MODIFICATION OF A 304 SS SURFACE WITH A TITANIUM FILM TO IMPROVE THE ADHERENCE OF CVD DIAMOND

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ABSTRACT

The results of diamond growth on a Ti film-304 stainless steel (304 SS) system are presented and discussed. The 304 SS (a specific steel) surface was previously modified by titanium adherent film to make a barrier against carbon diffusion. Diamond film were deposited on titanium film-304 SS system, at a temperature about 550° C, using Chemical Vapor Deposition from CH₄ / H₂ mixture in percentages of 2.5 wt% and 97.5 wt% respectively. This diamond film was characterized by SEM, Raman spectroscopy and X-ray diffraction. The cross sections of these CVD diamond film-Ti film-304 SS samples were analyzed by EDS. The results indicated the nucleation and growth of CVD diamond polycrystalline on Ti film-304 SS system with good quality but poor adherence.

1. INTRODUCTION

Steels with modified surfaces are widely used in a large variety of important technological applications, including cutting tools, machine components and molding dies, where their surfaces can be submitted to physical and/or chemical erosion [1-6]. The use of diamond polycrystalline films as protective coatings for steels is highly desirable and technologically relevant. However, nucleation of the diamond phase is extremely difficult on these material surfaces, mainly due to the high diffusivity of carbon ions into steel substrates at temperature used to obtain CVD diamond films, which consumes the carbon species needed for nucleation of diamond phase [7-9]. To enhance nucleation density, the growth of polycrystalline diamond films and the adhesion of these coatings on steel, the use an intermediary layer of a material that has a low diffusion coefficient for carbon, such as a thin deposited film, can be used [9-12]. The objective of this study, as can be seen in Figure 1, is to use the Ti film as an intermediate layer to improve the CVD diamond films adherence to steel substrates.

In this figure was shown a schematic representation interface profiles proposed in this work, with diamond film-Ti film defined interface and Ti film-304 SS substrate interface diffusion. The cross sections of the Ti film-304 SS samples were analyzed by EDS and the results have been indicating an interface diffusion promoted by the thermal actived diffusion process [13,14]. The CVD diamond film-Ti interlayer interface has been studied within chemistry iteration dominant.

TITANIUM

STEEL



Figure 1 - Schematic representation of the proposal of this work for atomic arrangement model adapted to diamond films-interlayer titanium film-steel substrate system.

2. EXPERIMENTAL PROCEDURE

DIAMOND

The substrates used for the diamond deposition were 304 SS stainless steel 3mm thick and 15mm of diameter. They were polished with a sequence of SiC sandpapers down to 1200# grid, polished with 1 μ m alumina and ultrasonically cleaned for 20min in acetone bath.

Before the diamond deposition, the substrates were coated with a titanium layer (approximately 0.5μ m thick) deposited by electron beam process at 210°C in vacuum, to make a barrier against carbon diffusion. Deposition of diamond film on Ti film-304 SS substrate was carried out by a conventional hot filament assisted technique, as described elsewhere [9]. The process gases were H₂ and CH₄ mixture in percentages of 2.5wt% and 97.5wt% respectively. The pressure inside the reactor was kept constant at 50Torr. Under these conditions, the substrate temperature was about 550°C. The substrate temperature was measured using a thermo-

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couple fixed to the bottom of substrate by a molybdenum grease. Diamond film was obtained with 4 hours of growth time. The surface morphology of the deposited CVD diamond was investigated by a JEOL scanning electron microscope (SEM) attached to an energy dispersive spectrometry (EDS). The quality of the diamond film was evaluated by Raman spectroscopy. This technique was used also to calculate the total residual stress in the CVD diamond film-304 SS modified surface interface. The cross section of the samples after CVD diamond deposition was investigated by EDS, from linescan analysis of the chemical elements. The CVD diamond-Ti film-304 SS substrate, Ti film-304 SS substrate and 304 SS substrate crystalline structure were obtained by X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

The sample with diamond film with approximately 0.5µm thickness was analyzed. As can be observed in Figure 2, the topographical observations by SEM of the CVD diamond film deposited on Ti film-304 SS system showed the film existence with characteristics of polycrystalline diamond.



Figure 2 - Surface morphology of the diamond film deposited on Ti film-304 SS system.

The curve obtained by Raman spectroscopy for the CVD diamond film indicated the presence of the characteristic diamond and graphite phase in the deposited film as shown in Figure 3.

There is a peak at about 1335.7cm⁻¹ which corresponds to the diamond peak. Raman bands around 1470 and 1550cm⁻¹ are attributed to sp²-bonded graphite. Raman spectroscopy was also carried out in order to study the total film stress. The shift of the stressed diamond Raman line relative to the

natural diamond line at 1332.5cm⁻¹ was used to calculate the total residual stress in diamond film. In comparison with that of natural diamond, experimental value of diamond line position exhibit a positive shift, indicating compressive stress. The shift of the diamond peak indicated the existence of a residual compressive stress of approximately 1.12Gpa. This stress value was calculated from the line position shift considering a linear line shift of 2.87cm⁻¹/GPa [15].



Figure 3 - Raman spectra of diamond film deposited on Ti film-304 SS system.

As can be seen in Figure 4, in the cross section near interface region was observed a little carbon diffusion in Ti film and 304 SS substrate. The Fe segregation was observed in Ti film that was associated a Fe diffusion in Ti. The carbon near interface served within barrier against diffusion this element in 304 SS substrate.



Figure 4 - EDS linescan analysis of the CVD diamond-Ti film-304 SS interface chemical elements.

XRD diffraction patterns, as can be seen in Figure 5, shows Ti film-304 SS surface before and after CVD diamond deposition. These result showed that after CVD diamond deposition on Ti Film-304 SS substrate, indicated the formation of titanium carbide (TiC). Titanium is an active carbide former. It is known that debonding of diamond film happens at the interface between the TiC layer and the diamond film as a result of high residual stress, particularly if the diamond film was relatively thick and the TiC layer relatively porous [16]. Cracking in the TiC layer also promoted cracking in the diamond film.



Figure 5 - XRD patterns of 304 SS substrate, Ti film on 304 SS substrate and CVD diamond on Ti film-304 SS surface.

4. CONCLUSION

This paper discussed the deposition of CVD diamond film on 304 SS substrate utilizing a titanium interlayer to make a barrier against carbon diffusion. Ti film deposited on 304 SS promoted carbon concentration near its interface serving as barrier against diffusion this element in 304 SS substrate. This explains the CVD diamond crystals formation on the 304 SS modified surface. A possible porous TiC formation caused weak interfacial bonding between the diamond and substrate. These results indicated the nucleation and growth of CVD diamond polycrystalline film on Ti film-304 SS system with excellent crystalline quality but poor adherence.

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REFERENCES

- NONO, M.C.A.; CORAT, E.J.; UEDA, M.; STELLATI, C.; BARROSO, J.J.; CONRAD, J.R.; SHAMIN, M.M.; FETHERSTON, P.; SRIDHARAN, K., Surface Coating Technology 112 (1999) 295.
- WINTERS, H.F.; CHANG, R.P.H.; MOBAB, C.J.; EVANS, J.; THORNTON, J.A.; YASUDA, H., *Materials Science and Engineering A* 70 (1985) 53.
- 3. SIOSHANSI, P., *Materials Science and Engineering A* 90 (1987) 373.
- 4. PEREPEZKO, J.; BREWER, L.; SCHAEFER, R., *Materials Science and Engineering A* 70 (1985) 9.
- MATTOX, D.M.; GREENE, J.E.; BUCKLEY, D.H.; SOMORJAI, G.A., *Materials Science and Engineering A* 70 (1985) 79.
- CONRAD, J.R.; RADTKE, J.L.; DOOD, R.A.; WORZALA, F.J.; TRAN, N.C., *Journal of Applied Physics* 62 nº11 (1987) 591.
- DAVANLOO, F.; PARK, H.; COLLINS, C.B., Journal of Materials Research 11 (1996) 2042.
- SCHÄFER, L.; FRYDA, M.; STOLLEY, T.; XIANG, L.; KLAGES, C. –P., *Surface Coating Technology* 116-119 (1999) 447.
- 9. VIEIRA, R.A., *Study 304 SS surface modification with polymeric and titanium films to improve the adherence of CVD diamond films.* Dissertação de Mestrado, 2000. Faculdade de Engenharia Química de Lorena, Lorena (SP).
- 10. FAN, Q.H.; FERNANDES, A.; PEREIRA, E.; GRÁCIO, J., *Vacuum* 52 (1999) 193.
- 11. FU, Y.; YAN, B.; LOH, N.L., Surface Coating Technology 130 (2000) 173
- FAN, Q. H.; PEREIRA, E.; DAVIM, P.; GRACIO, J.; TAVARES, C.J., Surface Coating Technology 126 (2000) 110.
- VIEIRA, R.A.; NONO, M.C.A.; CRUZ, N.C., *Physica Status* Solidi (b) 232 (2002) 116.
- VIEIRA, R.A.; NONO, M.C.A.; MATTOS, M.L.B., Acta Microscopica, B 8 (1999) 309.
- 15. BOPPART, H.; STRAATEN, J.V.; SILVERA, I.F., *Physical Review B*, 32 (1985) 1423.
- 16. YAN, B.; LOH, N.L.; FU, Y.; SUN, C.Q.; HING, P., Surface Coating Technology 115 (1999) 256.