Effect of Nitrogen on Cathode Spot Characteristics in Arc Ion-Plating of TiN

George Kim[1], Jean-Luc Meunier[1], Frank Ajersch[2]

[1]Plasma Technology Research Centre (CRTP), Department of Chemical Engineering, McGill University, Montreal, Canada H3A 2A7.
[2]Département de Métallurgie et de Génie des Matériaux, École Polytechnique de l'Université de Montréal, Montreal, Canada H3C 3A7.

Abstract

Experiments in vacuum , argon and nitrogen ambients were carried out in an arc ion-plating system designed and built to study the effects of low pressure nitrogen on a continuous, titanium arc. An increase in arc velocity with increasing nitrogen pressure was noted whereas an opposite trend was seen for argon. A critical nitrogen pressure (~ 1×10^{-3} Torr) was found where dramatic changes occurred. Some of the noted changes upon approaching and surpassing the critical nitrogen pressure were reduced erosion crater size and changes in crater shape. Erosion rate of the titanium cathode is found to decrease with conditions that promote cathode poisoning or contamination due to surface reactions with nitrogen. Erosion rates of steered arcs for argon and nitrogen are 38 and 15 μg/C, respectively.

Introduction

Arc ion-plating has proven to be a popular choice in reactively coating various base materials. Cathode erosion is the source of ions and microdroplets through vaporization and melting, respectively. The efficiency and quality of film depends largely on the vaporization and ionization of the cathode material. The high degree of ionization along with high ion energies makes this technique both unique and favourable. Microdroplet formation, on the other hand, is the main hinderance to the process and is currently being studied to minimize its deleterious effects on coating quality. Cathode erosion of vacuum and low pressure arcs has been studied in many non-reactive conditions [1-3]. The effect of a reactive gas on cathode erosion is not as frequently documented.

Rotating the arc through the use of permanent magnets allows for a study of the effects of both arc confinement and arc velocity on cathode characteristics. The aim of this study is to determine the influence of adding nitrogen into a titanium vacuum arc. Experiments with argon were also carried out to isolate the poisoning from the pressure effects.

Experiment

The experiments were performed in a cylindrical vacuum chamber, 19 cm in diameter and 34.5 cm long (Figure 1). A diffusion pump backed by a mechanical pump was used to evacuate the chamber down to a pressure in the 10^{-6} Torr range after which the optional introduction of nitrogen or argon to required pressures was carried out. An electromechanical piston-trigger was used for arc initiation.

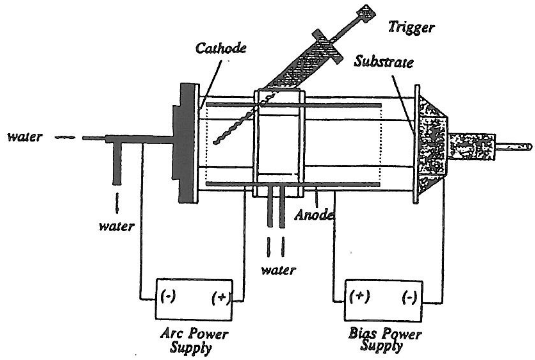

Fig. 1 Arc ion-plating setup.

Grade 2 titanium discs of 2 mm thickness and 11.5 cm diameter were used as cathodes which were used for single runs. Samarium/cobalt (SmCo 18) magnets were placed radially behind the cathode within a water-cooled cavity to confine and rotate the arc. A passive border of Carborundum's AX05 boron nitride was placed around the outer diameter of the cathode to avoid stray arcing. Although the chamber itself could have been used as an anode, a separate water-cooled anode was placed within the chamber.

Both arc current (60 A) and pressure were kept constant during arcing. The arc velocity was measured using two different methods: photographic and rotational frequency methods. Scanning electron microscope (SEM) was used to obtain micrographs of the region of arc rotation after arcing in different conditions. Cathode erosion rates were determined by weighing the cathode prior to and after arcing for 5 minutes. Knowing both the loss in mass and the total charge that passed through the cathode led to the calculation of the erosion rate.

Results

As can be seen in Figure 2, arc velocity evolutions with pressure for argon and nitrogen are in opposite directions. Argon shows a steady decrease in velocity until 0.1 Torr, afterwhich a sharp decrease is observed up to 1 Torr. Nitrogen shows almost an exact mirror image with an inverse trend at the same pressures.

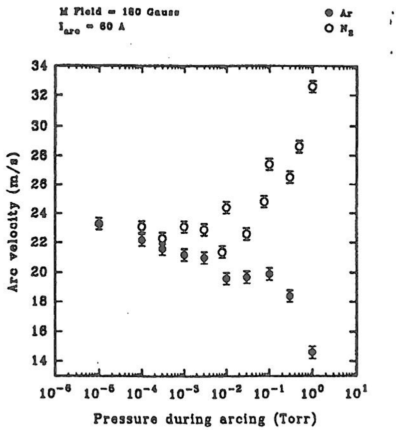

Fig. 2 Arc velocity versus pressure.

SEM micrographs of steered arc tracks reveal differences in both crater size and shape between experiments run in argon and nitrogen ambients (Figure 3). The crater diameters of argon are at least an order of magnitude greater than those of nitrogen (~ 100 μm). The craters resulting from argon possess rough rims with micropoints whereas the rims of craters formed in nitrogen are more rounded and smooth with no micropoints.

Erosion rates were measured for different arcing pressures of argon and nitrogen ambients (Figure 4). A constant arc current of 60 A and parallel field of 180 Gauss were maintained for each experiment. The curve for argon ambient very much resembles those found by many researchers [1, 2, 4]. In the inert gas environment, the erosion rate remained constant from vacuum (1 x 10^{-4} Torr) until just after 0.01 Torr. After this pressure erosion rate decreased fairly rapidly.

The plot for erosion rate in the presence of nitrogen shows both similarities and differences with that run in argon. The similarity lies in the fact that a distinct decrease in erosion rate occurs as pressure is increased from vacuum. However, unlike the argon case the decrease is not continuous but instead shows a pressure zone (~ 0.005 - 0.080 Torr) where the erosion rate stabilizes (~ 15 μg/C) followed by further decrease at higher pressures. These data were checked several times to validate the nature of this curve.

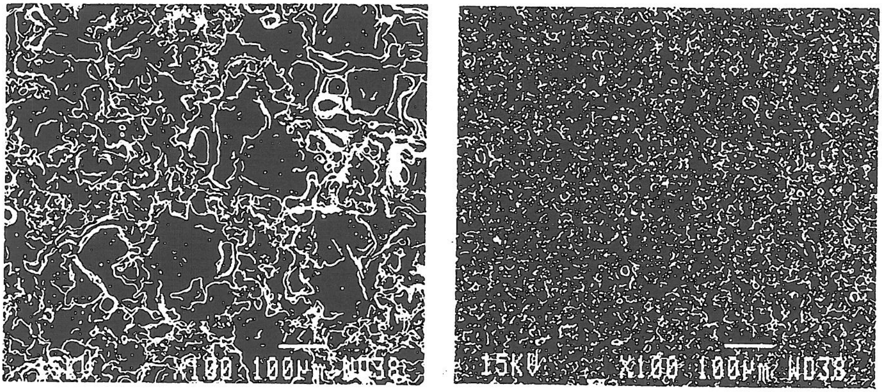

Fig. 3 Micrographs of steered arc track: P(Ar) = 0.8 Torr (left); $P(N_2)$ = 0.8 Torr (right).

Discussion

The results in Figure 2 shows the opposite effects of argon and nitrogen on arc velocity. However, we also see that the decrease and increase in velocity with an increase in argon and nitrogen pressure, respectively, is not linear. The difference in velocity between the conditions is greater at higher pressures which may result in larger differences in other characteristics. Reduction in work function and thickening of the contamination layer with increased nitrogen pressure may explain the nitrogen plot. Both of these changes will lead to a more favourable formation of new cathode spots, and hence, higher velocities. The decrease in arc velocity with argon pressure agrees with the findings presented by Murphree and Carter [5].

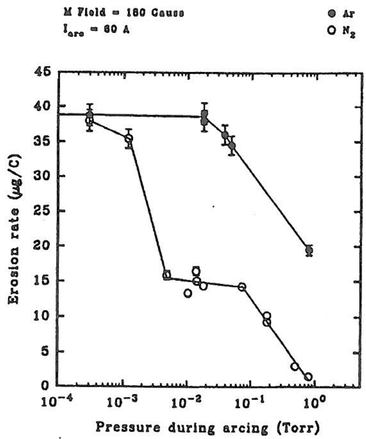

Fig. 4 Erosion rate versus pressure.

From the microstructures of steered arcs run in both ambients, the first thing to notice is the relative lack of distinct, individual crater structures due to repeated arcing of the same region. The smaller crater diameters with nitrogen ambient may be related to a change in arc spots from type 2 (clean cathode) to type 1 (poisoned cathode). The structure found in experiments at higher nitrogen pressures are complete in shape unlike the chainlike overlapping craters of type 2 spots (argon ambient). This is typical of type 1 spots which leave wide arc tracks respective to relatively small craters situated at a distance of several crater diameters from each other. The rounded, smooth rims without micropoints found after arcing in nitrogen may be a result of higher frequency of repeated arcing and/or higher surface temperature as a result of confinement. The higher cathode temperature means that the crater takes longer to cool or solidify, thereby allowing the rims to become smoother through the effects of surface tension forces. The centre of the crater also has the time to fill-in before solidifying.

A decrease in erosion rate was measured by Meunier and Drouet [1], and Kimblin [2] on copper cathodes when gas pressures were increased above the 10^{-2} Torr range. The pressure at which the erosion rate drop was observed in fact depends on the type of gas present in the chamber. The erosion rate evolution was shown to be independent of the type of gas when plotted as a function of the mass density of the gas in the vacuum chamber [1]. The drop in erosion rate was attributed to redeposition of some emitted metal vapour back onto the cathode in the cathode spot area. The cause of this redeposition phenomena was shown to be related to the increased metal vapour density in the cathode spot zone induced by the gas confinement [6]. The same type of evolution is observed here in argon for the titanium cathode.

In the nitrogen case, it seems as though a change in arc or cathode characteristic occurs at a critical pressure of around 0.001 Torr. Physical and chemical changes of the metal surface occurring at this nitrogen pressure may possibly decrease the erosion rate. Studies have shown that impurities on the surface tend to decrease properties such as the work function [7, 8] which facilitates emission of electrons leading to lower erosion rates. Therefore, nitriding or poisoning may have reached a certain chemical and/or thickness level where the cathode then resembles erosion of a different material, TiN. Coll and Chhowalla [9] have also obtained similar trends for titanium arcs run in nitrogen. They attribute the abrupt decrease in mass loss per coulomb at a critical pressure to the transition from unpoisoned to poisoned cathode. In the results presented here, the presence of another drop in erosion rate at nitrogen pressure greater than 0.1 Torr can be seen in Figure 4. This second part of the curve shows a behaviour very similar to the erosion rate decrease observed in argon and to the results of Meunier and Drouet [1]. This behaviour may hence possibly be attributed to a similar process. In this case however, the cathode shows a new, lower erosion rate value before the drop when compared to the argon case. This new value can be associated to a new material, erosion at the cathode spot location occurring not on a Ti cathode but on a new TiN surface.

Conclusions

The effect of nitrogen on a titanium cathode arc ion-plating system has been studied in detail. Changes in cathode surface, arc characteristics and emission properties have been noted. A critical nitrogen pressure has been found, at around 0.001 Torr, above which these changes commence.

Acknowledgements

Many thanks to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Québec and Hydro-Québec for their financial support.

References

[1] J.-L. Meunier and M. G. Drouet, "Experimental study of the effect of gas pressure on arc cathode erosion and redeposition in He, Ar and SF_6 from vacuum to atmospheric pressure", IEEE Trans. Plasma Sci., vol. PS-15, no. 5, pp. 515 - 519, Oct. 1987.

[2] C. W. Kimblin, "Cathode spot erosion and ionization phenomena in the transition from vacuum to atmospheric pressure arc", J. Appl. Phys., vol. 45, no. 12, pp. 5235 - 5244, Dec. 1974.

[3] A. E. Guile and A. H. Hitchcock, "The erosion of copper cathodes from vacuum to atmospheric pressure arcs", J. Appl. Phys., vol. 49, no.7, pp. 4275 - 4276, July 1978.

[4] P. R. Emtage, "Interaction of the cathode spot with low pressures of ambient gas", J. Appl. Phys., vol. 46, no. 9, pp. 3809 - 3816, Sept. 1975.

[5] D. L. Murphree and R. Carter, "Low-pressure arc discharge motion between concentric cylindrical electrodes in a transverse magnetic field", AIAA Journal, vol. 7, pp. 1430 - 1437, 1969.

[6] J.-L. Meunier "Pressure Limits for the Vacuum Arc Deposition Technique", IEEE Transactions on Plasma Science, Vol. 18, no. 6, pp. 904 - 910, Dec. 1990.

[7] S. Anders and B. Jüttner, "Influence of residual gases on cathode spot behaviour", IEEE Transactions on Plasma Science, vol. 19, pp. 705 - 712, 1991.

[8] R. N. Szente, "Erosion of Plasma Torch Electrodes", PhD Thesis, McGill University, Montreal, 1989.

[9] B. F. Coll and M. Chhowalla, "Modelization of reaction kinetics of nitrogen with titanium during TiN arc deposition", presented to us during a meeting prior to publishing, 1994.