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Diamond nucleation from the gas phase onto cold-worked Co-cemented tungsten carbide

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Abstract

Co-cemented tungsten carbide (WC–Co) substrates with fine (1 μm) and coarse (6 μm) grain size were sintered using 6 wt.% Co as a binder. The as-sintered samples were ground to the final geometry ($10 \times 10 \times 3$ mm^3). After the grinding treatment, the full width at half maximum (FWHM) of the WC X-ray diffraction (XRD) peaks indicated a high level of strain in a few micrometers thick surface layer, according to the penetration depth of Cu Kα radiation. The as-ground substrates were submitted to a two-step etching procedure with Murakami's solution, to roughen the surface, and 10 s acid wash to etch surface cobalt out. The Murakami's etching time was varied between 1 and 20 min. Fine- and coarse-grained substrates submitted to different chemical etching times were characterized by scanning electron microscopy and XRD, and then submitted to short diamond nucleation runs in a Hot Filament Chemical Vapour deposition reactor. Both FWHM of WC peaks and diamond nucleation density decreased by increasing the Murakami's etching duration, providing that the etched layer did not exceed 2 μm thickness. When a layer thicker than a couple of micrometers was removed by etching, diamond nucleation density was very low and no more dependent on etching time. This occurrence suggested that diamond nucleation density correlates well with the amount of residual strain at the substrate surface and can be tailored by a suitable control of strain-related defects produced by mechanical treatments.
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1. Introduction

Diamond nucleation from gas phase on non-diamond substrates occurs via the Volmer–Weber mode [1] since diamond has the largest surface energy of any known material. In most chemical vapour deposition (CVD) methods, heterogeneous diamond nucleation is a demanding process that requires the performance of a preliminary surface scratching with diamond powder and/or the presence of suitable nucleation sites at the substrate surface [2,3]. It is a well established fact that diamond nucleation onto untreated surfaces is usually both very difficult and slow.

Surface scratching by diamond powder allows to enhance the surface density of diamond nuclei. To justify the increase of surface activity after scratching two

hypotheses can be addressed: (a) residuals of diamond powder left at the surface act as seeds for subsequent diamond growth [4]; (b) the presence of defects produced by mechanical damage supplies suitable sites.

Several papers in the relevant literature have stressed the role of strain-related defects at the substrate surface on the diamond nucleation density. Ascarelli et al. [5], on the basis of X-ray photoelectron spectroscopy analyses, suggested that the well-known diamond nucleation enhancement caused by scratching pre-treatments could be ascribed to the observed formation of a certain degree of atomic disorder at the Si(1 0 0) substrate surface, rather than to diamond seeding. The Authors therefore hypothesized that the abrading pre-treatment could have been effective in providing Si dangling bond configurations at the substrate surface, suitable to match the diamond lattice. Hirakuri et al. [6] found that the diamond nucleation density on a Si(1 0 0) wafer mechanically stressed with a spring and a rod during CVD at 800 °C was affected by the applied stress. They

Table 1
Chemical compositions and properties of WC–Co substrates

WC–Co grade	Average size of WC powder (μm)	Nominal composition (wt.%)	Density (g cm^{-3})	Hardness (HV10)	Transverse strength (MPa)	Coercivity (Oe)
1	1	WC-5.8% Co-0.2% VC-0.2%TaC	14.91	1740	3350	275
6	6	WC-6%Co	14.89	1205	2800	74

measured nucleation densities up to 0.5 μm^{-2}, i.e. several orders of magnitude larger than the typical values reported in the literature for untreated Si(1 0 0)[2]. Polini et al. [7] found that diamond nucleation kinetics on plastically deformed Si(1 0 0) substrates, having a high dislocation density, was very fast and reached completion within 30 min deposition.

However, the correlation between diamond nucleation and strain-related defects has been mainly investigated in the case of single-crystalline Si substrates, which were chosen as model systems. In our knowledge, very few informations are given in the literature about similar effects when polycrystalline materials are concerned.

In this paper we first show that the nucleation of CVD diamond onto a technologically important material such as Co-cemented tungsten carbide (WC–Co) correlates well with WC X-ray diffraction (XRD) peaks broadening, which in turn is attributable to the presence of strain-related defects in the outermost layers of WC grains.

2. Experimental

Hard metal (WC–Co) $10\times10\times3$ mm^3 substrates with different grain size were supplied by F.I.L.M.S. SpA (Anzola d'Ossola, Italy) and used as substrates. The substrates were sintered according to usual powder metallurgy procedures. The final sintering step was performed in Ar atmosphere (35 bar) for 1 h at 1450 °C. Nominal chemical composition, density, hardness and coercivity of the sintered parts are given in Table 1.

After sintering the substrates were ground to the final geometry using a diamond grinding wheel (FEPA D 126, 106–125 μm diamond grit size) and then rinsed with acetone and ethanol. WC–Co samples were submitted to a two-step chemical etching with Murakami's reagent (10 g K$_3$[Fe(CN)$_6$]+10 g KOH+100 ml of water) and then with an acid solution of hydrogen peroxide (3 ml 96 wt.% H$_2$SO$_4$+88 ml 40% m v^{-1} H$_2$O$_2$, 10 s etching time) [8]. The duration of Murakami's etching was varied between 1 and 20 min. This allowed to tailor the weight loss (Δg) of the substrates after the first etching step and, therefore, the thickness, h, of the WC surface layer removed by chemical dissolution, according to the following equation [9]:

$$h=\left(\frac{\Delta g}{\rho_{WC}}\right)(V_{WC}S)^{-1} \tag{1}$$

where ρ_{WC} is the bulk density of tungsten carbide (15.73 g cm^{-3}), V_{WC} is the volume fraction of tungsten carbide in the sintered hard metal, and S is the substrate area (3.20 cm^2). According to previous data from our lab, the etching rate with Murakami's reagent at room temperature was 0.27 μm min^{-1}, independently of hard metal grain size [10]. However, we preferred to determine the value of the thickness of the WC removed layer by weighing each sample after the first etching step and by using Eq. (1).

Following each etching step, the substrates were ultrasonically rinsed with deionised water.

The substrates were labeled with a number (1 or 6, referring to the average grain size) followed by a letter (M) and a number indicating the duration (min) of the Murakami's etching.

All the substrates were analyzed by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360, with LaB$_6$ source), energy-dispersive spectroscopy (EDS, Link eXL II), and XRD (Philips X'Pert Pro). XRD spectra were collected using graphite-filtered Cu Kα radiation ($\lambda=1.54178$ Å) produced at 40 kV/40 mA, 0.75 s counting time for each 0.02° step in the 2θ region from 30 to 55°. For each substrate, and for as-ground and as-sintered samples as well, the full width at half maximum (FWHM) of WC(1 0 0) reflection was measured and corrected by instrumental peak broadening. We evaluated that the sampling depth of XRD analysis was 1.5 μm for the WC(1 0 0) peak (Bragg angle $\theta=17.8°$), as calculated from the mass absorption coefficient of WC–Co [11] and the optical path of the incident and diffracted beams.

Both fine- and coarse-grained substrates were submitted to 1.5 h diamond nucleation runs in the Hot Filament CVD reactor described elsewhere [12]. The gas phase was a mixture of hydrogen and methane with a CH$_4$/H$_2$ volume ratio fixed at 1.0%, activated by a carburized Ta filament (1 cm^2 area) held at 2180 °C and at 8 mm from the substrate surface. The total pressure of the gas mixture in the reactor was 4800 Pa and flow rate 300 standard cm^3 min^{-1}. The substrate temperature was 720 °C. Diamond nucleation densities were determined by SEM.
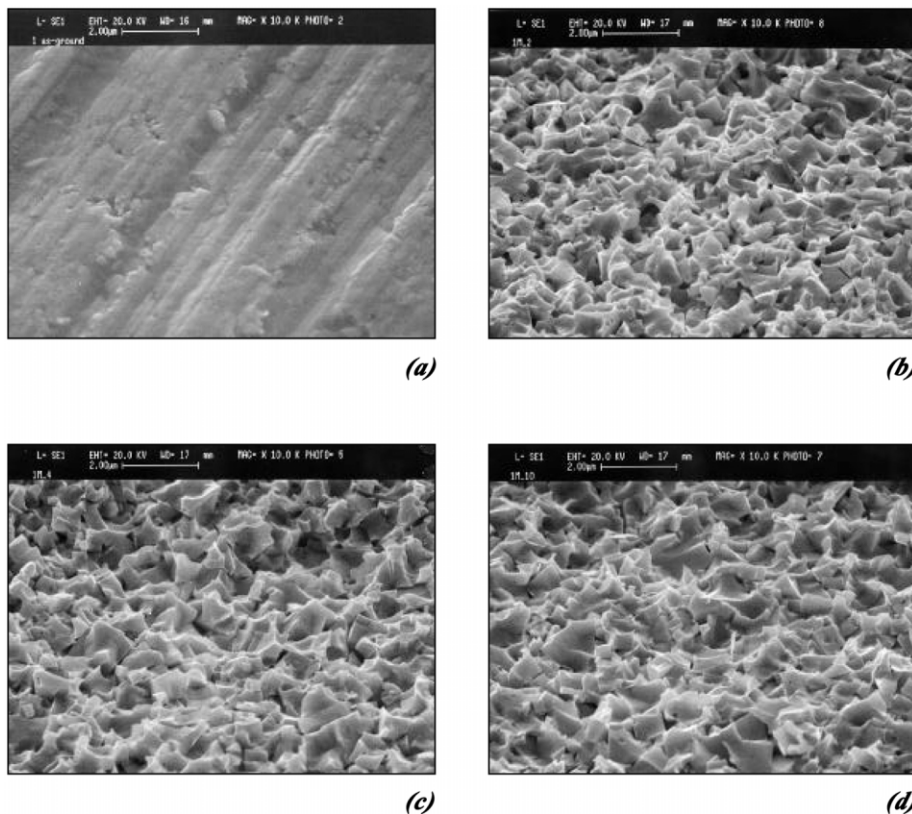
Fig. 1. SEM micrographs of fine-grained WC–Co substrates. Panel (a) shows the morphology of the as-ground surface; panels (b, c and d) show the surface morphology of substrates submitted to 2, 4 and 10 min etching with Murakami's reagent, respectively, and to further 10 s etching with $H_2O_2 + H_2SO_4$.

3. Results and discussion

3.1. Substrate characterization

Fig. 1 shows the SEM micrographs of as-ground (panel a) and fine-grained WC–Co samples after the two-step etching procedure, but submitted to 2, 4 and 10 min etching with Murakami's solution (panels b, c and d, respectively), being identical the subsequent etching time (10 s) with $H_2O_2 + H_2SO_4$. The data show that the two-step chemical pre-treatment led to surface roughening, but surface morphology was not significantly affected by the duration of Murakami's etching. The same results were also observed in the case of coarse-grained hard metal substrates. However, the duration of the chemical attack performed by the alkaline solution of potassium ferricyanide induced stronger changes in the XRD spectra. Fig. 2 shows the WC(1 0 0) diffraction peaks of several fine-grained samples. The scale is the same for all the plots. The bottom spectrum in the figure shows the sharp peak of as-sintered material. The broad WC(1 0 0) peak for as-ground substrates is also reported. It is known that grains, which are under stress, may exhibit anomalous diffraction patterns. The whole XRD pattern may be shifted to either lower or

higher interplanar spacings if the grains are under a compressive or tensile stress. If the stress is non-uniform, different grains or even different parts of the same grain may be deformed to different degrees and the diffraction pattern becomes broadened. This fact has to be attributed to lattice disorder, damage and micro-strain induced by the grinding process. In fact, even in the case of composite ceramics, grinding and polishing treatments with diamond abrasives induce plastic deformation with a region of dislocation activity close to the surface [13].

Fig. 2 also shows that the longer the etching time, the sharper the substrate diffraction peaks. Quite similar spectra were recorded also for coarse-grained substrates.

Fig. 3 shows the variation of the FWHM of WC(1 0 0) peak as a function of the thickness of the WC surface layer removed by etching with Murakami's reagent and calculated using Eq. (1). The data clearly show that the FWHM decreased with etching time and reached an almost constant value, comparable to the FWHM of as-sintered materials, and lower than 0.05° when the depth of etching overcame 2–3 μm. These observations strongly suggest that the grinding with diamond wheel produced a subsurface damage, confined within a couple of micrometers from the hard metal surface. The observed trends were identical for both
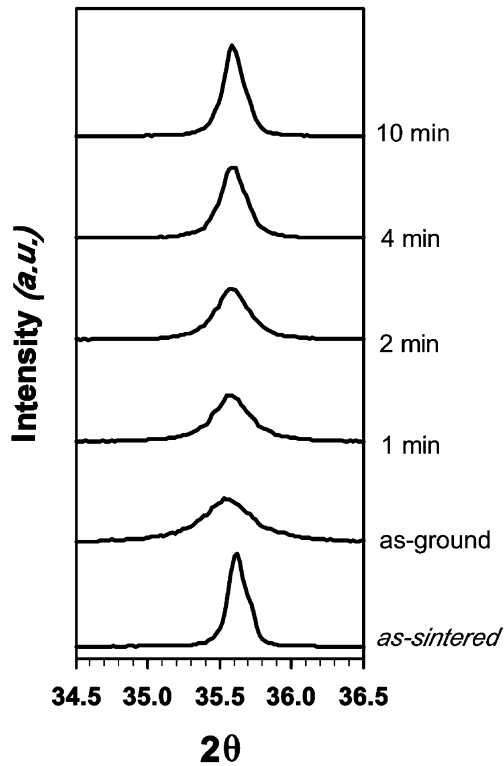
the depth of etching and (ii) the observed trend was independent of the hard metal grain size. Finally, when a WC layer thicker than 2 μm was removed by etching with Murakami's reagent, nucleation density was found to be independent of the etching time.

Therefore, by comparing Figs. 5 and 3, it is evident that diamond nucleation density was affected by the FWHM of WC diffraction peaks which in turn depends on the amount of residual stresses in the outermost layer of cold-worked hard metal substrates. The thickness of this layer can be reduced by increasing the etching time with Murakami's reagent. Since the residual stress is induced by surface machining with diamond wheel, we infer that the grinding treatment led to a concentration gradient of defects, like dislocations, twinning and/or intragranular cracks, whose density decreases from the surface to the bulk of the substrate. The observed strict correlation between nucleation density and depth of etching suggests that suitable surface sites exist at the intersection of the substrate surface created by etching and defects produced by grinding, which caused broadening of XRD peaks.

Few papers studied the diamond/WC interface [14–16]. Echigoya et al. [16] showed that diamond can directly grow on pure WC, with a 23% lattice misfit at the interface. Therefore, strain-related defects could provide atomic arrangements which minimize this lattice misfit, providing pseudomorphic stabilization and nucleation enhancement of CVD diamond onto tungsten carbide.

4. Conclusions

Residual stress and subsurface damage is present in ground WC–Co materials, as witnessed by a quite

Fig. 2. Evolution of WC(1 0 0) XRD peak of as-ground 1 μm-grained WC–Co substrates as a function of the etching time with Murakami's reagent. Etching times are indicated in the figure. For sake of comparison, a line corresponding to the spectrum of the as-sintered material is also reported.

fine- and coarse-grained substrates and this occurrence did not allow to ascribe the observed peak broadenings to grain size effects, thus supporting the hypothesis that large peaks were due to residual stresses in the outermost region of the machined material.

3.2. Diamond nucleation

Fig. 4 shows the SEM micrographs of diamond nuclei formed onto fine-grained substrates which were submitted, after the grinding treatment, to 1, 2, 4 and 10 min etching times with Murakami's reagent. The data clearly show that diamond nucleation density decreased with increasing the etching time. According to XRD results, the diamond nucleation density decreased with the sharpening of the XRD peaks.

Fig. 5 shows quantitative nucleation data. For sake of comparison, also the nucleation density measured after 1 h deposition onto an as-ground coarse-grained (6 μm) substrate, which was not submitted to Murakami's etching, is reported. However, prior to deposition the substrate was etched with $H_2O_2 + H_2SO_4$ in order to avoid the deleterious effect of Co on diamond nucleation.

It is worth noting that (i) nucleation density decreased by about two orders of magnitude with the increase of
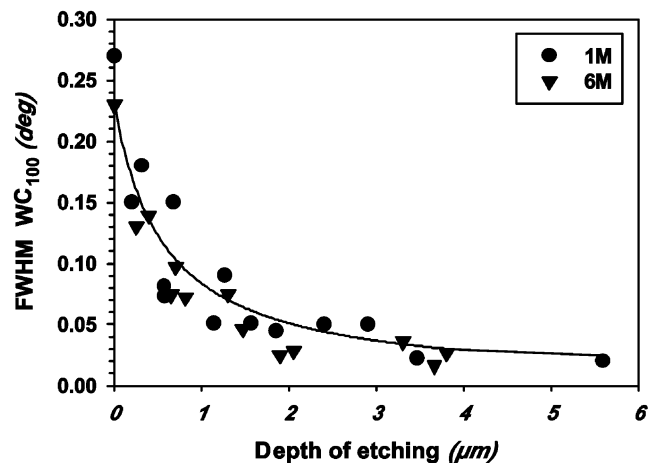
Fig. 3. FWHM of the WC(1 0 0) peak of fine- (1 M) and coarse-grained (6 M) substrates as a function of the thickness of the WC surface layer removed by etching with Murakami's reagent.
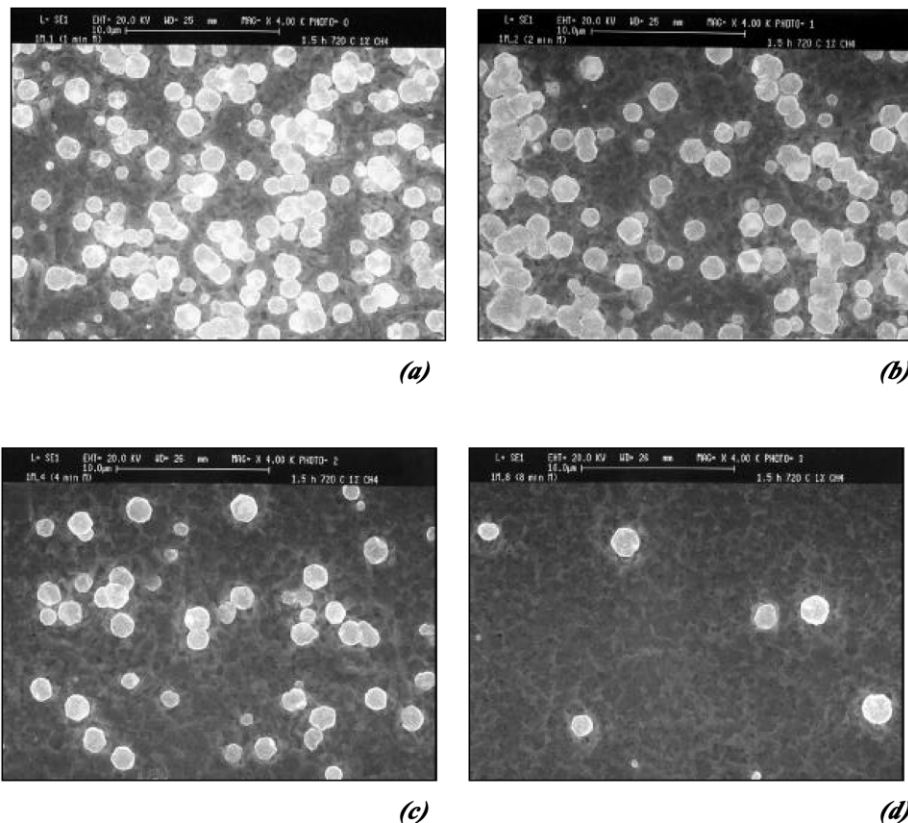
Fig. 4. SEM micrographs of fine-grained substrates submitted to 1 (panel a), 2 (panel b), 4 (panel c) and 10 min (panel d) etching time with Murakami's reagent and to 1.5 h diamond deposition at 720 °C (1% CH$_4$). Prior to CVD the samples were also etched with H$_2$O$_2$ + H$_2$SO$_4$ (10 s) and Co was not detectable by EDS.

evident broadening of WC XRD peaks. The FWHM of these peaks decreased with increasing the amount of WC removed by chemical dissolution, thus suggesting
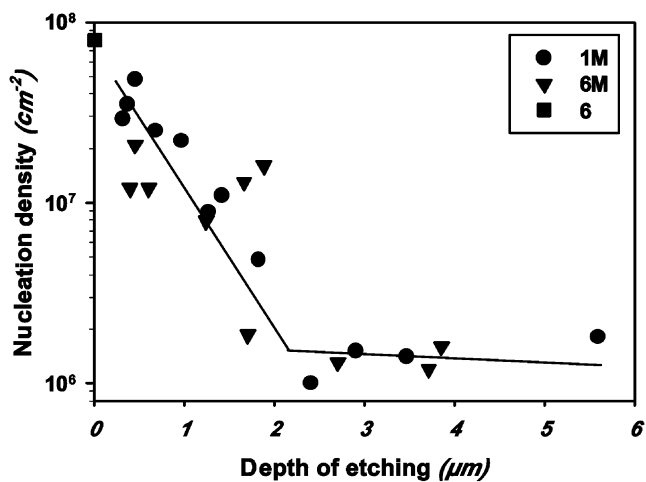

Fig. 5. Diamond nucleation density as a function of the thickness of the WC surface layer removed by etching as-ground substrates with Murakami's reagent. Full square shows the nucleation density measured after 1 h deposition onto an as-ground 6 μm-grained substrate, which was etched only with H$_2$O$_2$ + H$_2$SO$_4$ to wash surface Co out.

that the grinding treatment induced a concentration gradient of defects. If a WC layer thicker than 2 μm is removed, the FWHM resembles that of as-sintered hard metal parts, independently of hard metal grain size. This fact implies that the subsurface damage in ground WC–Co is confined within a couple of micrometers. Diamond nucleation density was found to decrease to a limit value with increasing the amount of cold-worked WC etched away by Murakami's reagent. This fact suggests that stress-related defects produced by machining could act as suitable nucleation sites for diamond. Therefore, a careful control of residual stresses could allow to tailor CVD diamond nucleation density on technologically important polycrystalline substrates.

Acknowledgments

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