CVD OF ALTERNATED MICROCRYSTALLINE (MCD) AND NANOCRYSTALLINE (NCD) DIAMOND FILMS ON WC-TIC-CO SUBSTRATES[1]

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Abstract

CVD Diamond coating of WC-TiC-Co cutting tools has been an alternative to increase tool lifetime. Experiments have shown that residual stresses produced during films growth on WC-TiC-Co substrates significantly increases with increasing film thickness up to 20 µm and usually leads to film delamination. In this work alternated micro- and nanocrystalline CVD diamond films have been used to relax interface stresses and to increase diamond coatings performance. WC-TiC-Co substrates have been submitted to a boronizing thermal diffusion treatment prior to CVD diamond films growth. After reactive heat treatment samples were submitted to chemical etching in acid and alkaline solution. The diamond films deposition was performed using HFCVD reactor with different gas concentrations for microcrystalline (MCD) and nano-crystalline (NCD) films growth. As a result, we present the improvement of diamond films adherence on WC-TiC-Co, evaluated by indentation and machining tests. Samples were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) for qualitative analysis of diamond films. X-ray Diffraction (XRD) was used for phases identification after boronizing process. Diamond film compressive residual stresses were analyzed by Raman Scattering Spectroscopy (RSS).

Key words: Cutting tools; HFCVD; Diamond films; Thermal diffusion.

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1 INTRODUCTION

Considerable interest exists concerning diamond films coatings on tungsten cemented carbides (WC-TiC-Co), mainly to manufacture cutting tools and metal forming dies. The physical and chemical set of outstanding characteristics presented by diamond make it a potential candidate for many industrial applications, being particularly attractive for coating WC-TCi-Co machining tools. In this context there are still fundamental technological stages to overcome, concerning both to diamond films growth and to its adherence to substrate. The principal objective for coating tools with diamond films is to increase its lifetime. For such purpose it's also necessary a relatively high thickness.[1] However, the growth of CVD diamond films on non-diamond substrates generate residual thermal stresses in the film-substrate interface.[2] These stresses increase linearly with film thickness, frequently resulting in diamond film peeling off. To avoid this problem, some authors propose growth in alternated steps of film deposition and sample cleaning.[3] In this work we used alternated growth of microcrystalline (MCD) and nanocrystalline (NCD) diamond, with the nanocrystalline diamond film promoting residual stresses relaxation. Another difficulty in the CVD diamond films deposition on WC-TiC-Co substrates is related to the presence of cobalt in the matrix. Specific chemical interactions between Co and carbon atoms during chemical vapor deposition of diamond films[4,5] result in the formation of a graphitic phase on the surface, which inhibits direct deposition of CVD diamond films on WC-TiC-Co without pre-treatment.

The boronising technique[6] forms an intermediate barrier that blocks Co diffusion to surface, minimising the Co binder negative effects for diamond growth. The boronising process is one of the pre-treatments used in this work for diamond film deposition on WC-TiC-Co. It consists on boron thermodiffusion from heated powders mixed according to pre-established mass proportions. After boronising, the sample is submitted to chemical etching, first with acid solution (H_2SO_4 + H_2O_2) to remove free Co from sample surface, followed by alkaline etching using Murakami's solution[7] to improve surface roughness and diamond film adherence.

2 MATERIALS AND METHOD

Commercially available WC-TiC-Co cutting tool inserts (Brassinter S.A) were used as substrate for diamond coating in this work. WC medium grain size in WC-TiC-Co was 3 µm in all experiments. The sample surface was polished successively with diamond polishing pastes, grit sizes of 6µm and 1µm. The powders used in the boronising process and its respective concentrations were: B_4C - 15% (boron carbide); KBF_4 - 10% (potassium fluoroborate); 5% (C) – graphite; 70% (SiC) – silicon carbide. The boron carbide will act as boron source to form the boride interlayer. As boron has high chemical affinity with oxygen to form boron oxide it is necessary to add SiC in excess (diluting agent), to avoid boron oxide formation and boron consumption during initial phase of the thermodiffusion process. Graphite is added to the salt bath to keep carbon equilibrium on substrate surface, due to deficiency of carbon on WC-Ti-Co matrix. Potassium fluoroborate acts as an activator, reducing temperature needed to supply boron to thermodiffusion process.

WC-TiC-Co boronised samples were submitted to chemical etching, first with acid solution with concentration 2:8 of H_2SO_4 + H_2O_2, for 20s, to eliminate free cobalt remaining from boronising process.[8] Subsequently they were exposed to Murakami's alkaline reactant KOH + $K_3[Fe(CN)_6]$ + H_2O, concentration 1:1:10, for

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10 min, to increase surface roughness and to improve diamond film adherence. Both chemical etching were performed in ultrasonic bath. Samples were then pre-treated in ultrasonic bath with 0.25 µm diamond powder suspension in n-hexane for 1 h to increase nucleation rate.

Diamond films deposition were performed in a HFCVD using six straight 125 µm diameter tungsten filaments, 3 mm equidistant one from each other, at 2200 ºC. Total pressure was 6.5 x 10^3 Pa and gas flow rate was 100 sccm (standard cm^3 min^{-1}). Growth conditions for the growth of MCD and NCD are listed in Table1.

Table1. NCD and MCD growth conditions

Films	Time [h]	H_2 [%]	CH_4 [%]	Ar [%]	Temp [ºC]
MCD	5	98	2	-	700-900
NCD	24	24.5	0.5	75	550-600

The experimental apparatus has an independent substrate heating system, located in the substrate holder. This system provides an extra heating of the substrate in the range of 600 to 800ºC. Substrate temperature is measured by a chromel-alumel thermocouple in contact with sample lower surface.

The adherence tests were performed in a Rockwell C (HRC) universal hardness testing device, using a 120° cone angle diamond indenter with 200 µm tip radius. Loads were gradually increased to determine the critical load to initiate lateral crack.[9-11] It allows direct comparison from our adherence results to most results previously presented in literature.[12-14] The machining tests were conducted using uncoated and diamond coated inserts. Samples cutting performance in Al -1060 alloy were evaluated using a lathe model Mascote MS-175 (Nardini). Machining tests parameters were:

- Cutting velocity – 250m/min
- Feed – 0.01mm/rev
- Depth of cut – 0.5mm

3 RESULTS AND DISCUSSIONS

Substrate microstructure is shown in Fig. 1, evidencing WC and TiC grain size and distribution. Fig. 2 shows X ray identification of WC, TiC and Co phases in the substrate. After polished, the samples were submitted to boronising process. Once mixed, powders were placed in a stainless steel crucible and heated to 1000 ºC. The mixture was kept at this temperature for 15 min before inserting the WC-TiC-Co sample. After inserting the sample, temperature was kept at 1000 ºC for a period of 5 h. Boron reacts with Co and W from substrate surface to form the ternary compound CoWB. Fig. 3 shows X-ray diffractogram of the WC-TiC-Co sample, prior and after the boronising process, showing the CoWB and Co_3B phases formed. Co_3B is formed due to the presence of residual Co on the surface.[15] Fig. 4 shows the boronised layer microstructure of WC-TiC-Co substrate.

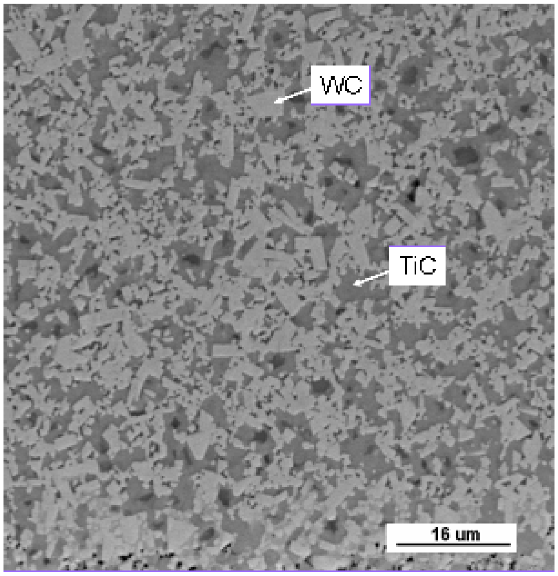

Figure 1. Image (SEM) of uncoated WC-TiC-Co cross section.

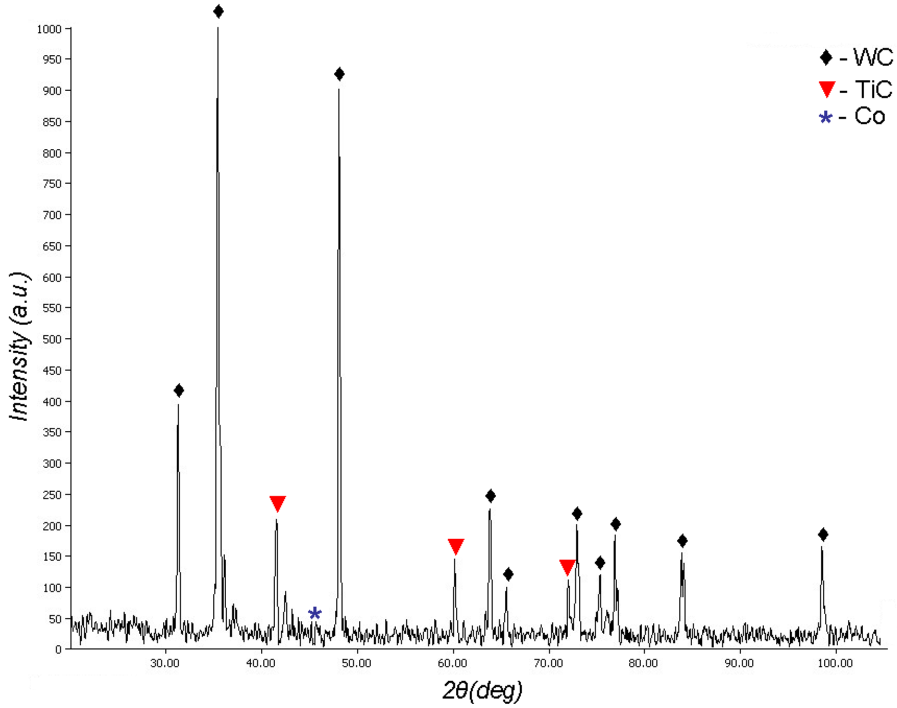

Figure 2. X-ray diffractogram of WC-TiC-Co sample prior to boronising.

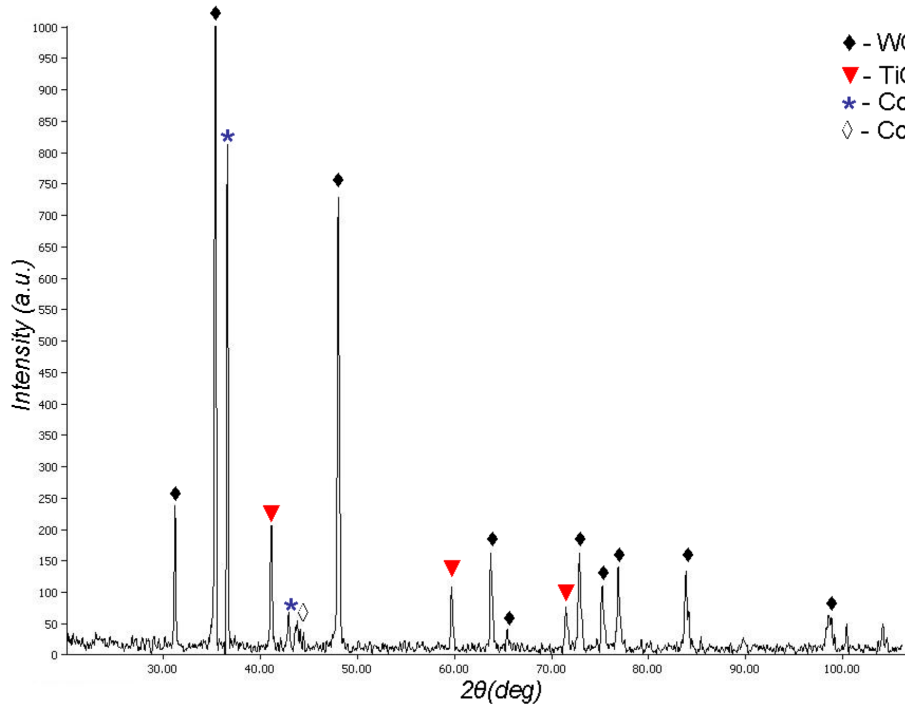

Figure 3. X-ray diffractogram of WC-TiC-Co sample after boronising.

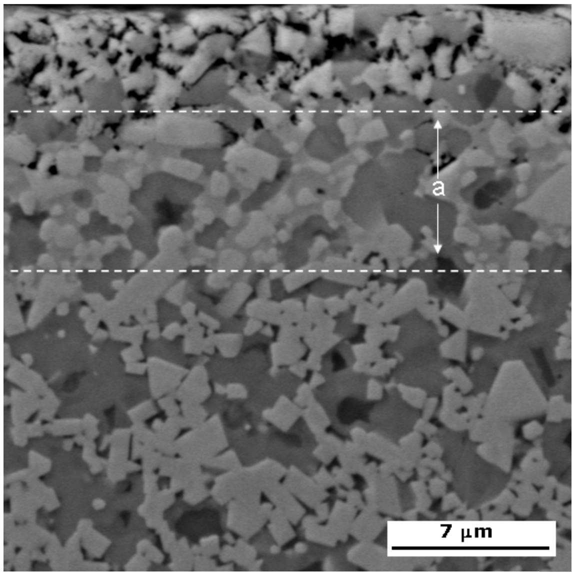

Figure 4. Image (SEM) of the boronised layer on WC-TiC-Co substrate. Detail (a) shows the boride interlayer that blocks Co diffusion to surface.

After etching in acid and Murakami solutions the sample surface becomes free of residual Co and shows enhanced roughness. In the first stage of substrate coating MCD films were grown according to conditions described in Table 1.

Fig. 5 shows the morphology of microcrystalline diamond film grown on WC-Ti-Co inserts with a boride interlayer. MCD deposition rate was approximately 2 µm/h and deposition time was 5h. The Raman spectrum (Fig. 6) of the diamond film deposited on WC-TiC-Co substrate with boride interlayer shows a peak shift of about 8 cm^{-1}, correlated to residual stresses in the diamond lattice. These stresses, typically compressive, are due to the low thermal expansion coefficient of diamond.

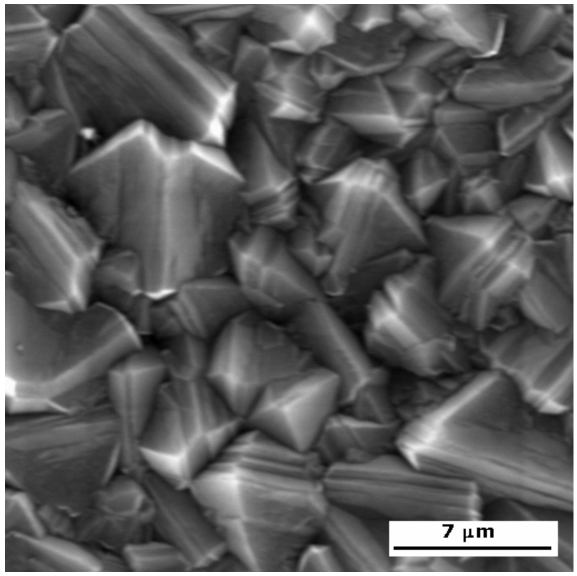

Figure 5. Image (SEM) of diamond film deposited on WC-TiC-Co boronised surface.

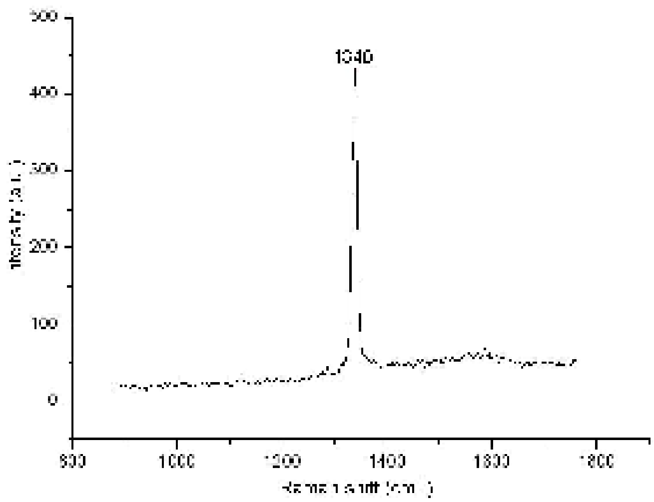

Fig. 6. Raman spectrum of MCD diamond film on WC-TiC-Co with boride interlayer.

The residual stresses can be evaluated from Raman peak shift related to natural unstressed diamond. In this case, the peak was centered at 1340 cm^{-1}, corresponding to a shift of 8 cm^{-1} from the characteristic peak of diamond (1332 cm^{1}). Residual stresses imposed to the diamond film can be calculated from Eq. 1, developed by Ager and Drory.[16,17]

$$\sigma = - 0.567(\nu_m - \nu_0) \qquad (1)$$

Where ν_0 is the characteristic Raman peak of diamond and ν_m corresponds to the Raman shift obtained from sample analysis. This leads to stresses of -4.5 GPa in the deposited diamond film, minus signal standing for compression.

Fig. 7 shows the morphology of the NCD film grown for 24 hours on the MCD film and the Raman spectrum is shown in Fig. 8. Growth conditions are described in Table 1. Fig. 8 shows a significant reduction in the Raman peak shift and the stress relieve in the film. The broad band assigned to sp^2 cluster is slightly observed at around 1550 cm^{-1}.[18,19] The upper layer of the coating was MCD film, corresponding to the third layer.

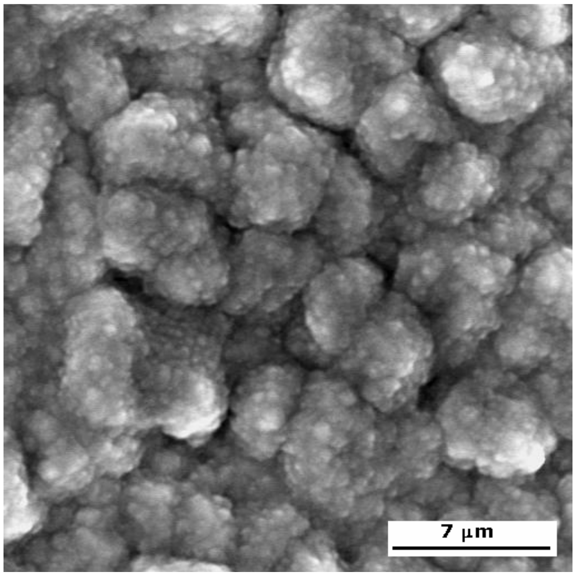

Figure 7. Image (SEM) of NCD diamond film deposited on MCD diamond film.

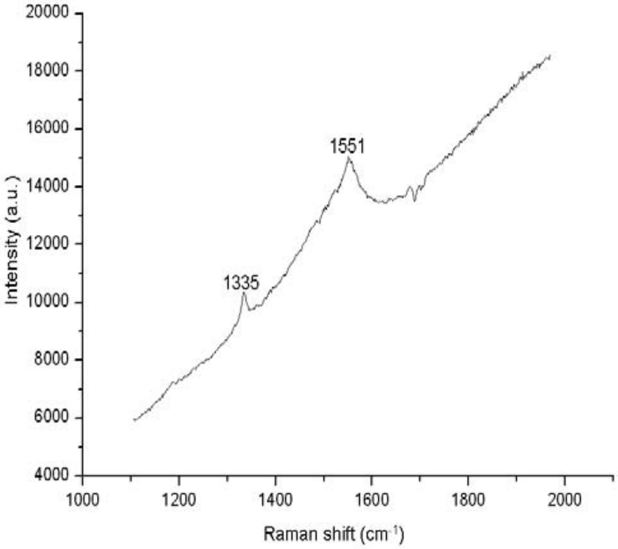

Figure 8. Raman spectrum of NCD diamond film on MCD diamond film.

Machining tests showed a significant improvement in the wear resistance of WC-TiC-Co inserts coated with diamond CVD film when compared to uncoated inserts, as presented in Fig. 9 and Fig. 10. Fig. 9(a - b) shows the cutting edge of the uncoated tool, (a) before and (b) after machining test, pointing local wear by cratering (crater wear), which is a typical failure of cemented carbide inserts. It's shown the cutting edge after 4 min and 12 min of machining, respectively. After 25 min of machining wear on cutting edge increased significantly. The multilayer NCD-MCD coated tools did not exhibit edge wear for the same machining time and there has been no peeling or wear of the diamond film (Fig. 10a and 10b). The coated tool preserved its initial edge geometry for 30 min in the machining test. In addition to machining tests, coatings resistance were evaluated by indentation, using standard Rockwell C conical diamond indenter.

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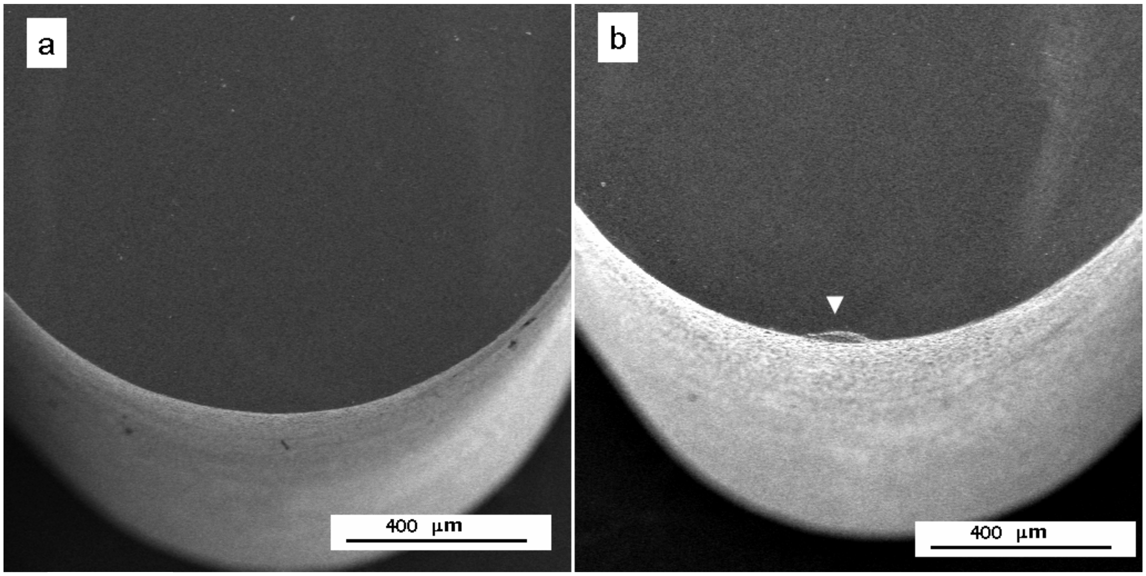

Figure 9. Image (SEM) of uncoated tool cutting edge, (a) before and (b) after machining tests.

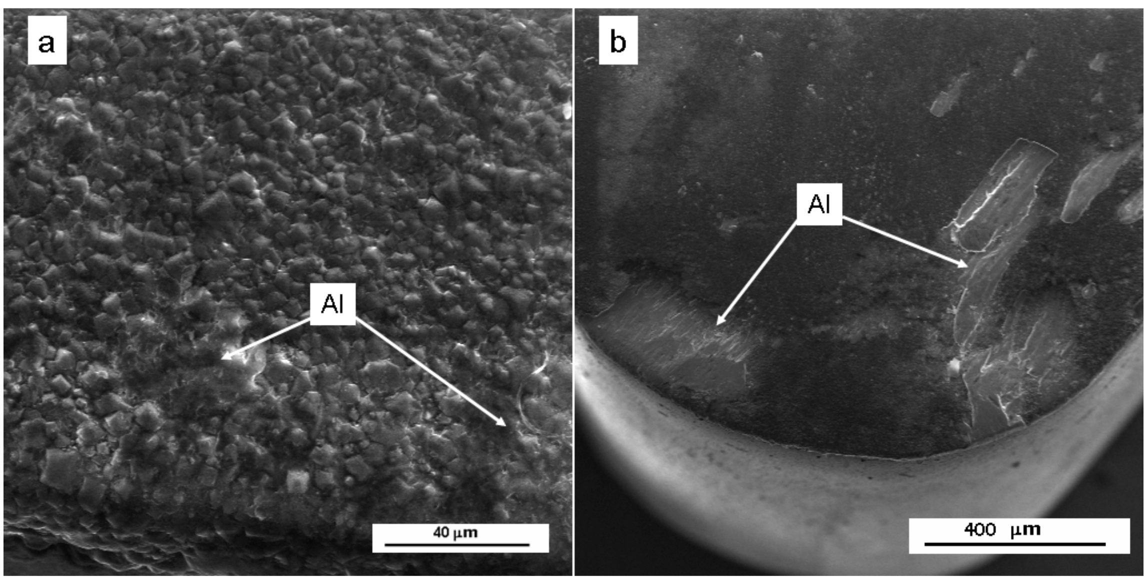

Figure 10. Image (SEM) of coated tool cutting edge after (a) 4 min and (b) 12 min machining.

Fig. 11 shows resulting surface from the Rockwell indentation test at 588 N load of, with no lateral cracks. This correlates to high adhesion of the MCD film growth to WC-TiC-Co substrate.[20]

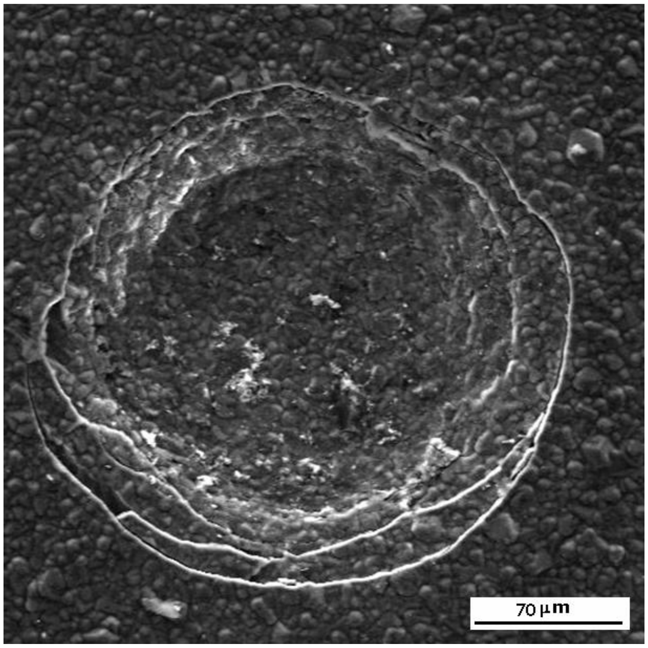

Figure 11. Image (SEM) of diamond film deposited on WC-TiC-Co substrate with boride interlayer, loaded at 588 N a Rockwell C indenter.

4 CONCLUSION

The combination of chemical etching, thermal diffusion treatment and alternated MCD and NCD growth of CVD diamond films on WC-TiC-Co substrates improved adhesion between diamond film and the substrate and contributed to relieve coating residual stresses. Acid etching after boronisation is fundamental to remove free cobalt excess from surface prior diamond film growth. Alkaline etching has shown to be effective to increase surface roughness and improve diamond film adherence. The Raman spectrum shift analysis of NCD and MCD combined films showed reduction in the residual stress level. Turning tests performed on Al -1060 alloy showed an increase of three times in tool lifetime, for diamond-coated inserts compared to uncoated cemented carbide.

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