[Article ID] 1003- 6326(2002)04- 0629- 06

Wear and isothermal oxidation kinetics of nitrided TiAl based alloys ①

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[Abstract] Gas nitridation of TiAl based alloys in an ammonia atmosphere was carried out. The evaluation of the surface wear resistance was performed to compare with those of the non-nitrided alloys. It is concluded that high temperature nitridation raised wear resistance of TiAl based alloys markedly. The tribological behaviors of the nitrided alloys were also discussed. The oxidation kinetics of the nitrided TiAl based alloys were investigated at 800~ 1 000 ℃ in hot air. It is concluded that nitridation is detrimental to the oxidation resistance of TiAl based alloys under the present conditions. The nitrided alloys exhibit increased oxidizing rate with the prolongation of nitridation time at 800 ℃. However, alloys nitrided at 940 ℃ for 50 h display a sign of better oxidation resistance than the other nitrided alloys at more severe oxidizing conditions. The parabolic rate law is considered as the basis of the data processing and interpretation of the mass gain vs time data. As a comparison with it, attempts were made to fit the data with the power law. The oxidation kinetic parameter k_n, k_p and n were measured and the trends were discussed.

[Key words] intermetallic compound TiAl; nitridation; oxidation; wear
[CLC number] TG 146.2 **[Document code]** A

1 INTRODUCTION

The intermetallic compound TiAl has a great potential as light-mass high-temperature materials for aerospace and automobile industries[1~4]. In the development of high performance TiAl, great efforts have been made to improve room temperature ductility and oxidation resistance[5~11].

As we know, tribological problems are always involved in the structural materials, especially in case of a turbine engine or a turbocharger rotor. Titanium nitride is a suitable hard material for improving wear resistance, and coating of TiN by chemical vapor deposition(CVD) or physical vapor deposition(PVD) is often applied to tool steels to improve the service life of cutting tools in wear application[12, 13]. Because TiN is more thermodynamically stable than AlN, TiN layers can be formed on TiAl by direct nitridation in different atmospheres[14, 15] by implantation with N[16] and by ion nitridation[17].

However, as to its oxidation resistance after nitridation, the systematic study has not been carried out. The effect of nitrogen on the oxidation behavior of TiAl alloys has been noticed[8~11]. Wu et al[11] showed that TiN formation was favored in the Ti_3Al based alloys with Nb after exposure in hot air. Hanrahan et al[18] observed that the TiN layer was a diffusion barrier to oxygen in titanium-tantalum alloys. However, Choudhury et al[19] concluded that the faster oxidation of TiAl in air as compared with that in oxygen was due to the presence of nitrogen in air. Meier et al[20] observed that protective alumina scales formed on TiAl upon exposure in oxygen up to 1000 ℃, while the same exposure in air resulted in the formation of titania-rich scale exhibiting faster growth rate. Meier et al also suggested that the presence of nitrogen caused formation of a nitride layer that prevented the development of a continuous alumina scale. It was concluded that formation of nitride layer was favored in Ti_3Al based alloys, but for the high Al content alloys, e. g., TiAl based alloys, it was another story. The oxidation rate of the TiAl based alloys in oxygen was in general lower than that in air. However, exceptions had been also observed[8]. The formation of a nitride layer, in particular TiN, obviously favored the formation of a protective Al_2O_3 layer, because it decreased the Ti activity and increased the Al activity of the metal phase. However, it was only one aspect of the nitrogen effect.

The role of nitride on the oxidation kinetics of TiAl based alloys is not quite clear, especially of these alloys after nitridation. Compared with the non-nitrided TiAl based alloys, this paper describes investigations regarding the wear resistance and isothermal oxidation behavior of nitrided TiAl based alloys in order to get a better understanding of the role of nitride.

2 EXPERIMENTAL

A conventional tungsten arc melting technique was employed to prepare titanium aluminide alloy.

① **[Foundation item]** Project (98JC14016) supported by the Science and Technology Commission of Shanghai Municipal Government
[Received date] 2001- 10- 08

Ti-47Al-2Nb-2Cr-0.2Si (mole fraction, %) was cast and homogenized at 1 050 ℃ for 100 h. Specimens with dimensions of 6 mm × 6 mm × 10 mm for the wear test and d10 mm × 2 mm for the oxidation test were cut from the homogenized ingots followed by surface polishing. After washed carefully in the acetone and alcohol to remove grease, all specimens were hung in a high-temperature quartz reaction tube for nitridation. The tube was evacuated repeatedly and finally filled with argon. The specimens were heated to 800~ 940 ℃. The nitridation time was 10h, 30h and 50h, respectively. And then argon was replaced with ammonia flowing at the rate of 5~ 10cm^3/s. When the required period had been attained, the specimens were cooled down in argon to room temperature. The details about the nitride layers characterization were reported in the other paper[21~ 23].

The wear test was performed on an Amsler test machine using block-on-ring setup. The counter ring was made of carbon steel containing 0.45% C and surface electroplated with hard chromium with a hardness of HRC65. The load for the wear tests was 13 N, and the sliding speed was 0.523 m/s under unlubricated conditions. The sliding distance was 314 m. X-ray diffractometry (XRD) using CuK$_\alpha$ radiation and scanning electron microscopy (SEM) were used to study the microstructure and morphologies of the nitrided alloys. SEM and optical microscopy (OM) were employed to investigate the wear traces, the trace edge and the wear debris.

Isothermal oxidation was performed in an open air for 5~ 100 h at different temperatures from 800 to 1 000 ℃. Oxidation kinetics was measured by an electrobalance with the precision of 0.1mg. After oxidation, the phase constitutions of the scales in the surface of the specimens were characterized by X-ray diffractometry (XRD) using CuK$_\alpha$ radiation. SEM and energy dispersive X-ray spectroscopy (EDX) were employed to investigate both the surface morphology and the cross-section of the scale formed on the alloys.

3 RESULTS AND DISCUSSION

3.1 Wear resistance

Wear properties are generally related to the surface hardness of the alloys. Formation of the nitride layers increased the Knoop hardness and was also thought to be able to improve the wear resistance of the alloys. According to optical micrographs of the TiAl based alloys, the width of wear traces of the non-nitrided specimens (as shown in Fig. 1(a)) was wider than that of specimens nitrided at 940 ℃ for 50h (as shown in Fig. 1(b)), and its wear trace depth was also deeper. It shows severe plastic deformation along the edge of the traces of the non-nitrided alloys (as shown in Fig. 2(a)) compared with that

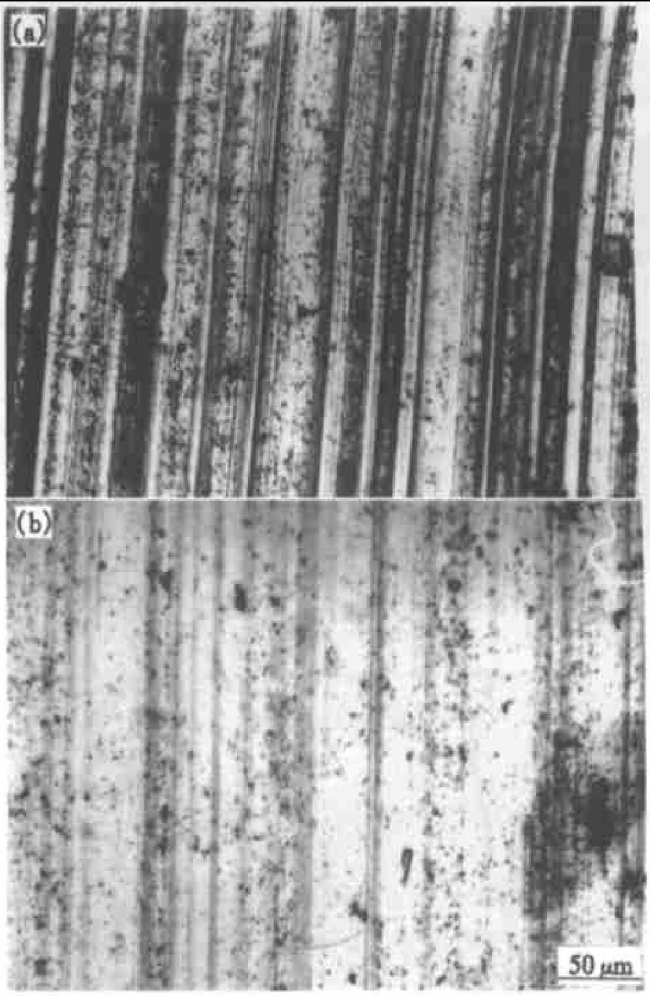

Fig. 1 Wear traces of TiAl based alloys
(a) —Non-nitrided alloys;
(b) —Alloys nitrided at 940 ℃ for 50 h

Fig. 2 Edges of wear traces
(a) —Non-nitrided alloys;
(b) —Alloys nitrided at 860 ℃ for 50 h

of the alloys nitrided at 860 ℃ for 50 h (as shown in Fig. 2(b)), which indicates the progressive loss of the wear trace. Two types of debris feature were observed. Fig. 3 shows debris of the non-nitrided alloys exhibits the signs of peeling and rupturing during wear testing.

Fig. 3 Debris of TiAl based alloys nitrided at 940 ℃ for 50 h

The comparison of the wear loss for different specimens is shown in Fig. 4. As can be seen the wear resistance of the specimens nitrided at different temperatures and time was better than that of the non-nitrided alloys. For the nitrided alloys, the wear resistance increased with increasing nitridation temperature and time. The wear loss of the specimen nitrided at 940 ℃ for 50 h was only half as large as that of the non-nitrided alloys. The variation of the mean dynamic friction coefficients displayed the same trend as their Knoop hardness and wear resistance. The friction coefficient of the non-nitrided alloy was 0. 74, while that of the alloy nitrided at 940 ℃ for 50 h was 0. 53.

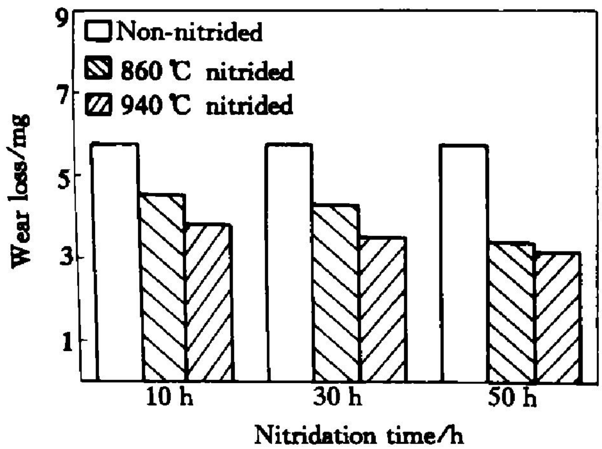

Fig. 4 Comparison of wear loss of nitrided alloys with that of non-nitrided alloys

Wear mechanisms of TiN coating on steel in dry sliding contact in a pin-on-disk wear tester was investigated in Ref. [24]. Three wear regimes were identified: 1) transfer and build up of oxidized pin debris on the coating at 20N load, 2) increased polishing damage and brittle spallation failure of the TiN at 50~100 N and 3) a sharp transition to plastic deformation and microploughing of TiN at loads greater than 100N. In the present experiment, the wear mechanism of the nitrided alloys was similar to the second regime because of the more austere wear conditions than those in Ref. [24]. As a result, the nitrided alloys show the signs of increasing wear loss and damage of the nitride layers after the wear test. However, without the protection of the nitride layers, the non-nitrided alloys displayed severe abrasive wear and plastic deformation (as shown in Fig. 2(a)).

3. 2 Oxidation kinetics at 800 ℃

The results of isothermal exposure at 800 ℃ in air up to 100 h are summarized in Fig. 5. The overall mass gain of the nitrided TiAl based alloys at the various temperatures and time is higher than that of the non-nitrided alloy. The alloys nitrided at 940 ℃

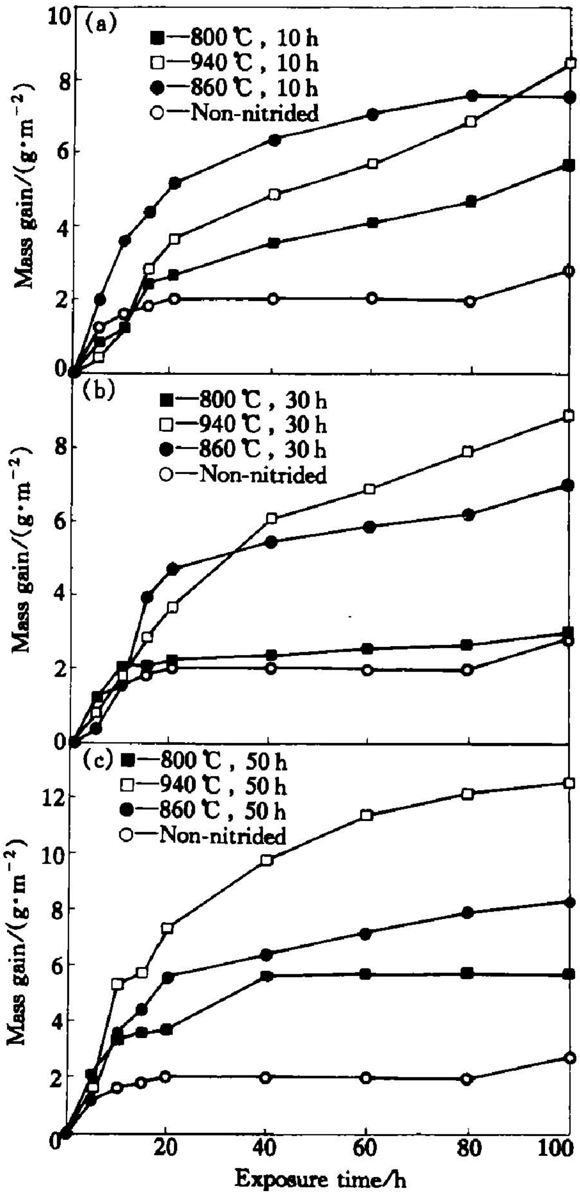

Fig. 5 Mass gain—time relationship of various TiAl based alloys after exposure in air at 800 ℃

(a) —Nitrided for 10 h; (b) —Nitrided for 30 h; (c) —Nitrided for 50 h exhibit a gradually weakened oxidation resistance with the elongation of nitridation time. As to the alloys nitrided at 940 ℃ for 10 h, its mass gain exceeds that of the other two nitrided alloys after 90h exposure time (as shown in Fig. 5(a)). The alloys nitrided at 940 ℃ for 30 h lasts about 35 h (as shown in Fig. 5(b)), and less than 10 h for the alloys nitrided at 940 ℃ for 50 h (as shown in Fig. 5(c)). Generally, the non-nitrided alloys exhibit the best oxidation resistance. Those nitrided at 800 ℃ do better than the alloys nitrided at 860 ℃. The nitrided alloys display the weakened oxidation resistance by increasing nitridation time. The largest mass change of the alloys nitrided at 940 ℃ for 50h was almost five times the value as found for the non-nitrided alloys, which was very low and in the order of 3 g/m^2. Under the present conditions, no spallation happened in all the alloys. And it took about 20 h for all the alloys to form a protective layer after transient oxidation.

3.3 Oxidation kinetics at 900 ℃

Compared with the results at 800 ℃, there was a slight difference among the mass gains of the nitrided alloys exposed at 900 ℃ for the same exposure time. Fig. 6 is a typical one which shows the oxidation results of the alloys nitrided at various temperatures for 50 h. Relatively, the alloys nitrided at 940 ℃ showed the improved resistance as compared with that at 800 ℃. The non-nitrided alloys still exhibited better oxidation resistance than the nitrided alloys. For the alloys nitrided at 940 ℃ for 50 h, a rapid transient oxidation was observed during the initial 5h of exposure, followed by a slower oxidation rate than those of all the other alloys including the non-nitrided alloys. All the alloys exhibited more rapid corrosion rates at 900 ℃ than at 800 ℃. For the alloys nitrided at 800 ℃, their mean mass gains at 900 ℃ were approximately four times as large as those at 800 ℃. However alloys nitrided at 860 ℃ and 940 ℃ acted better and it was about twice. After exposure at 900 ℃ for 60 h most of the specimens appeared the sign of spallation. It spent 15 h for the alloys to form a protective layer to reduce the corrosion rate.

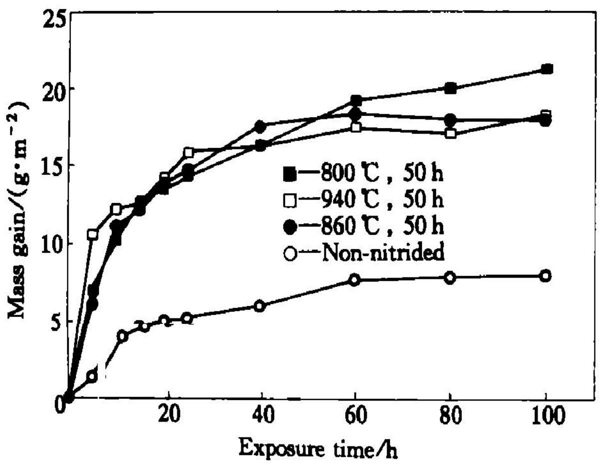

Fig. 6 Typical mass gain—time relationship of nitrided TiAl based alloys exposed in air at 900 ℃

3.4 Oxidation kinetics at 1 000 ℃

When exposure at 1 000 ℃, the alloys nitrided at 940 ℃ show a clear trend as a rapid transient oxidation during the initial 5 h, followed by a more slow rate than all the other alloys. Furthermore, alloys nitrided at higher temperatures show better oxidation resistance than those nitrided at the lower temperatures (as shown in Fig. 7). Fig. 7(a) and Fig. 7(c) exhibit that alloys nitrided at 940 ℃ show a slower oxidation rate than the other two nitrided alloys. It was no doubt that alloys displayed worse oxidation resistance at 1 000 ℃ than at 900 ℃. But the ratio of the mass gains between those at 1 000 ℃ for 100 h and those at 900 ℃ are small. That of the alloys

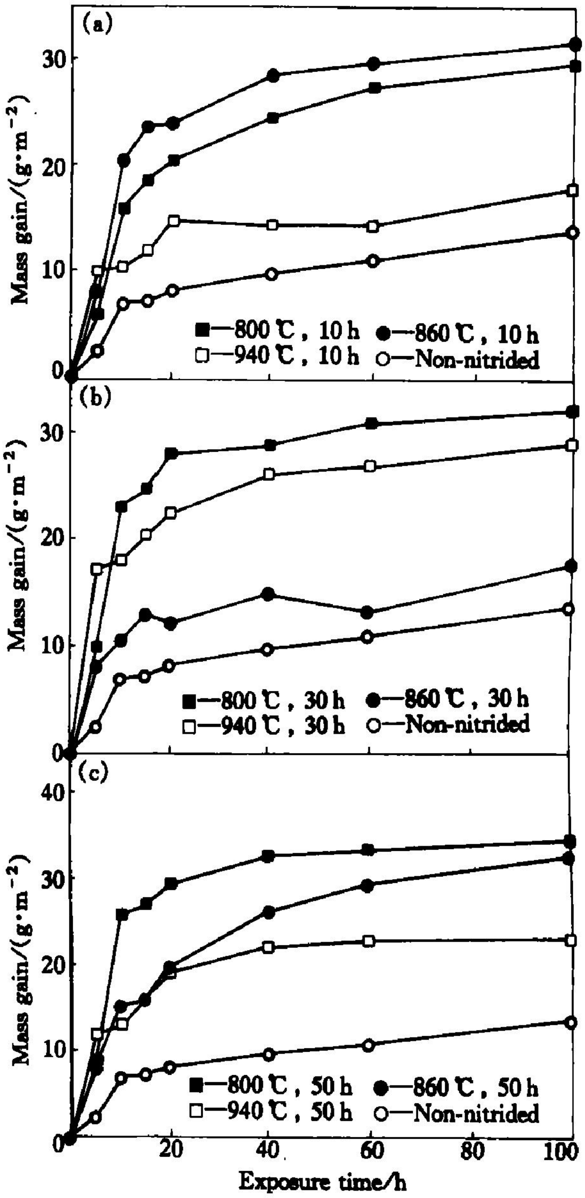

Fig. 7 Mass gain—time relationship of various TiAl based alloys exposed in air at 1 000 ℃ (a) —Nitrided for 10 h; (b) —Nitrided for 30 h; (c) —Nitrided for 50 h

nitrided at 800 ℃ and 860 ℃ was about twice, yet it was only 1.3 for those nitrided at 940 ℃.

As a consequence, the oxidation resistance of the nitrided alloys exposed for upon 100 h at 800, 900 and 1 000 ℃ displayed the following characteristics:

1) Under the present conditions, non-nitrided alloys still exhibit the superior oxidation resistance to the nitrided alloys. Although the formation of a nitride layer, in particular TiN, the formation of a protective Al_2O_3 layer is obviously favored because of the formation of an Al enriched layer[8, 21~23]. However, this only one aspect of the nitridation. The nitride layers were easily oxidized above 500 ℃[25]. It was also considered that the further nitridation happened during the oxidation tests, which prevented the continuous Al_2O_3 layer from forming. As a result, more Al content on the surface of the non-nitrided alloys accelerated the formation of Al_2O_3 that protected the substrate from further oxidizing, while the nitrided alloys lost more during the oxidation tests.

2) Among the nitrided alloys, it was concluded that the high-temperature nitrided alloys displayed a sign of better oxidation resistance at more severe oxidizing conditions. Those nitrided at lower temperatures exhibited better resistance at 800 ℃, but at higher temperatures they were inferior. That was mainly due to the rapid transient oxidation at the initial stage that was beneficial to the quick formation for the protective layers at 1 000 ℃.

3.5 Oxidation kinetic parameters of nitrided TiAl based alloys

A review of earlier investigations on oxidation kinetics of the TiAl based alloys revealed that the parabolic rate law was considered as the basis of data processing and interpretation of the mass gain vs time data. With a comparison with the parabolic rate law, attempts were made to fit the data with law as follows.

$$(\Delta m/A)^n = k_n t \quad (1)$$

Where $\Delta m/A$ was mass gain per unit surface area of specimen, t was exposure time and k_n was the rate constant. The rate constant k_n and exponent n were evaluated from linear regression fitting of $\lg(\Delta m/A)$ vs $\lg t$ data.

The processing results of the kinetic parameters of TiAl-based alloys at 800 ℃ for 100 h showed that the difference between k_n values for duplicate sets was larger than that of k_p which was the parabolic rate constant. The difference between k_n values and that of k_p could be neglected. It was also concluded that the nitrided alloys oxidized at 800 ℃ approximately showed the parabolic rate law. However, the difference between the values of k_n and k_p became larger at 900 ℃ and 1000 ℃ after 100 h exposure time, and the values of n was also larger than 2, especially those oxidized at 1 000 ℃. The departures from the parabolic law can be ascribed to the variation in uniformity and composition of scale in process of oxidation, such as the changes on scale porousness, adherence, nature of defects, cracking etc[10]. However, the k_p values for duplicate sets were observed to be similar. On the other hand, the difference between k_n values for duplicate was large, too. The values of n also exhibited a lot of scatter. But with the variation of temperature, it showed the trends of gradual increase. The range of values of n was from 3 to 5 at 900 ℃ for 100 h, and from 4 to 6 at 1 000 ℃. The nitrided alloys showed a singular rate law during their early stage of oxidation for 10 to 15 h, especially when they were oxidized at 900 ℃ and 1 000 ℃.

Values of k_n and k_p were obtained from the slopes of regression-fitted straight lines $(\Delta m/A)^2$ vs t data and $\lg(m/A)$ vs $\lg t$ data. Such as those presented in Fig. 8(a) and Fig. 8(b), the parabolic and power plots of samples mass gain for oxidation of TiAl based alloys nitrided at 940 ℃ for 50h and at 800 ℃ in the hot air are shown respectively. It was concluded that the power law fits the experimental data better. Furthermore according to Fig. 8(b), different oxidation stages, such as the transient oxidation at the initial stages and the followed slower oxidation could be identified easily, which was helpful for the understanding of alloys oxidation behaviors. However, it was indicated in the Ref. [10] that evaluation

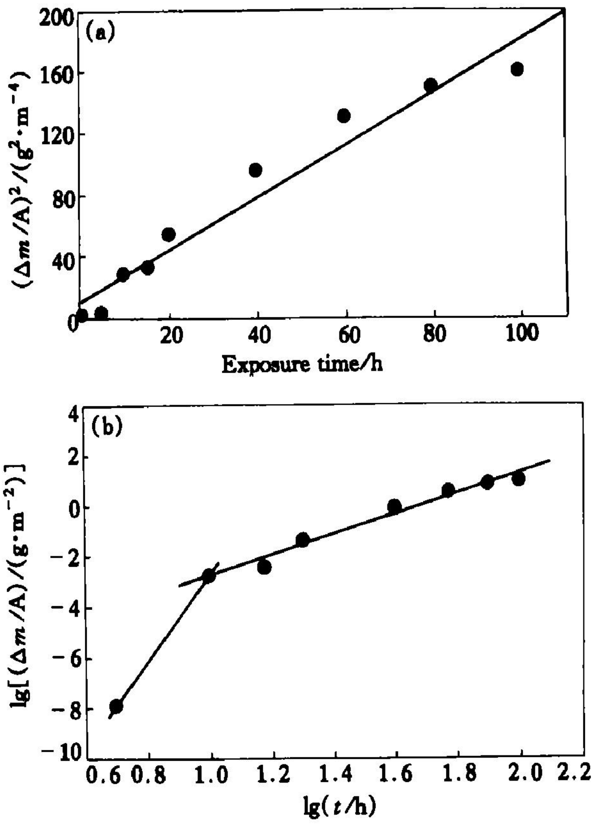

Fig. 8 Parabolic (a) and power (b) plots of samples mass gain for oxidation of TiAl based alloys nitrided at 940 ℃ for 50 h at 800 ℃ in hot air respectively

of the rate constant on the basis of parabolic law was more reliable as compared to the use of the empirical Eqn. (1). Moreover, the parabolic rate constant had a theoretical basis, hence it could be used for comparison with the literature.

4 CONCLUSIONS

1) Mechanical tests shows that high-temperature nitridation can obviously increase the sliding wear resistance of the TiAl based alloys. When the nitriding time prolonged to 50 h at 940 ℃, its wear loss is only half as large as that of the non-nitrided alloys.

2) Alloys nitrided at 800 ℃ for 10 h exhibit better oxidation resistance at the lower oxidizing temperature than the other nitrided alloys. But by increasing the oxidation temperature, those alloys nitrided at the higher temperature for a longer time show an improved oxidation resistance, especially the alloys nitrided at the oxidation temperature of 1 000 ℃ for 100 h. It also indicated that they undergo the slowest oxidation rate after a rapid transient oxidation among all the alloys including the non-nitrided alloys.

3) At 800 ℃ the nitrided alloys approximately show the parabolic rate law. But great departures from the parabolic law happen at the 900 ℃ and 1 000 ℃, which could be ascribed to the variation in uniformity and composition of scale in process of oxidation. The fitting results show that the power law fits the experimental data better. However, the parabolic rate constant has a theoretical basis, so it can be convenient for comparison with other literatures.

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(Edited by YANG Bing)