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Cite as: AIP Conference Proceedings **866**, 233 (2006); https://doi.org/10.1063/1.2401502
Published Online: 01 December 2006

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Nitrogen Plasma Ion Implantation of Al and Ti alloys in the High Voltage Glow Discharge Mode

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Abstract. Enhanced surface properties can be attained for aluminum and its alloys (mechanical and tribological) and Ti6Al4V (mainly tribological) by Plasma Immersion Ion Implantation (PIII) technique. The main problem here, more severe for Al case, is the rapid oxygen contamination even in low O partial pressure. High energy nitrogen ions during PIII are demanded for this situation, in order to enable the ions to pass through the formed oxide layer. We have developed a PIII system that can operate at energies in excess of 50keV, using a Stacked Blumlein (SB) pulser which can nominally provide up to 100 kV pulses. Initially, we are using this system in the High Voltage Glow Discharge (HVGD) mode, to implant nitrogen ions into Al5052 alloy with energies in the range of 30 to 50keV, with 1.5µs duration pulses at a repetition rate of 100Hz. AES, pin-on-disc, nanoindentation measurements are under way but x-ray diffraction results already indicated abundant formation of AlN in the surface for Al5052 treated with this HVGD mode. Our major aim in this PIII experiment is to achieve this difficult to produce stable and highly reliable AlN rich surface layer with high hardness, high corrosion resistance and very low wear rate.

Keywords: plasma immersion ion implantation, high voltage glow discharge mode, Al5052, Ti6Al4V.
PACS: 52.77Dq

INTRODUCTION

Aluminum and its alloys are highly demanded materials in the modern industries, especially in applications requiring light-weight, high corrosion resistance and reasonable toughness, as in aerospace components [1].

Because of its excellent combination of properties regarding mechanical and chemical stability, Ti6Al4V is one of the mostly used titanium alloys in aeronautical and biomedical applications [2, 3]. However, Ti6Al4V presents inadequate tribological properties. To improve them, ion implantation has been used previously [4, 5].

Possibilities of nitrogen ion implantation in the surface of Al alloys to produce AlN compound layer opened up new hopes to manufacture industrial components made of Al alloys with even more enhanced surface properties (both mechanical and tribological). In the case of the Ti alloy, compounds as TiN or Ti_2N are produced to favor improved surfaces.

Plasma immersion ion implantation (PIII) is a well suited technique for this transformation in reasonably complex shaped or large area components. However, it has been shown by many recent experiments that Al and its alloys are prone to rapid contamination by oxygen not only in air but also in relatively low O partial pressures (as residual gas during plasma treatments) [6, 7]. This results in a fast build-up of alumina layer which blocks the nitrogen ion penetration into the bulk, for low energy implantations. One way to circumvent this problem is to use sufficiently high energy nitrogen ion, of the order of 30keV or more, to pass through this oxide layer [8].

CP866, *Ion Implantation Technology,*
edited by K. J. Kirkby, R. Gwilliam, A. Smith, and D. Chivers

We have developed a PIII system that can operate at energies in excess of 50keV, using a Stacked Blumlein (SB) pulser which can nominally provide up to 100 kV pulses [9]. Initially, we are using this system in the High Voltage Glow Discharge (HVGD) mode, to implant nitrogen ions into Al5052 alloy with energies in the range of 30 to 50 keV, with 1.5 µs duration pulses at a repetition rate of 100 Hz. For Ti alloys, the problem of oxide layer is less severe.

In both cases of Al and Ti alloys, the thickness of the treated layer is usually small for implantation of nitrogen at such energies, unless hybrid process combining implantation with a diffusive process is used. Typically ~ 100 nm layers are useful for many applications. For Ti alloys, PIII at 800ºC is highly effective to achieve treated layers as thick as 3 µm [10, 11].

EXPERIMENTAL

A schematic drawing of high energy PIII (HEPIII) system including all its components is shown in Fig.1. Using typical nitrogen gas pressures of $5x10^{-3}$ mbar, firstly, the filament is turned-on to start the glow discharge plasma with the electrode located at the upper part of the 180 liter volume stainless steel vacuum chamber. A base pressure of $5x10^{-6}$ mbar is achieved with a turbomolecular/mechanical pumping system. High voltage (HV) pulses are applied to the sample support through a high voltage feedthrough. Plasma parameters (T_e, n_e) were determined by using a double Langmuir probe. Typical parameters were $n_e \sim 5x10^9$ cm^{-3} and $T_e \sim 5$ eV.

The HV pulses originates from a high voltage pulse generator with an expected performance of 100kV/200A, based on a Stacked Blumlein technology, which is usually used in applications such as x-ray generation, breakdown tests, etc [12]. According to our design, the output pulse should reach voltages of 150 kV. However, in practice, corona discharges (between metallic structure and connection) have limited the output voltages to up to 100 kV at most. Electrical details of the Blumlein pulser can be found elsewhere [13].

To characterize the Al5052 and Ti6Al4V samples submitted to the HEPIII system in the high voltage glow discharge mode (explained later), we used x-ray diffraction (Philips 3410 diffractometer in the Seeman-Bohlin 2θ mode) for microstructure information and Auger Electron Spectroscopy (FISONS Instruments Surface Science, model MICROLAB 310-F).

RESULTS

For the results shown here, the HV pulser was operated at 35 kV for Ti alloy and at 48 kV for Al alloy, with pulse duration of 1.5 µs and 100 Hz repetition frequency, for both cases, with the plasma load. When HEPIII system is activated in such a condition, with the working pressure above $5x10^{-3}$ mbar, the ion implantation occurs by means of a high voltage glow discharge (HVGD) mode (i.e., the plasma is produced by the HV pulse itself).

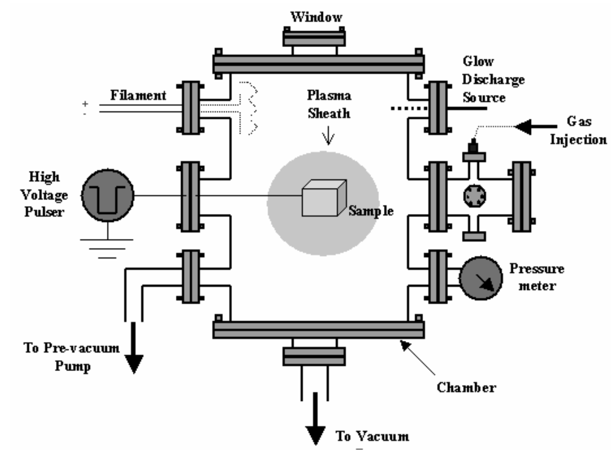

FIGURE 1. Schematic drawing of high energy PIII system

Typical voltage and current waveforms for the HEPIII system operated in the HVGD mode is shown in Fig.2(a) and (b), respectively. The voltage peak reaches 48 kV and the current peak, about 10A, at the implantation phase (excluding the first peak which is mainly due to displacement current). The inversion of the polarity in the voltage signal, after the main pulse, could be eliminated by using free-wheeling diodes that should also cut-off the negative current part. Voltage overshoot in this case is due to a mismatch between the characteristic impedance of the line and the plasma impedance.

In Fig. 3 we present the result of AES analysis performed in a sample of Al5052 treated with nitrogen PIII at 48 kV, 1.5 µs pulse duration, 100 Hz frequency, for a period of 1 h. Nitrogen implantation with ~ 10% atomic percent peak concentration and penetration of nitrogen of up to around 100 nm was achieved. Large concentration of oxygen was implanted (up to 50% atomic concentration) and its penetration was near 60 nm. It is clear from this result that insufficient amount of nitrogen was implanted because of two reasons: low delivered dose and very thick oxygen barrier to nitrogen influx formed as a native layer or during the

PIII processing. Increased total treatment time and cleaning of the surface by argon bombardment should allow better implantation of nitrogen in such condition of treatment. This is necessary for a successful formation of AlN layer with good mechanical and tribological properties. Preliminary measurements of corrosion resistance showed improved performance of the implanted surface compared to the unimplanted one.

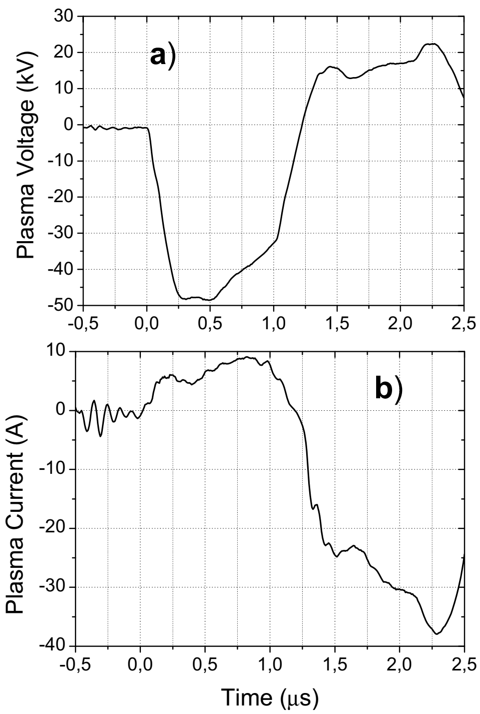

FIGURE 2. Typical voltage (a) and current (b) waveforms for the HEPIII system operated in the HVGD mode.

In Fig.4 AES analysis of Ti6Al4V treated at 35 kV, 1.5 μs, 100 Hz, for 1 h is shown. Besides the profiles of atomic concentration of normal elements in the alloy, Ti, V, Al, we can also notice the presence of O and Fe that are impurities introduced during the treatment. Most importantly, we can see the profile of N which indicates near 20% atomic concentration at the peak and penetration depth of up to 40 nm. The oxygen contamination is very high, reaching 55% near the surface. Once again, the oxygen atoms come from the native oxide layer and the residual gas in the treatment chamber. This result is comparable to one obtained under typical PIII conditions [14] in Ti6Al4V samples without diffusion effects.

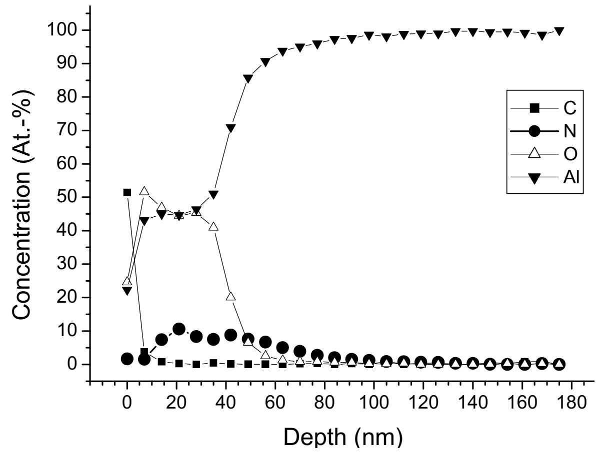

FIGURE 3. Atomic concentration profiles for the sample of Al5052 treated with nitrogen PIII, 48 kV/1.5μs/100Hz/1h.

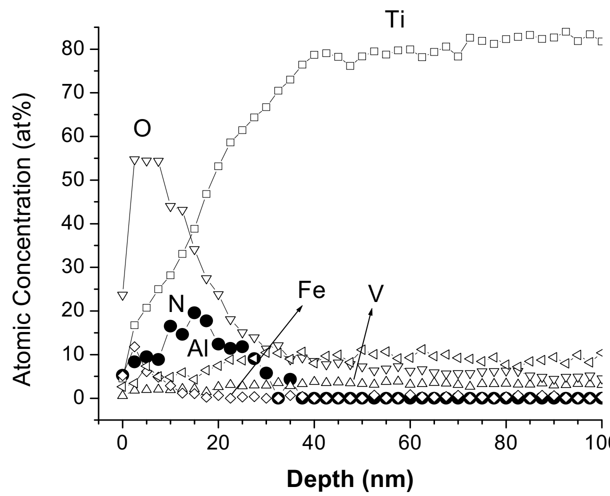

FIGURE 4. Atomic concentration profile for the Ti6Al4V treated at 35 kV/ 1.5 μs/ 100 Hz/ 1h.

CONCLUSIONS

Al and Ti alloys were implanted by nitrogen PIII at energies of 48 and 35 keV, respectively, with frequencies of 100 Hz and very short pulses (1.5 μs), for up to 1 h. High voltage glow discharge mode was used for these treatments. High concentration of O was co-implanted as a result of native oxided layer and residual gas during the treatment, in both cases, being more critical in the case of Al alloy.

For better nitrogen implantation, attempts are underway to reduce the oxygen contamination by Ar cleaning before the PIII treatment of Al alloy, and also to increase the retained dose by longer treatments. For improved nitrogen implantation in Ti alloy, we are performing high temperature PIII with successful results [15].

ACKNOWLEDGEMENTS

This project is supported by FAPESP, MCT and CNPq from Brazil.

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