Improvement of the oxidation resistance of TiAl Alloys by Metal plasma-based ion implantation

Takaya Ishii, Kazutugu Murakami, Kazuhisa Fujita and Yutaka Hibino

Ion Engineering Research Institute Corporation, 2-8-1, Tsuda Yamate, Hirakata, Osaka, Japan Fax: 81-072-859-6299, e-mail: ishii@ion-eng.jp

Abstract

Plasma based ion implantation (PBII) system has been studied to achieved a uniform ion implantation to a three-dimensional workpiece. Up to date, PBII system with gas plasma has been used to improve anti-corrosion and tribological properties. In order to expand the application area of PBII, metal plasma source has been investigated for the surface modification in several materials. However, metal plasma-based ion implantation (Me-PBII) has some problems such as film deposition during ion implantation. Recently, we have developed the Me-PBII system with a pulse arc system to reduce the film deposition.

In this study, improvement of the oxidation resistance of TiAl alloy is reported. Niobium and Mo ions were implanted into Ti50%Al50% (at.%) alloys by using Me-PBII system. The oxidation behavior of TiAl alloys was then investigated in air at 850°C. The depth profile of implanted Nb and Mo atoms were evaluated by Auger electron spectroscopy. The results showed that after the ion implantation, Nb and Mo ions were located in a very shallow surface region with a peak concentration at 40nm. The oxidation test revealed that TiAl treated by PBII showed a very low oxidation weight loss of 1.0 mg/cm² at 200 hours, and a protective continuous Al_2O_3 scale formed on the surface. Me-PBII treatment proves to be a promising surface modification method for improving the oxidation resistance of TiAl alloys.

Key words: Plasma based ion implantation, TiAl alloy, Nb ion implantation, Mo ion implantation, oxidation resistance

1. INTRODUCTION

 γ -TiA1 based on intermetallic alloys are promising candidate materials for use as high-temperature structural applications because of the unique combination of their low density and high specific strength at elevated temperatures[1]. The potential use of TiA1 alloys is expected for blades in gas turbine engines, and for valves and turbocharger rotors in car engines[2].

However, the oxidation resistance of TiAl alloys is insufficient for industrial applications. Ion implantation has been utilized as an effective method for improving the oxidation behavior of TiAl alloys. For example, implantation of Nb, Mo, F and Cl etc., can favor formation of an $A1_2O_3$ -rich oxide scale on the surface, thereby leading to the improvement of the oxidation resistance of TiAl[3-7].

However, conventional beam-line ion implantation is limited for modification of flat substrates with small area and not suited for industrial applications. Plasma based ion implantation (PBII) system has been developed to achieved a uniform ion implantation to a three-dimensional workpiece.[8,9] In this work, PBII was applied to improve oxidation behavior of TiA1 alloys.

2. EXPERIMENTAL

2.1 PBII equipment



Fig.1 Schematic diagram of PBII system

Schematic diagram of PBII equipment is shown in Figure 1. The substrate was pulsed biased to a negative voltage of $10 \sim 40$ kV through a feedthrough with a pulsed voltage supplier. The length of the pulsed voltage was 100μ s with a repetition rate of 100 pps. Gas plasma was produced from RF coil for Ar ion cleaning treatment. The plasma was produced from metal target with a metal plasma source.

2.2 Metal ion source

A schematic diagram of the metal ion source is shown in Fig.2. The metal ion source is connected with a pulse trigger power supply and a arc power supply. The metal target is biased negative relative to the anode. A metal ion was produced by applied trigger pulse from water cooled metal cathode. It triggered a arc discharge between the cathode and the anode plate.

High voltage for generating the trigger pulse was 4kV between the cathode and the trigger ring. The specifications of the metal ion source are as follow.

1)Arc voltage / current : -300V(max) / 100A(max) (Wave form : Rectangular shape)

- 2)Arc voltage pulse width : $10 \sim 100 \mu s$
- 3)Pulse frequency : 1~100pps
- 4)Specifications of trigger system
- II h and the mention of the gen system

High voltage pulse : -4kV / 100A, $12\mu s$ 5)Cathode metals : Nb, Mo, Ti, Cr, W



Fig.2 Schematic diagram of metal ion source

2.3 Specimen and evaluate

The materials were nused Ti50%Al50%(at.%) alloys, which were prepared by vacuum arc-melting followed by hot forging and without any further heat treatment. TiA1 specimens measuring $15\times 10\times 2$ mm were cut from the forged sheets. The specimens were polished with SiC paper up to 1500 grit and finally by using diamond powders for a mirror finish. Prior to ion implantation PBII treatment, the specimens were ultrasonically cleaned in ethanol.

The high voltage pulse of -10kV to -40kV with 100pps were applied the substrate. The specimens were treated by Me-PBII for 10min.

AES (Auger electron spectroscopy) and SIMS (Secondary ion Mass Spectroscopy) were employed to determine the elemental depth profiles for the as-treated TiA1.

Oxidation experiments were carried out in a vertically mounted furnace with a platinum-made basket holder. TiA1 specimens were oxidized at 850°C in the static air. For one cycle test, TiA1 specimens were inserted into the hot zone of the furnace at 850°C for a initial period of 15min, then hold at 850°C for 20hr, and finally removed out from the furnace for a fina1 period of 15min. The specimen mass was measured after each cycle.

3. RESULTS AND DISCUSSION

3.1 Waveforms of voltage and current

Fig.3 shows a waveform of applied high voltage and current during metal ion implantation. The pulse arc current for generating the arc current is 100A. The pulse voltage applied to the substrate is -20kV. The waveform of voltage pulse shows a rectangular form. The current applied to the substrate is 5A. Pulse frequency is 100 pps (pulse per sec.) and voltage pulse width is $100\mu s$. In this work, waveform is selected single pulse mode.



(a) Multi pulse



Fig.3 Waveform of applied voltage and current

3.2 Depth profile

Figure 4 and Figure 5 show depth profile of implanted Nb and Mo atoms for TiAl were evaluated by auger electron spectroscopy.

Figure 4 shows depth profiles of implanted Nb atoms for TiAl at 30 kV by PBII. Nb ions exhibited a peak concentration of about 35 at % with a distribution depth of about 150 nm.

Figure 5 shows depth profiles of implanted Mo atoms for TiAl at 30 kV by PBII. Mo ions exhibited a peak concentration of about 18 at %with a distribution depth of about 80 nm.

Oxygen was also observed to distribute in this modified surface region, which gradually decreased from 40 at % at the surface, indicating the presence of a thin oxide layer on the surface. It is apparent that the modified layer containing Nb was extremely thin before oxidation.



Fig.4 AES depth profile of Nb implanted in TiAl alloy



Fig.5 AES depth profile of Mo implanted in TiAl alloy

3.3 Cyclic oxidation behavior

Cyclic oxidation curves of TiAl in air are shown in Fig. 6 and Fig.7. The untreated TiAl showed a rapid mass gain for up to about 80 hr, and after this initial period of high oxidation rate, a rapid mass decrease was observed due to the scale spallation. In contrast, a very low mass gain was observed for TiA1 implanted with Nb ions by PBII, especially for the TiAl treated at -40 kV. It is obvious that PBII treatment of Nb led to a significant improvement in oxidation resistance of TiAl. The oxidation test revealed that TiAl treated by PBII showed a very low oxidation weight loss of 1.0 mg/cm² at 200 hours, Nb ion implantation can be expected as a promising method for modifying TiAl alloys in the industrial field.



Fig.6 Oxidation mass change of Nb ion implanted in TiAl alloy



Fig.7 Oxidation mass change of Mo ion implanted in TiAl alloy

TiA1 implanted with Mo ions by PBII showed a little high oxidation rate, compared with TiA1 alloy.Me-PBII treatment proves to be a promising surface modification method for improving the oxidation resistance of TiAl alloys.

For TiAl alloys, severe TiO_2 scale spallation occurs during the cyclic oxidation, and large mass loss is observed. For the Nb, Mo ion implanted TiAl alloys, a thin protective Al_2O_3 scale is formed on the surface. Thus, Nb and Mo ion implantation results in a significant improvement in the oxidation resistance of TiAl alloys. [7]

4.CONCLUSIONS

1) TiAl alloys were implanted with Nb and Mo ions by PBII process. We have developed the Me-PBII system with a pulse arc system to be implanted metal ions into TiAl alloy.

2) The oxidation test revealed that TiAl treated by PBII showed a very low oxidation weight gain of 1.0 mg/cm2 after 200 hours.

3) Me-PBII treatment proves to be a promising surface modification method for improving the oxidation resistance of TiAl alloys.

ACKOWLEDGMENT

This work was supported by NEDO(New Energy and Industrial Technology Development Organization), the Ministry of International Trade and Industry of Japan. REFERENCES

[1] K.kawanabe, T.kanai, O.Izumi, *Acta.Met.*,33,1335 (1985).

[2] M.Schutze, M.Hald, *Mater.Sci.Eng.*,A234-240,847-858(1997)

 [3] S.Taniguchi, K.Uesaki, Y.-C.Zhu, H.-X.Zhang and T.Shibata, *Mater.Sci.Eng.*, A249,223-232(1997).
 [4]Yao-Can Zhu, Yoshiro Matsumoto, Kazuhisa Fujita

and Nobuya Iwamoto, *Materials Trans, JIM* Vol.41,No.5,May,(2000).

[5]Yao-Can Zhu, X.Y.Li, K.Fujita, N.Iwamoto, Y.Matsunaga, K.Nakagawa, S.Taniguchi, *Surface and Coating Technology*, 158-159, 503-507,(2002).
[6]U. Hornauer, R.Gunzer, 12th International Conference of SMMIB 2001, I-14.

[7]S.Taniguchi, *MateriaJapan*, Vol.37, No.3, 175-178 (1998).

[8]H. Takigawa, The Journal of The Institute of Electrical Engineers of Japan, Vol.121, No.5, 312-315,(2001).

[9]K. Yukimura, The Journal of The Institute of Electrical Engineers of Japan, Vol.121, No.5, 316-319,(2001).

(Received December 21, 2002; Accepted March 26, 2003)