

Formation of titanium nitride on γ -TiAl alloys by direct metal–gas reaction

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Abstract Two alloys, Ti-47Al-2Nb-2Cr (MJ12) and Ti-47Al-2Nb-2Mn + 0.8TiB₂ (MJ47), were nitrided in purified ammonia for 3.6×10^3 – 3.6×10^4 s (1–10 h) at a temperature range of 800–1,000 °C. The nitridation process can successfully improve alloy hardness which increased with an increase of the nitridation temperature and time. Hardness values of MJ12 and MJ47 with 1,000 °C nitridation for 3.6×10^4 s were the highest at 700.5 ± 9.0 and 694.7 ± 21.8 kg mm⁻², respectively. The wear rate and friction coefficient were significantly reduced by the nitridation process. Wear resistance of both alloys increased by two orders of magnitude after nitridation compared to the corresponding alloys without nitridation. In addition, the alloys were analyzed using XRD, SEM, EDX and an optical microscope.

Introduction

γ -TiAl alloys have shown the potential for use as engineering materials at high temperature due to their low density, high temperature strength, high strength to weight ratio, and high resistance to oxidation and hydrogen absorption [1–5]. They have been used in moving structural applications such as the following. Turbine blades

are used to replace superalloys due to their lower densities and higher operating temperatures [4, 5]. Valves are used in automotive engines due to their lightweight and high-temperature resistance. The engines are able to run at higher revolutions per minute and the efficiency is at the maximum [5]. Turbocharger rotors show the greatest advantage in that the reduction of time needed to reach the optimal operating speed leads to a decrease in CO₂ soot particles in the exhaust [5]. In addition, γ -TiAl alloys can be used in industries to meet environmental requirements and standards such as reduction of CO₂ emissions, higher efficiency of combustion engines and power units, weight reduction and improved quality of critical components [5]. However, the alloys have poor surface properties at high temperature and have very limited ductility at room temperature [6]. The nitridation process may be used for the improvement of these properties. Titanium nitride is well known for having excellent tribological properties [7–11]. Coating of titanium nitride can be made by chemical vapor deposition (CVD) or physical vapor deposition (PVD) [8, 10]. The CVD and PVD of titanium nitride are rather expensive. They need very low vacuum systems and toxic chemicals. Titanium nitride can be formed by direct metal–gas reaction, which is an inexpensive and non-toxic process. The purpose of the present research is to improve the tribological properties of γ -TiAl alloys by the direct metal–gas nitridation at high temperatures.

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Experiment

Two γ -TiAl alloys used for the experiment were Ti-47Al-2Nb-2Cr (MJ12) and Ti-47Al-2Nb-2Mn + 0.8TiB₂ (MJ47) which were processed by hot isostatic pressing at 1,260 °C

and 172 MPa pressure for 1.44×10^4 s (4 h). Their compositions are shown in Table 1. The alloys, supplied as 15.5-mm diameter rods, were cut into 1–2 mm thick disks, polished down to 0.3-micron alumina powder and degreased with alcohol. They were put in a high temperature reaction chamber made of high-alumina porcelain and fired at 1,300 °C. A water-cooled copper cap was tightly closed on top as shown in Fig. 1. The air was removed by evacuation to 17.33 kPa absolute pressure and purified argon was slowly fed into the chamber. The process was repeated ten times. The residual content of oxygen in the chamber before starting the nitridation was calculated using the equation of state of an ideal gas and 20 vol% O₂ in ambient atmosphere and found to be not more than 5 ppb. The chamber was then put into a furnace. The alloys were heated in argon until the test temperature was obtained. Then the argon was replaced with purified ammonia flowing at 10 mL s⁻¹. The nitridation process proceeded for 3.6×10^3 – 3.6×10^4 s (1–10 h). At the end of the process,

the furnace was turned off and the ammonia was replaced by argon. The alloys were cooled down to room temperature and brought for further analysis using an XRD (Jeol: JDX-8030, operated at 45 kV and 35 mA and using the K_α line from a Cu target) in combination with JCPDS software [12], a SEM equipped with an EDX (Jeol: JSM-6335F, operated at 15.0 kV), an optical microscope (Zeiss: Axio-tech 100HD and Sony CCD: SSC-M370CE), a Knoop hardness tester (Matsuzawa Seiki: MXT-α7, 50 gf load) and a pin-on-disk wear tester (Implant Science: ISC 200, radius of WC pin = 3.175 mm, load = 50 gf, linear speed = 40.0 mm s⁻¹, sliding distance = 60 m and wear track radius = 4.5 mm).

Results and discussion

Knoop hardness

Knoop hardness (HK) of the alloys was measured ten times. The average value and standard deviation were calculated and are shown in Fig. 2. HK of the alloys was successfully improved by the nitridation process and increased with an increase of the nitridation temperature and time. HK values of non-nitrided MJ12 and MJ47 were 343.2 ± 22.4 and 447.3 ± 35.3 kg mm⁻², respectively. The maximum HK

Table 1 Nominal composition (at %) of the alloys

Alloys	Ti	Al	Nb	Cr	Mn	TiB ₂
MJ12	Balance	47	2	2	–	–
MJ47	Balance	47	2	–	2	0.8

Fig. 1 High temperature reaction chamber with water-cooled copper cap on top

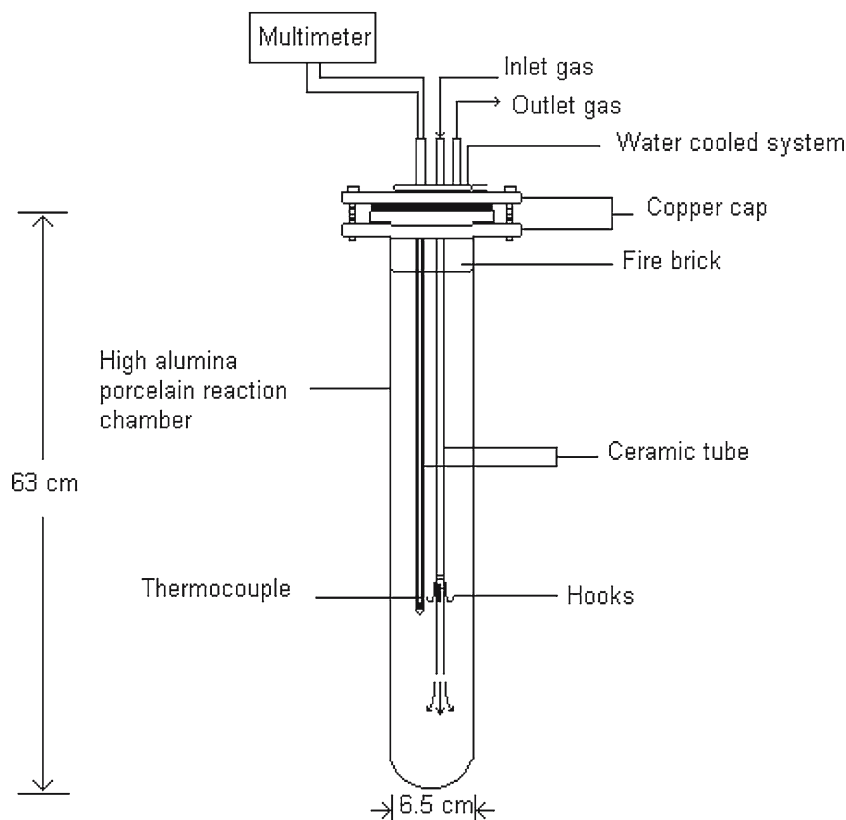
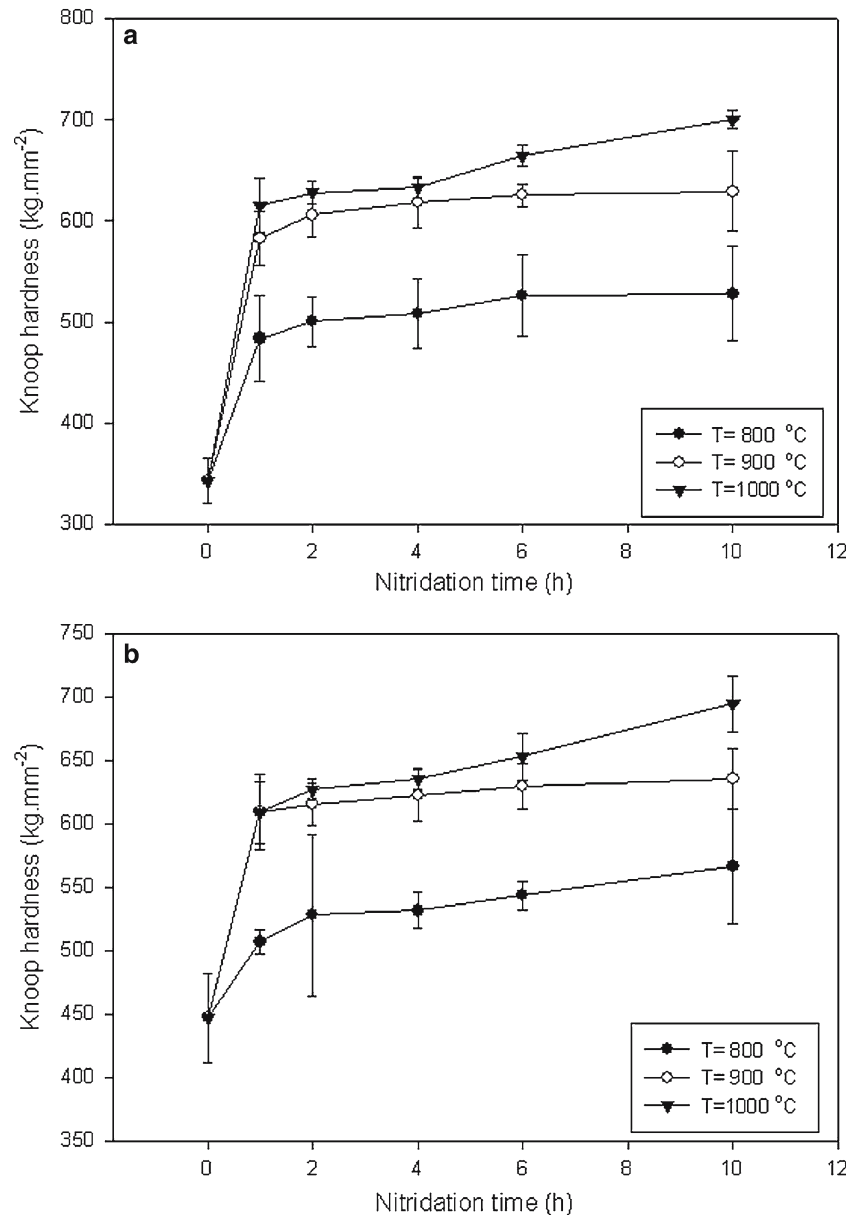


Fig. 2 Knoop hardness of (a) MJ12 and (b) MJ47 for 50 gf load



values of MJ12 and MJ47 with 1,000°C nitridation for 3.6×10^4 s were at 700.5 ± 9.0 and 694.7 ± 21.8 kg mm⁻², respectively. At the initiation of the nitridation process, reactive gas directly adsorbed onto the alloy surfaces, which were very shiny and fresh. The potential of the reactive gas to react with the fresh alloys was very high. Therefore, HK values rapidly increased during the first hour of the nitridation. Comparing among 800, 900 and 1,000 °C nitridation within one hour, the average rate of HK increase for MJ12 and MJ47 with 1,000 °C nitridation were the largest at 0.0755 and 0.0450 kg mm⁻² s⁻¹, respectively. During the nitridation process, there were products deposited on the alloy surfaces which could protect the alloys from contacting the reactive gas and could delay the underneath

alloys from nitridation. As time proceeded, the rate of nitridation slowed down. HK values increased parabolically with an increase of the nitridation time. It shows that hardness of the alloys was controlled by the diffusion process in the nitrided products, which are solid phases. Therefore, HK values were controlled by temperature and time including a variety of deposited phases.

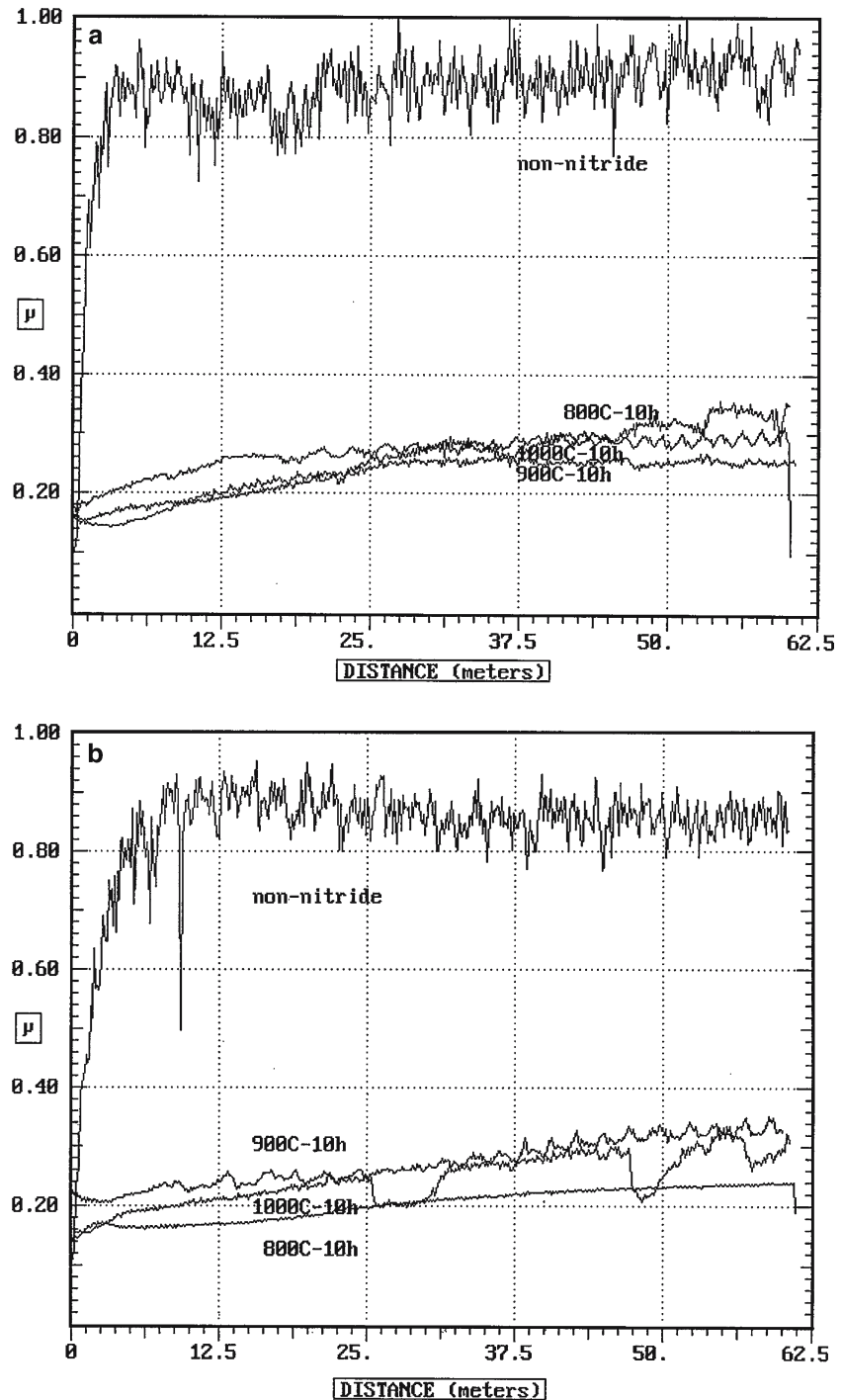
Coefficient of friction

Coefficient of (sliding) friction of MJ12 and MJ47 without and with 800–1,000 °C nitridation for 3.6×10^4 s (10 h) versus sliding distance is shown in Fig. 3. During wear testing, the coefficient of friction

varied with the sliding distance that the WC pin moved. The coefficient of friction of both MJ12 and MJ47 without nitridation rapidly increased from zero to about 0.88 within the first 6 m. Then, they continued to fluctuate around this value until the completion of the test. The coefficient of friction of MJ12 and MJ47 with 800–1,000 °C nitridation for 3.6×10^4 s rapidly increased within a very short distance to about 0.16 and slowly

increased until reaching a constant value between 0.24 and 0.35. The change in the friction coefficient was irregular due to the different phases formed on the alloys at different temperatures and the vibration of the WC pin. Comparing the alloys without and with 800–1,000 °C nitridation, the coefficient of friction of the alloys without nitridation showed more fluctuation than that of the alloys with high temperature nitridation.

Fig. 3 Coefficient of friction (μ) of (a) MJ12 and (b) MJ47 without and with 800–1,000 °C nitridation for 3.6×10^4 s



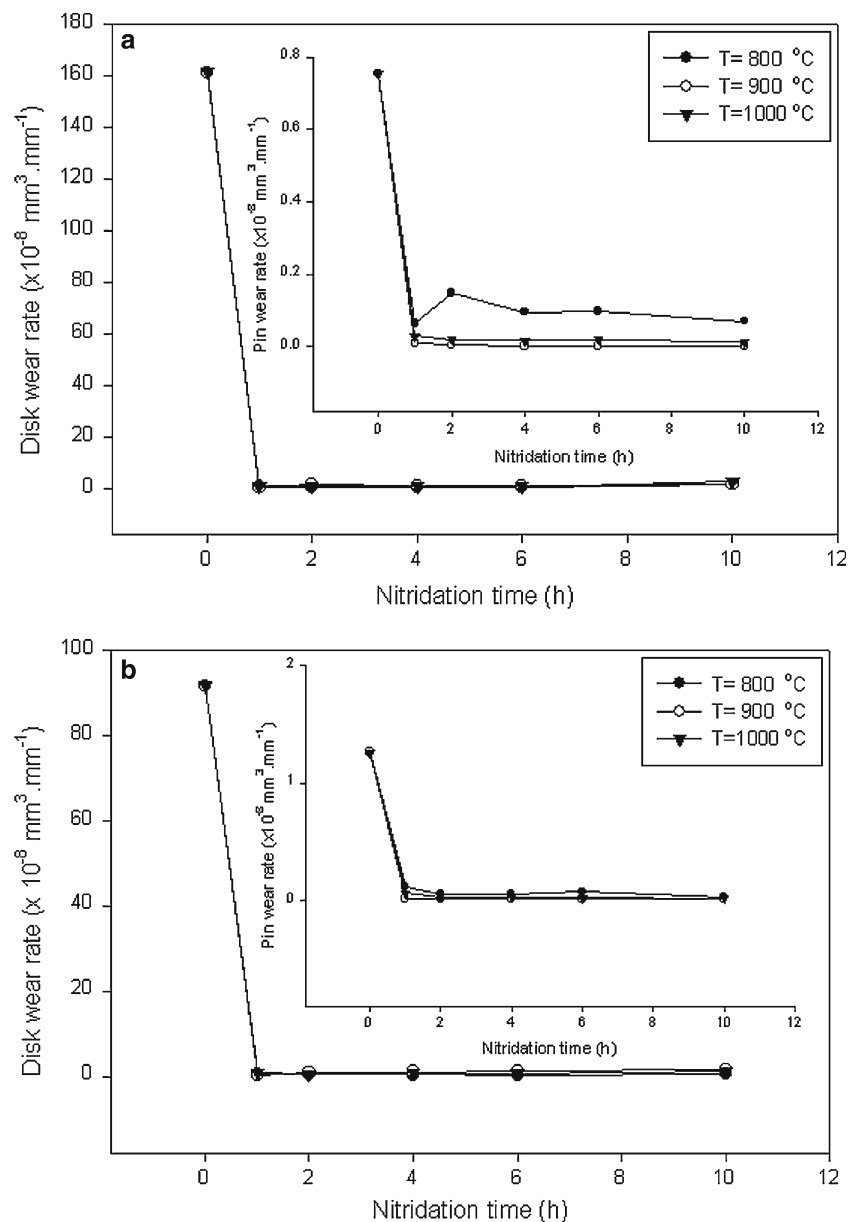
Disk and pin wear rates

Wear rates of the disks and the WC pin are shown in Fig. 4. For the alloys without nitridation, wear rates of MJ12 and MJ47 are $161.63 \times 10^{-8} \pm 9.09 \times 10^{-8}$ and $91.67 \times 10^{-8} \pm 6.26 \times 10^{-8} \text{ mm}^3 \text{ mm}^{-1}$, respectively. Wear resistance of MJ12 is less than that of MJ47. The results are in accord with the hardness of the two alloys. It shows that hardness and wear resistance have the same tendency. Wear rates of MJ12 and MJ47 with 800–1,000 °C nitridation for 3.6×10^3 – $3.6 \times 10^4 \text{ s}$ were reduced by two orders of magnitude after nitridation in comparison with the alloys without nitridation. The 800–1,000 °C nitridation process can improve both hardness and wear resistance. At differ-

ent nitridation temperature and time, wear rates of the alloys were irregular due to the irregularity of wear tracks. The irregularity could be the width, the depth or the shape of the wear tracks. The results are in agreement with those for the friction coefficient of the corresponding alloys, as previously explained. The nitridation temperature could play a role in the formation of different phases and compositions which reflect the irregularity of wear resistance as well.

Wear rates of the WC pin used for measuring wear resistances of MJ12 and MJ47 without and with 800–1,000 °C nitridation were between $0.12 \times 10^{-10} \pm 0.01 \times 10^{-10}$ and $125.79 \times 10^{-10} \pm 13.33 \times 10^{-10} \text{ mm}^3 \text{ mm}^{-1}$. The values of the wear rates were irregular due to vibration of the pin

Fig. 4 Disk and pin wear rates of (a) MJ12 and (b) MJ47



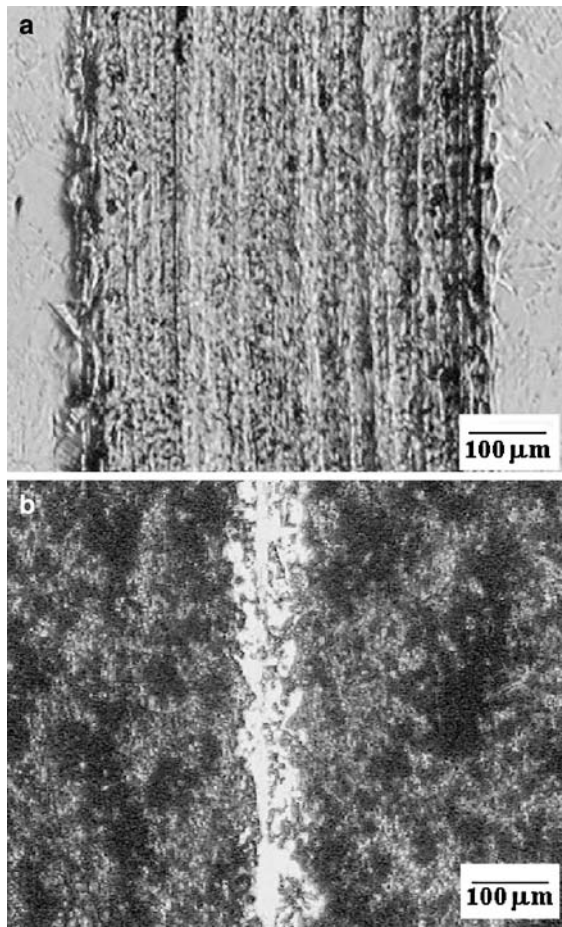


Fig. 5 Wear tracks on MJ12 (a) without and (b) with 800 °C nitridation for 2.16×10^4 s

during testing. Pin wear rates used for measuring the alloys without nitridation were higher than those used for measuring the alloys with 800–1,000 °C nitridation. The results could be due to vibration of the pin, the characteristics of the tracks, and the different phases formed on the alloys.

Optical micrographs

After wear testing, external morphologies of wear tracks on the alloys and wear scar on the WC pin were examined using an optical microscope. The results are shown in Figs. 5–7. The width of the tracks on MJ12 and MJ47 without nitridation were 507.4 ± 9.5 and 420.0 ± 9.6 μm, respectively. After 800 °C nitridation for 2.16×10^4 s (6 h), wear tracks on MJ12 and MJ47 were 80.8 ± 9.5 and 63.0 ± 7.5 μm, respectively. The track on MJ12 was larger than that on MJ47. This result is consistent with the hardness and wear rate of the alloys. In addition, the characteristics of the wear tracks on the alloys without and with 800 °C nitridation are different. The tracks of the alloys without nitridation show the characteristics of

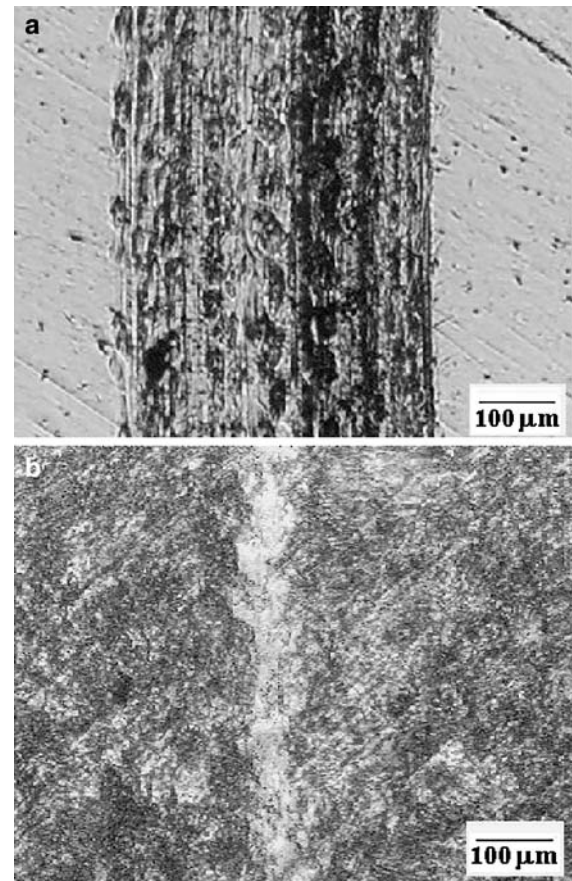


Fig. 6 Wear tracks on MJ47 (a) without and (b) with 800 °C nitridation for 2.16×10^4 s

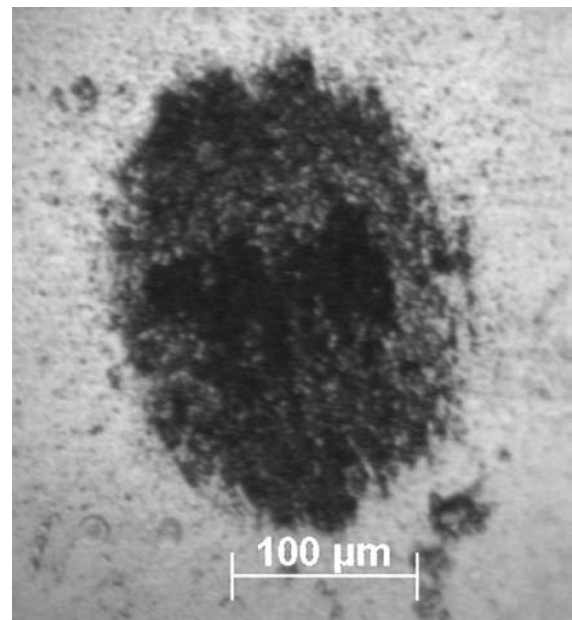


Fig. 7 Wear scar on WC pin used for testing on MJ47 with 800 °C nitridation for 2.16×10^4 s

ductile metals. There are a number of small parallel traces of different depth and width on the tracks. But for the alloys with 800 °C nitridation, the tracks show characteristics of brittle materials. There are worn protrusions of the nitridation products occurring along the tracks. In addition, the optical micrograph of the wear scar on the WC pin shows that it was worn by the disks and is irregular.

SEM

Cross-section and top view of the alloys are shown in Figs. 8 and 9. There are single layers deposited on top of MJ12 and MJ47 that are 1 and 2 μm thick, respectively. Both of these layers are irregular showing that the reactive gas reacted with the alloying elements at random. This random reaction leads to surface roughness which reflects the tribological properties of the alloys.

EDX

By using EDX, the elemental spectra of MJ12 and MJ47 without and with 800–1,000 °C nitridation for 3.6×10^4 s

are shown in Fig. 10. Ti, Al and Nb were detected on both alloys. Additional Cr and Mn were detected on MJ12 and MJ47, respectively. Atomic mass of B is 10.81 g mol^{-1} ; therefore, no B was detected on MJ47. The results are consistent with the composition of the alloys shown in Table 1. During 800–1,000 °C nitridation, NH_3 decomposed into N and H. Due to its light element, no H was detected. Additional N and O were detected on the two alloys. The presence of O is likely to be from the reaction between ammonia and the high-alumina porcelain reaction chamber. Some N and O dissolved into the alloy matrices and some formed compounds with the alloying elements.

XRD

The alloys with 800–1,000 °C nitridation for 3.6×10^4 s were analyzed using an XRD and the spectra are shown in Fig. 11. A variety of phases are summarized in Table 2. At 800 °C, only TiAl was detected on both alloys. No TiN was detected. The nitridation temperature could be so low that no TiN can form. Its concentration could be too low to be detected as well.

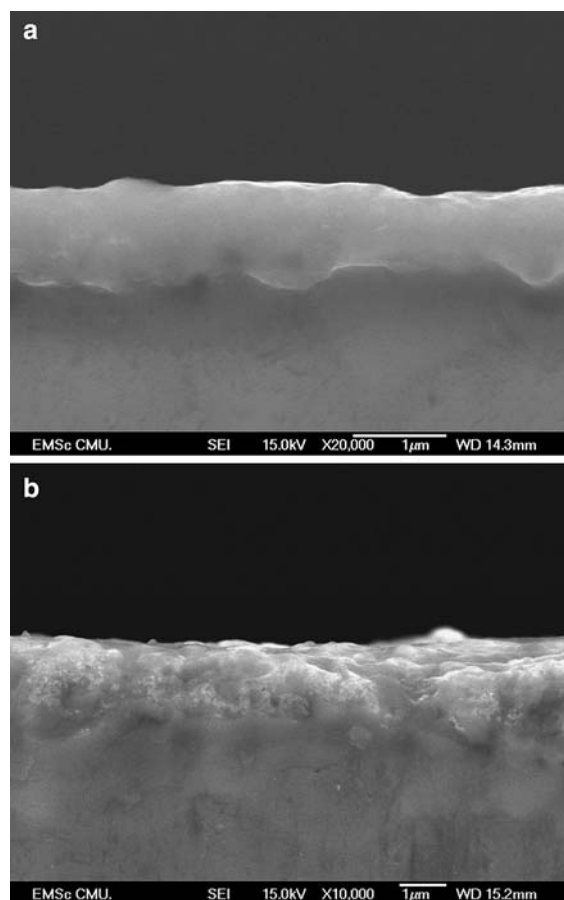


Fig. 8 Cross-section of (a) MJ12 and (b) MJ47 with 1,000 °C nitridation for 3.6×10^4 s

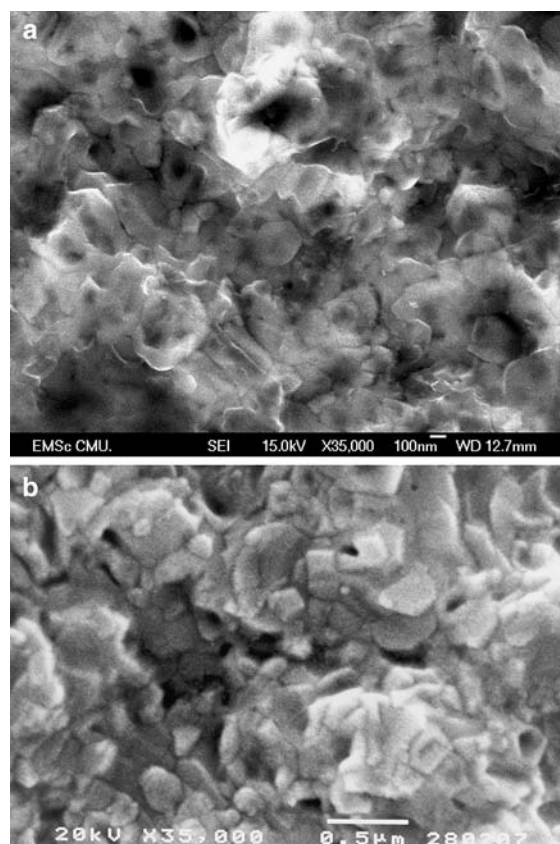


Fig. 9 Top view of (a) MJ12 and (b) MJ47 with 1,000 °C nitridation for 3.6×10^4 s

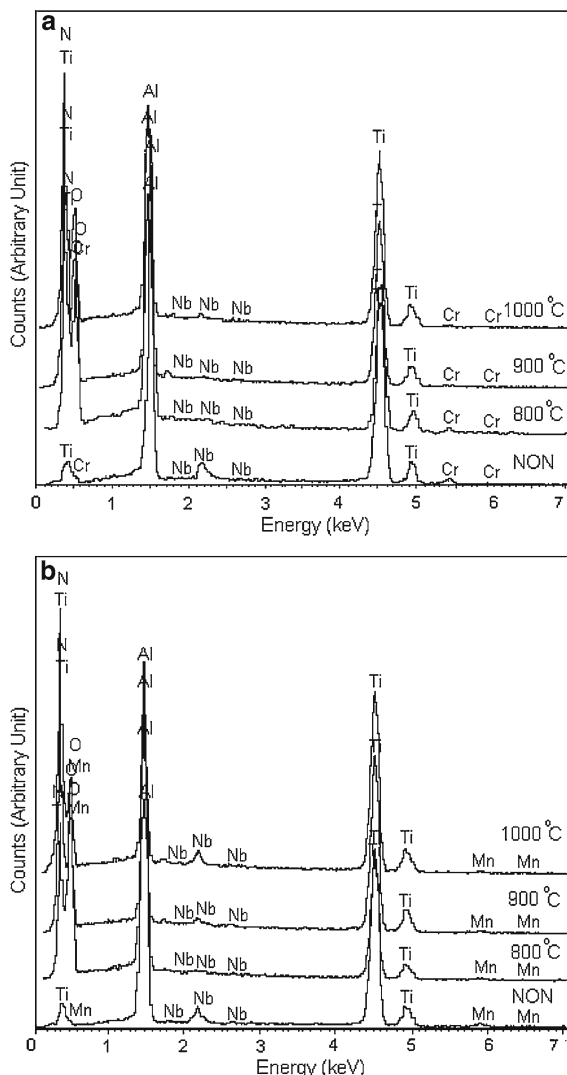
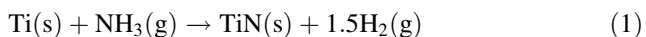


Fig. 10 EDX spectra of (a) MJ12 and (b) MJ47 without and with 800–1,000 °C nitridation for 3.6×10^4 s

At 900 and 1,000 °C, Ti–Al phases, TiN, Al₂O₃ and Al were detected. The detection of different phases on the alloys can be explained as follows:

TiAl: Nitrided layers could be too thin to shield the underneath alloy matrices and TiAl was detected.

TiN: At 900 and 1,000 °C, TiN is more thermodynamically stable than AlN [13, 14]. During the nitridation process, ammonia reacted with titanium to form nitride by the reaction,



TiN(s) deposited on the alloy surfaces and H₂(g) drained off into the ambient atmosphere.

Al₂O₃: At the very beginning of the nitridation process, residual oxygen in the high temperature reaction chamber was not more than 5 ppb; therefore, the content of oxygen

Table 2 A summary of phases on MJ12 and MJ47 with 800–1,000 °C nitridation for 3.6×10^4 s

T (°C)	Phases	
	MJ12	MJ47
800	TiAl	TiAl
900	TiAl, Ti ₃ Al, TiN, Al ₂ O ₃	TiAl, TiN, Al ₂ O ₃
1,000	TiAl, Ti ₃ Al, TiN, Al ₂ O ₃	TiAl, Ti ₃ Al, TiN, Al ₂ O ₃ , Al

was not enough to form Al₂O₃ that can be detected by the XRD. Silica in the high alumina porcelain chamber is likely to be reduced by NH₃; therefore, nascent oxygen developed and reacted with Al to form Al₂O₃.

Ti₃Al: Nitridation could play a role in Ti and Al concentrations leading to phase transformation of TiAl into Ti₃Al. When the alloys cooled down to room temperature, there was Ti₃Al phase left and detected.

Al: The formation of Al on MJ47 with 1,000 °C nitridation was due to the reaction between Ti and NH₃ as shown in Eq. (1). TiN developed and Al in TiAl matrix was released. Some of Al reacted with O to form Al₂O₃ and some Al was left and detected.

No TiB₂ was detected on MJ47 although TiAl was detected. The concentration of TiB₂ underneath the nitrided layer could be too low to be detected by the XRD.

A variety of phases at different temperatures is the factor that controls tribological properties of the alloys.

Conclusions

Hardness of γ -TiAl alloys was successfully improved by 800–1,000 °C nitridation in ammonia and increased with an increase of the nitridation temperature and time. The tribological test showed that wear resistance and friction coefficient are significantly improved by the nitridation process. The improvements are in accord with the TiN formation analyzed by the XRD and N detection analyzed by the EDX. SEM micrographs show that the alloys are covered with a single layer of deposited phases of which roughness reflects the surface properties.

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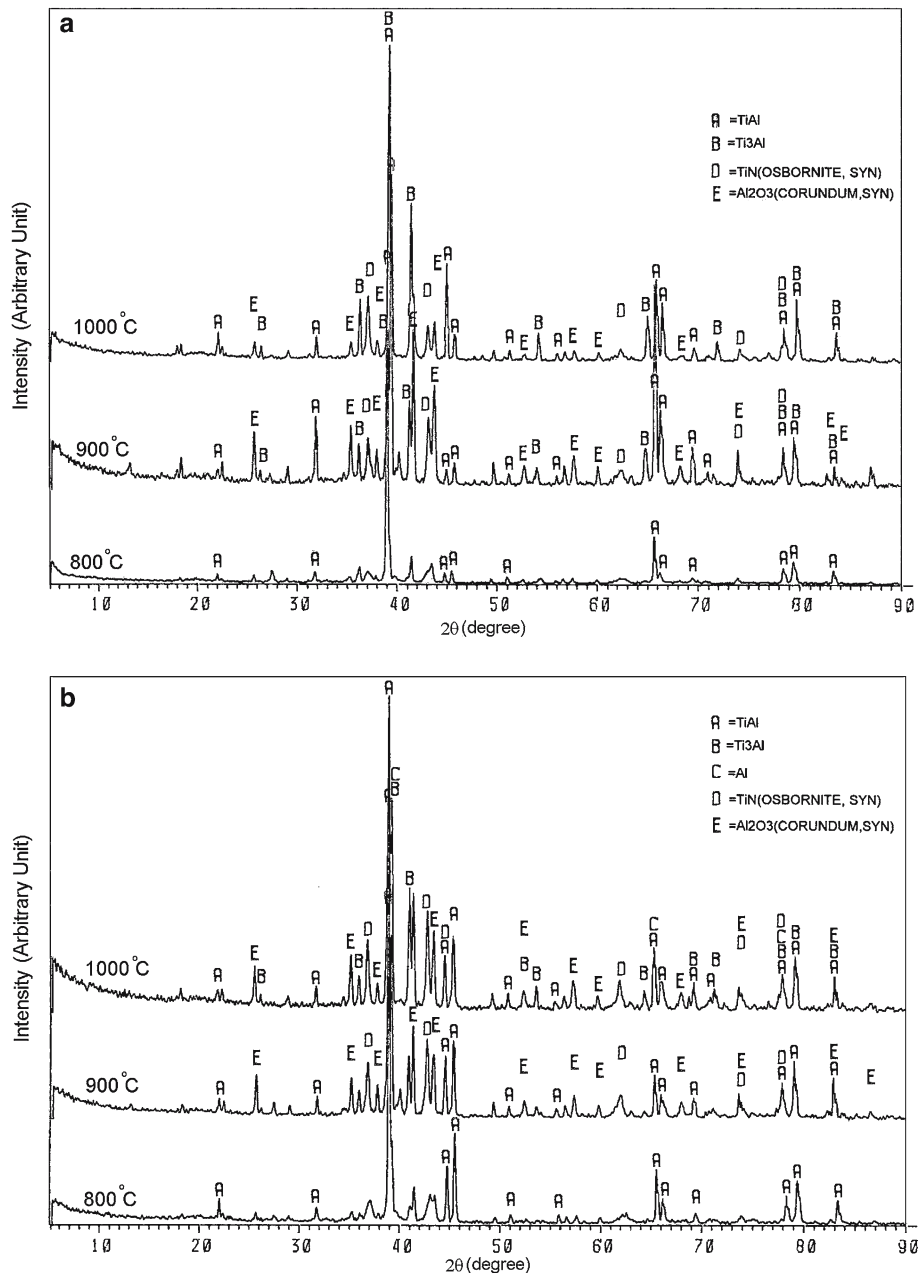


Fig. 11 XRD spectra of (a) MJ12 and (b) MJ47 with 800–1,000 °C nitridation for 3.6×10^4 s

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