_3 -rich layer failed to protect the $\gamma\text{-TiAl}$ during prolonged high-temperature oxidation. The weight gain of the oxidized specimens (Fig. 2) increased with increased oxidation time, and accelerated beyond 100 h. A simple diffusion mechanism of the oxidation of $\gamma\text{-TiAl}$ was theoretically fitted (solid line in Fig. 2) using a simple parabolic scale growth law. However, oxidation of $\gamma\text{-TiAl}$ showed accelerated weight gain beyond 100 h compared to the standard parabolic behavior (open circles in Fig. 2) due to combined scale growth mechanisms [10], and spallation and fracture of the oxide scales. Oxidation rate accelerated beyond 100 h owing to breakdown of the Al_2O_3 -rich layer [14].

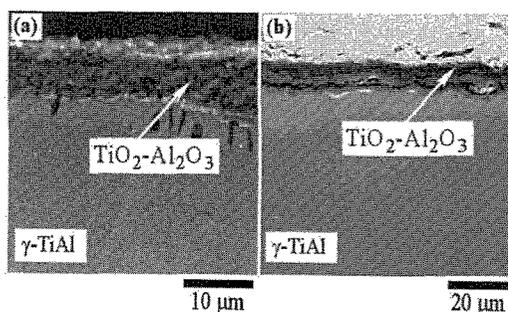


Fig. 1. SEM cross-sectional micrographs of $\gamma\text{-TiAl}$ oxidized at 1050 °C for (a) 10 h, and (b) 100 h.

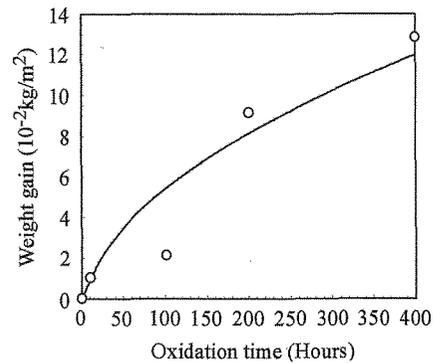


Fig. 2. Weight gain of $\gamma\text{-TiAl}$ oxidized at 1050 °C for 10-400 h (Solid line: fitted data; open circles: experimental data).

The phase compositions of the oxidized surfaces were identified from XRD patterns (not shown). The scales formed consisted almost solely of TiO_2 , Al_2O_3 , and some nitrides. Accordingly, providing protective coating on the $\gamma\text{-TiAl}$ with oxidation-resistant materials is necessary to improve performance at prolonged operational times.

3.2. Formation of NbSi_2 coatings on $\gamma\text{-TiAl}$

NbSi_2 layers ($\text{NbSi}_2/\text{Nb}/\gamma\text{-TiAl}$) were prepared using molten salts. Phase composition of the coating and SEM cross-sectional micrograph of a NbSi_2 -coated $\gamma\text{-TiAl}$ grown at 900 °C for 10 h are shown in Fig. 3. The XRD surface pattern of the NbSi_2 -coated $\gamma\text{-TiAl}$ (Fig. 3a) confirmed formation of single phase hexagonal NbSi_2 . No signals from the underlying Nb and $\gamma\text{-TiAl}$ were observed, indicating that the coating was deposited uniformly, and at good thickness. The SEM micrograph (Fig. 3b) showed that the NbSi_2 coating and its Nb film were well joined to the underlying $\gamma\text{-TiAl}$ without propagation of cracks or defects at the interface.

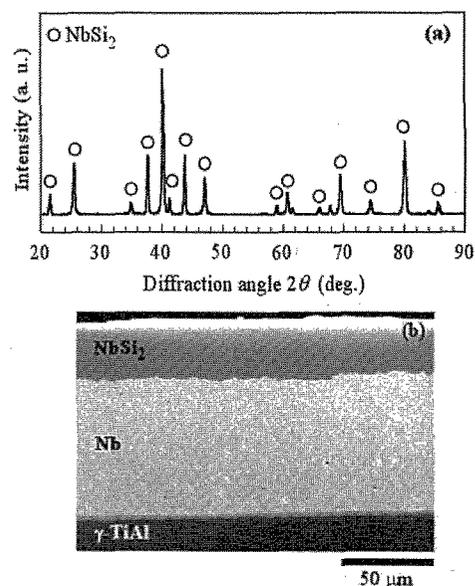


Fig. 3. NbSi_2 -coated $\gamma\text{-TiAl}$ ($\text{NbSi}_2/\text{Nb}/\gamma\text{-TiAl}$) prepared at 900 °C for 10 h in molten salts: (a) XRD pattern, and (b) SEM cross-sectional micrograph.

Growth kinetics of the NbSi₂ coatings was governed by a parabolic mechanism as shown in Fig. 4; experimental data were fitted into a parabolic equation (solid line in Fig. 4). Filled circles in Fig. 4 show the average measured thickness of the NbSi₂ coatings. Homogeneous growth kinetics prevailed, which explains the uniformity and flatness of the silicide coatings.

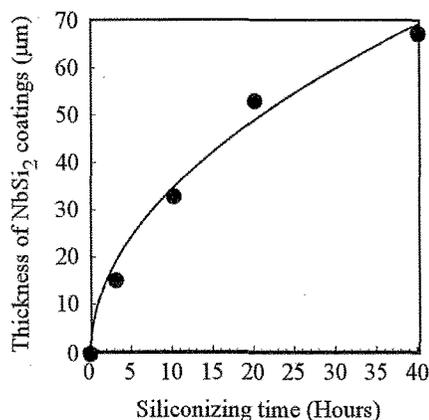


Fig. 4. Average thickness of the NbSi₂ coatings as function of silicizing time (3-40 h) at 900 °C using the molten salts siliconizing.

3.3. Oxidation behavior of NbSi₂ coatings

Oxidation of NbSi₂/Nb/γ-TiAl in air. XRD pattern of an oxidized NbSi₂-coated γ-TiAl (NbSi₂/Nb/γ-TiAl) revealed that the oxide scale consisted of a mixture of Nb₂O₅ and crystalline tridymite (SiO₂) along with the NbSi₂ (Fig. 5). SEM and EDX cross-sectional micrographs with elemental profiles (Fig. 6) of the oxidized NbSi₂/Nb/γ-TiAl showed the elemental distribution (Si, Nb, and O) after oxidation at 1050 °C for 10 h. The novel NbSi₂ coating protected the underlying γ-TiAl surface by preventing penetration of oxygen at high temperature (1050 °C). Likewise, the NbSi₂/Nb layers successfully provided oxidation barrier and prevented oxidation of the γ-TiAl. During oxidation at high temperatures, development of both the composition and microstructure of the NbSi₂ coatings observed from Figs. 5 and 6. Interaction of NbSi₂ coating with air at high temperature forms an oxide layer, consisting of a mixture of Nb₂O₅ and SiO₂.

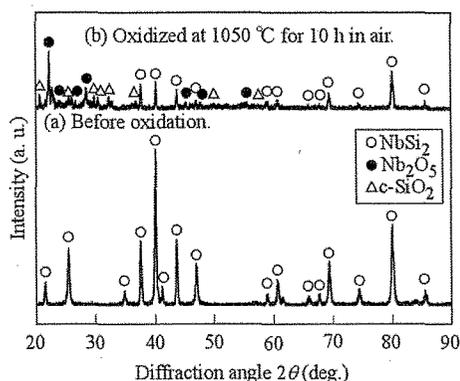


Fig. 5. XRD patterns of NbSi₂-coated γ-TiAl: (a) unoxidized, and (b) oxidized at 1050 °C for 10 h in air.

The Nb₂O₅ and SiO₂ were detected in the XRD surface pattern (Fig. 5). Beneath the oxide scale, a defects-free NbSi₂ coating supported the oxidation resistance of the combination and protected the γ-TiAl. During oxidation, Si diffused into the NbSi₂/Nb interface forming Nb₅Si₃, which is important to bridge any differences in coefficients of thermal expansion between the NbSi₂ coating and Nb, and prevents crack formation [13]. The graded structure (NbSi₂/Nb₅Si₃/Nb) helped in relieving thermal stresses and improving oxidation resistance of the coating.

Prolonged intrinsic oxidation of NbSi₂ in air: To investigate the intrinsic oxidation resistance of NbSi₂ coatings for prolonged exposure times, NbSi₂-coated Nb (NbSi₂/Nb) were siliconized at 900 °C for 40 h. The obtained NbSi₂ coatings were thick, uniform in thickness, and flat (Fig. 7). Phase composition of the obtained coatings was confirmed using XRD. The XRD surface patterns obtained showed that single phase hexagonal NbSi₂ layers were present, which were similar to the pattern shown in Fig. 3a.

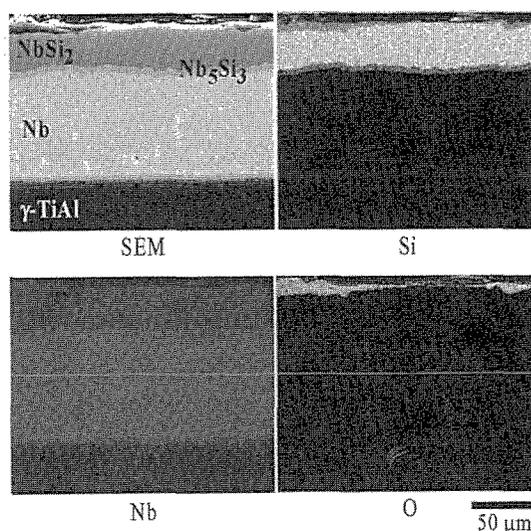


Fig. 6. SEM and EDX cross-sectional micrographs with elemental profiles of an oxidized NbSi₂/Nb/γ-TiAl surface (oxidized at 1050 °C for 10 h in air).

SEM and EDX cross-sectional micrographs (Fig. 8) with elemental profiles of an oxidized NbSi₂-coated Nb (NbSi₂/Nb) surface showed formation of an oxide scale and penetration of oxygen into the Nb surface was hindered by the oxide scale. The oxide scale consisted of Nb₂O₅ and SiO₂ similar to Fig. 5b. The oxide scale was adherent to the underlying Nb surface. It was inferred that NbSi₂ coatings have good oxidation resistance at 1050 °C for exposure up to 400 h. The oxidized coatings did not show delamination from the underlying surfaces after continuous oxidation at 1050 °C for up to 400 h, and no crack propagation was observed (Fig. 8). Consequently, NbSi₂ coatings formed by molten salts siliconizing can be adopted to improve oxidation resistance of γ-TiAl subjected to extended oxidation, due to the formation of a slow growth and condensed oxide scale containing the protective SiO₂.

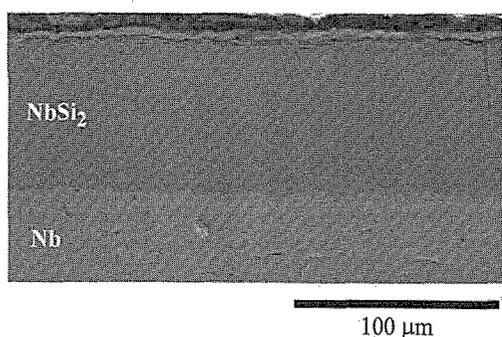


Fig. 7. SEM cross-sectional micrograph of a NbSi₂-coated Nb (NbSi₂/Nb) siliconized at 900 °C for 40 h.

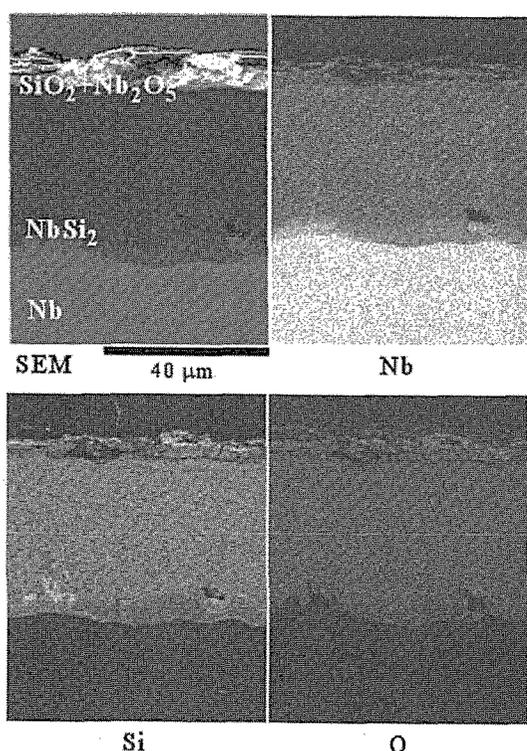


Fig. 8. SEM and EDX cross-sectional micrographs with elemental profiles of an oxidized NbSi₂-coated Nb specimen (Oxidized at 1050 °C for 400 h in air).

The XRD and EDX analyses confirmed that NbSi₂ coatings can be selected and used at elevated temperatures to protect and improve the oxidation resistance of γ -TiAl.

4. CONCLUSIONS

The preparation and high temperature oxidation behavior of the NbSi₂-coated γ -TiAl, and the intrinsic oxidation of NbSi₂ coating were investigated in an effort to develop oxidation-resistant coating suitable for γ -TiAl at high temperature. The results of this study are:

1. Oxidation resistance of γ -TiAl at 1050 °C was inadequate at prolonged exposure, with development of scale spallation and accelerated

oxidation at prolonged exposure times.

2. The prepared NbSi₂/Nb coatings adhered well to the γ -TiAl. Single phase hexagonal NbSi₂ coatings were formed using molten salts siliconizing at 900 °C for 3-40 h.
3. Isothermal oxidation tests of the NbSi₂-coated γ -TiAl (NbSi₂/Nb/ γ -TiAl) showed improved oxidation resistance at 1050 °C in air.
4. Prolonged oxidation tests of NbSi₂ coatings (NbSi₂-coated Nb) showed enhanced intrinsic oxidation resistance up to exposure time of 400 h. In addition, no crack propagation or spallation was observed.
5. Based on the experimental results of this work, NbSi₂ coatings showed potential use at 1050 °C to protect γ -TiAl alloys, thus widens their applications as ecomaterials.

ACKNOWLEDGEMENTS

Our thanks to Mr. K. Kikui of Tottori Institute of Industrial Technology for his help with the SEM/EDX measurements and to Dr. B. Roser of Shimane University for his helpful discussions on the manuscript.

REFERENCES

- [1] H. Kestler, H. Clemens, "Titanium and Titanium Alloys: Fundamentals and Applications", Ed. by C. Leyens, M. Peters, Wiley-VCH, Weinheim (2003) pp. 351-92.
- [2] T. Tetsui, S. Ono, *Intermetallics*, **7**, 689-97 (1999).
- [3] M. Yoshihara, Y.-W. Kim, *Intermetallics*, **13**, 952-8 (2005).
- [4] T. Noda, *Intermetallics*, **6**, 709-13 (1998).
- [5] K. Halada, *Current Opinion in Solid State and Materials Science*, **7**, 209-16 (2003).
- [6] C. Leyens, R. Braun, M. Fröhlich, and P. Eh. Hovsepian, *JOM Journal of the Minerals, Metals, and Materials Society*, **58**, 17-21 (2006).
- [7] F. Appel, M. Oehring, Titanium and Titanium Alloys: Fundamentals and Applications, Ed. by C. Leyens, M. Peters, Wiley-VCH, Weinheim (2003) pp. 90-3.
- [8] M.P. Brady, B. Gleeson, I.G. Wright, *JOM Journal of the Minerals, Metals, and Materials Society*, **52**, 16-21 (2004).
- [9] X.Y. Li, S. Taniguchi, Y. Matsunaga, N. Nakagawa, K. Fujita, *Intermetallics*, **11**, 143-150 (2003).
- [10] C. Leyens, Titanium and Titanium Alloys: Fundamentals and Applications, Ed. by C. Leyens, M. Peters, Wiley-VCH, Weinheim (2003) pp. 187-230.
- [11] C. Milanese, V. Buscaglia, F. Maglia, U. Anselmi-Tamburini, *Acta Mater.*, **51**, 4837-46 (2003).
- [12] T. Tetsui, *Intermetallics*, **10**, 239-45 (2002).
- [13] R.O. Suzuki, M. Ishikawa, K. Ono, *J. Alloys Comp.*, **336**, 280-5 (2002).
- [14] J.D. Sunderkotter, H.J. Schmutzler, V.A.C. Haanappel, R. Hofman, W. Glatz, H. Clemens, M.F. Stroosnijder, *Intermetallics*, **5**, 525-34 (1997).

(Received September 6, 2007 ; Accepted January 16, 2008)