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Cobalt Diffusion in Different Microstructured WC-Co Substrates during Diamond Chemical Vapor Deposition

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Our investigation on diamond deposition using cemented tungsten carbide (WC-Co) has shown that diamond particles deposit at different rates onto micrograin and coarse-grain WC-Co substrates. Diamond deposition was carried out using a parallel-plate plasma-enhanced chemical vapor deposition system, which utilized the bias-enhanced growth (BEG) process. BEG was performed at four different times: 15, 20, 25, and 30 min. The resultant diamond-based deposits were characterized for morphology, microstructure, and crystallinity using scanning electron microscopy. It was found that diamond nucleation initiated at the grain boundaries of the substrates. The present article discusses the possible reasons that can potentially explain our key findings. In particular, the CO diffusion from the bulk material through the grain boundaries and onto the substrate surface using a theoretical approach.

1. Introduction

Cemented WC-Co hard metals containing WC grains in the submicron (i.e., 0.5-0.8 μm) to ultrafine (i.e., 0.2-0.5 μm) range and also containing 6 to 16 mass% of cobalt (Co) generally find use in micromachining applications, dental burs, surgical tools, microdrills, and punches used in the pharmaceutical industry.[1] The performance of such hardmetals during service and their lifetime is not ideal for many of the applications. Improvements in such areas can be achieved by the application of an ultrahard coating onto the component. Diamond films display an extraordinary combination of properties that enable them to be used in many different applications.[2-6] The task of direct diamond deposition onto grades of cemented WC-Co, consisting of submicron or ultrafine grains of WC and/or high content of Co (i.e., >8 wt.%) becomes an even more difficult endeavor. Because diamond deposition onto cemented WC-Co consisting of fine-sized WC grains and content with a high percentage of Co is difficult, relatively less work has been done on these grades of material.[7-9] However, many articles can be found in the open literature reporting diamond deposition onto coarse-grain WC-Co substrates with Co contents of <8%.[1-15] The major cause of concern that prevents the successful deposition of diamond onto WC-Co is the negative influence of Co on diamond sp^3 carbon (C) formation.[16,17] Generally, the surface pretreatment methods used to remove the Co from the substrate surface and suppress its negative effects on film growth can be classed into three groups: (1) chemical treatments[12]; (2) stable CO compounds[18]; and (3) intermediate metallic-ceramic layers.[19]

In this investigation, chemical methods were used to pretreat the substrates, and the recently introduced process by Sharda et al.,[20,21] called *bias-enhanced growth* (BEG), to deposit diamond onto micrograin and coarse-grain WC-Co substrates using 15, 20, 25, and 30 min of BEG time.

2. Experimental

The substrates of WC-Co used in this investigation were 6 mm in diameter by 3 mm in thickness. The grade of substrate material used was K10: WC-6mass%Co with average WC grain sizes of 0.8 μm (micrograin) and 4 μm (coarse-grain). All of the samples were polished with diamond paste (containing diamond particle sizes of 15, 7, 3, and 0.25 μm) prior to BEG to achieve similar surface roughness/smoothness. Surface profilometry was used to measure the surface roughness (Ra values) of the cemented WC-Co substrates. Following each polishing step, the substrates were washed with deionized water, and subsequently were chemically cleaned in acetone and ethanol using ultrasonic vibrations. To increase the roughness of WC grains, the samples were etched using Murakami's reagent (10 g of $K_3[Fe(CN)_6]$ + 10 g of KOH + 10 mL of water) for 2 min. Subsequently, the samples were treated for 1 min with acid etching ($HNO_3 + H_2O_2$ 9:1) to remove surface CO. Following each etching step, the substrates were washed with deionized water, acetone, and ethanol in an ultrasonic vessel.

A conventional direct current parallel-plate plasma chemical vapor deposition (CVD) system was used to deposit diamond particles/film onto the two types of WC-Co substrates. The conditions used during the BEG experiments were: methane flow, 5 standard cubic centimeters per minute (sccm); hydrogen flow, 150 sccm; argon flow, 11.7 sccm; pressure, 30 Torr; substrate temperature, 800 to 900 °C; deposition time, 15, 20, 25, and 30 min; emission

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current, 20 mA; and voltage of plates, 400 V. The samples were characterized using scanning electron microscopy (SEM) (model 4100 microscope; Hitachi, Tokyo, Japan).

3. Results and Discussion

3.1 Scanning Electron Microscopy Analysis

The deposits produced during the BEG process were confirmed for sp^3 diamond-C phase presence by Raman spectroscopy studies (results not shown). Raman peaks centered at around 1332 cm^{-1} wavenumbers were found on the spectra for all the samples. Raman spectroscopy is a widely used technique for the characterization of diamond films for C-phase purity. Figure 1 displays SEM micrographs showing the densities of diamond particles deposited on coarse-grain (Fig. 1a-d) and micrograin (Fig. 1e-h) WC-Co substrates after 15, 20, 25, and 30 min of BEG time. It is clear that the density of diamond particles deposited on both grades of substrates generally increased with BEG time. This can be expected because with BEG the diamond particles develop and transform into crystals before coalescing to form a continuous layer of diamond film. The results showed that the minimum time required to form the first continuous, homogeneous diamond film layer on the micrograin WC-Co substrate was within the range of 25 to 30 min. However, using the coarse-grain substrate the continuous diamond film did not form even after 30 min of BEG.

Figure 2 displays the SEM micrograph showing the film morphology of the as-deposited diamond film grown on the micrograin WC-Co substrate after 30 min of BEG time. The average diamond crystallite size of the film shown in Fig. 3 was calculated to be ~10 nm. It was noted in both cases that diamond clusters were formed on the substrate surfaces, and each cluster consisted of nano-sized diamond crystallites. Typically, this type of structure is generated when diamond is deposited under a higher concentration of methane in the vacuum reactor, which results in the formation of a ballas-like morphological structure consisting of nano-sized diamond grains.[22] Figure 3 indicates that diamond nucleation was initiated at the boundaries of the WC grains and subsequently the diamond particles grew to form clusters consisting of many nano-sized diamond grains. The initiation of diamond nucleation at the grain boundaries, in between and underneath the WC grains, and the production of nano-sized diamond grains by the BEG process are advantageous in producing adherent diamond coatings on WC-Co tools by improving the mechanical interlock at the substrate-film interface. It is obvious that there is a greater network of grain boundaries present in the micrograin WC-Co substrate than in the coarse-grain substrate. These sites (grain boundaries) provide suitable centers for the adsorption of gaseous precursors and the formation of sp^3-C clusters. Therefore, with micrograin WC-Co substrates the density of the diamond cluster formation is expected to be higher than in coarse-grain substrates.

In explaining the authors' findings, it should be noted that the differences in the diamond deposits produced on micrograin and coarse-grain WC-Co substrates at different BEG times are due to the "substrate effects." The fact that identical BEG conditions were used during deposition on micrograin and coarse-grain WC-Co substrates ruled out the influence of any contributions from the growth process results of this study. The four main and influential factors contributing to the substrate effects are: (1) substrate grain size; (2) CO diffusion from the bulk material to the substrate surface during diamond BEG; (3) substrate roughness; and (4) substrate residual stresses. Factors 1 and 2 will be discussed in section 3.2. The substrates used in this study were prepared such that the surface roughness was kept approximately equal in both cases prior to loading the substrates in the CVD chamber by using different grades of polishing abrasives. Concerning the substrate residual stress, Hegeman et al.[23] reported that the substrate residual stress increased after grinding the substrate surfaces with a diamond wheel. In this work, the grinding residual stress was quantified by x-ray measurements, and their findings indicated the existence of a detached surface layer with a thickness of 1.5 μm. More recently, Polini et al.[24] showed that the grinding process induces a concentration gradient of defects in the substrate, which can act as suitable nucleation sites for diamond deposition. However, when a layer of 5 μm was removed from the substrate surface by Murakami's reagent, this influence became very small or even nonexistent. Therefore, in this case, because the investigation focused on a comparative study, it was necessary to reduce the grinding residual stresses in both substrates to similar values. During sample preparation, 3 μm of the layer were removed from the surface of the substrates using diamond paste polishing followed by the removal of a further 3 μm of WC during the chemical pretreatment involving the Murakami's reagent.

3.2 Cobalt Diffusion

It is commonly believed that the binder material, Co, in WC-Co diffuses from the bulk material to the substrate surface during diamond CVD. Although the chemical compositions of the two types of substrates used were similar, the average WC grain size values for micrograin and coarse-grain substrates used were 0.8 and 4 μm, respectively. It is anticipated that the rates of outward Co diffusion from the bulk material to the substrate surface during film deposition is different for micrograin and coarse-grain WC-Co substrates. In this section, we attempt to explain theoretically the diffusion of Co from the bulk material during diamond CVD.

During sample characterization using SEM, the authors observed the presence of drops on the substrate surfaces (see Fig. 4 for micrograin; and Fig. 5 for coarse grain). The images in Fig. 4 and 5 represent the micrograin and coarse-grain substrates, respectively, after 15 min of BEG time. This observation has been frequently reported by other workers.[25-27] Despite the Co fraction volume, with both types of substrates being the same the coarse-grain substrate showed greater density of such drops. Because the temperature of the coatings is below the liquid phase formation during cemented carbide sintering, it is expected that the drop formation (Fig. 4, 5) is related to Co diffusion from the bulk material and the diffusion through the vapor phase is due to the relatively higher vapor pressure of the binder material,

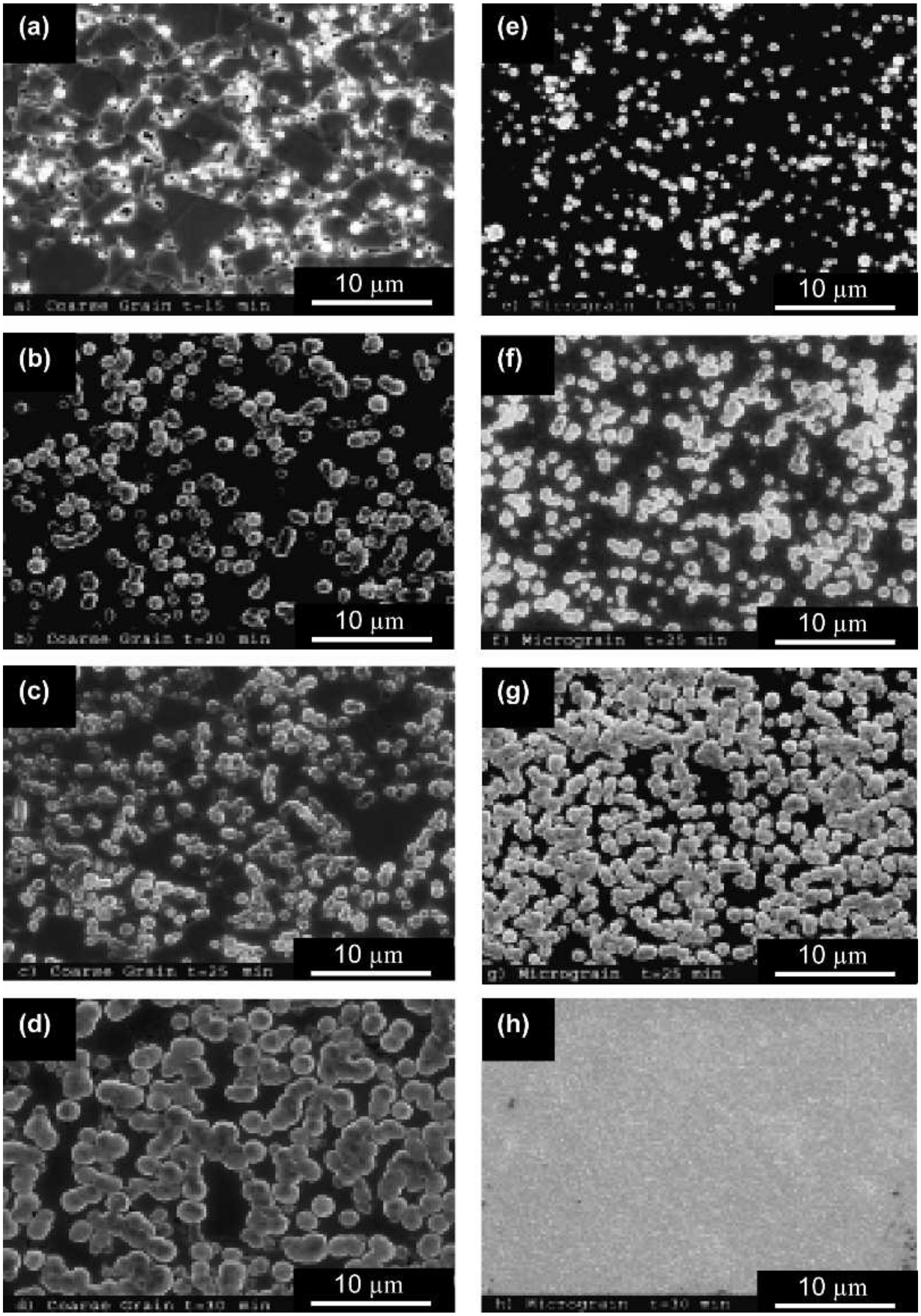

Fig. 1 SEM images showing the diamond deposits produced after BEG times of 15 min (a and e), 20 min (b and f), 25 min (c and g), and 30 min (d and h). (a-d) deposits on coarse-grain substrates; (e-h) deposits on micrograin substrates

combined with the surface forces. This behavior can be attributed to two causes. First, the presence of a higher number of Co droplets observed on the WC surfaces can be held responsible for suppressing the diamond nucleation on such sites and for favoring the catalyzed formation of sp^2 C. Figures 4 and 5 indicate that Co out-diffusion is faster in the

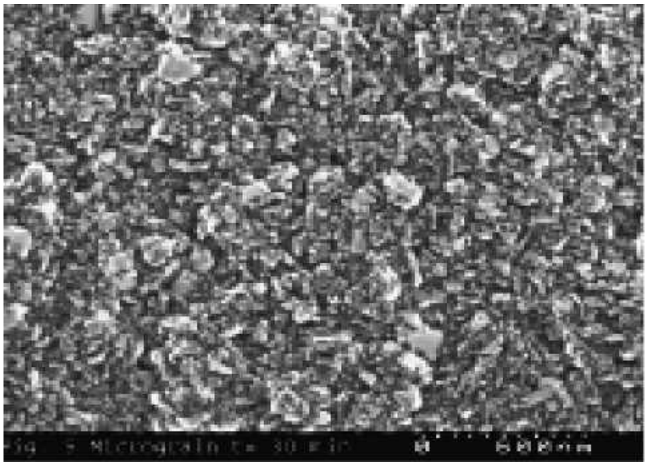

Fig. 2 As-deposited nanocrystalline diamond coating deposited after 30 min of BEG on micrograin WC-Co grade hardmetal. The average grain size is ~10 nm.

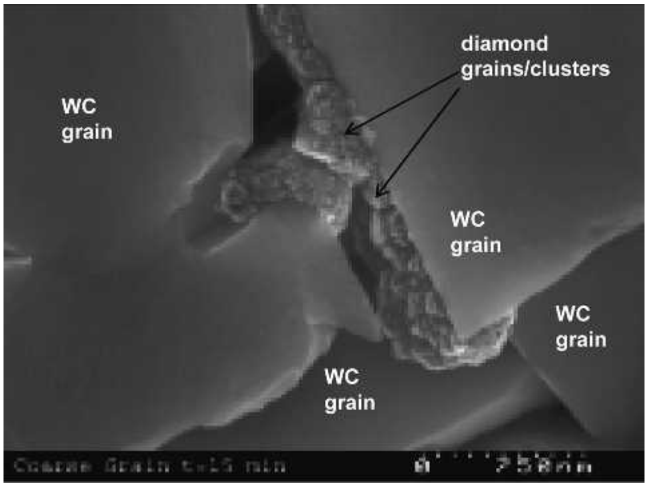

Fig. 3 SEM micrograph showing diamond nucleation occurring at the WC-WC grain boundaries after 15 min of BEG on coarse-grain substrate

coarse-grain substrate compared with micrograin WC-Co material under CVD processing conditions.

From a thermodynamic and kinetic point of view, it is expected that Co diffusion in WC-Co, D_{Co}, has a temperature-dependent Arrhenius expression[28]:

$$D_{\text{Co}} \propto \exp\left(-\frac{Q}{RT}\right) \qquad \text{(Eq 1)}$$

where Q and T represent the activation energy and temperature, respectively. Because of the presence of dispersed phases of WC in the Co matrix, the diffusion paths are partially blocked. This effect can be overcome by considering the effective diffusivities created by introducing the term *labyrinth factor*, ξ, which leads to the reduction of the diffusivity:

$$D^{\text{WC}}_{\text{Co\_eff}} = \xi \times D_{\text{Co}} \qquad \text{(Eq 2)}$$

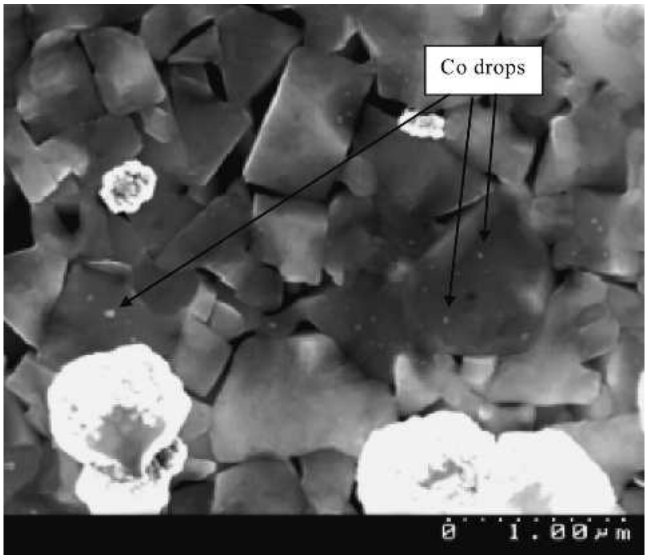

Fig. 4 SEM micrograph showing the surface of the micrograin substrate after 15 min of BEG

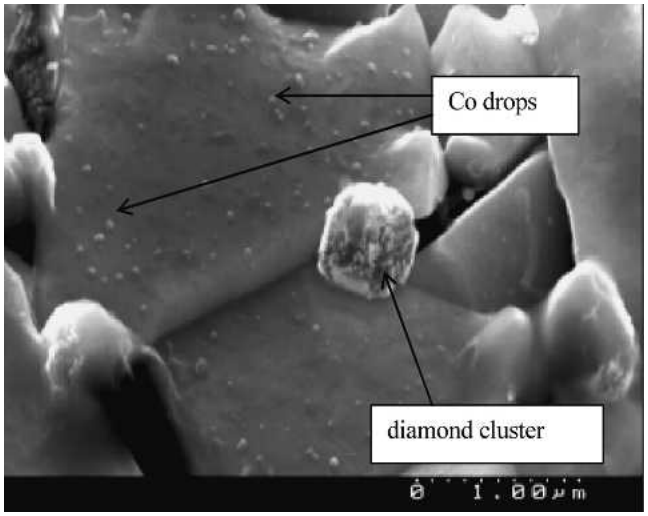

Fig. 5 SEM micrograph showing the surface of the coarse-grain substrate after 15 min of BEG

The value for ξ increases with smaller sized WC grains in the micrograin substrate, according to the following relationship:

$$\xi \propto \frac{1}{G_{\text{WC}}} \qquad \text{(Eq 3)}$$

The microstructure of metal matrix materials is often described in terms of (a) the average grain size of the hard particles, G_{WC}, (b) the mean free path (MFP) in the binder, λ, and (c) the volume fraction of the binder phase, ν_{Co}. Usually G_{WC} and λ are measured by the line-intercept method. These parameters can be related to the Co volume fraction according to the following equation, which was used by Underwood[29]:

$$\upsilon_{Co} = \frac{\lambda}{(G_{WC} + \lambda)} \qquad \text{(Eq 4)}$$

From Eq 2, 3, and 4, we arrive at Eq 5, which indicates that the effective diffusivity of Co increases with Co content and smaller values of MFP for the microstructure.

$$D^{WC}_{Co\_eff} \propto \frac{\upsilon_{Co}}{\lambda \times (1 - \upsilon_{Co})} \times \exp\left(-\frac{Q}{RT}\right) \qquad \text{(Eq 5)}$$

The flux of Co diffusing through a cross section of the material can be expressed by the multicomponent extension of Fick's law multiplied by the volume fraction of the binder:

$$J_{Co\_eff} \propto -\frac{\upsilon_{Co}}{\lambda \times (1 - \upsilon_{Co})} \times \exp\left(-\frac{Q}{RT}\right) \times \frac{\partial c_{Co}(z,t)}{\partial z} \qquad \text{(Eq 6)}$$

In this case, it is very likely that the flow of Co through the WC-Co substrate is higher for substrate grades with higher volume fractions of the binder phase and/or higher MFP (i.e., larger grain size substrates). Polini et al.[26] showed that the nucleation of diamond on WC-Co substrates, which were pretreated in a way that was similar to the pretreatments used in this investigation, was independent of substrate grain size. However, in their study they used a conventional hot-filament CVD system to deposit the diamond films. In this case, the authors used a different type of CVD setup, in which a glow discharge is generated between the two molybdenum parallel plates during the BEG process. Therefore, in this system, the plasma chemistry involved during the BEG of diamond in the reactor is expected to be significantly different from the conditions generated in a conventional hot-filament CVD reactor. Unfortunately, at this stage of the investigation, there is insufficient experimental evidence that gives detailed information about the mechanisms involved at the energetic sites on the grain boundaries during the BEG of diamond deposits onto different grades of WC-Co. However, the authors are currently investigating further to gain a detailed understanding about the mechanisms involved during the BEG of diamond deposits, and the key findings will be reported in our forthcoming publications.

4. Conclusions

Diamond deposits were produced on micrograin and coarse-grain WC-Co substrates, at 15, 20, 25, and 30 min of BEG time, using a plasma-enhanced CVD system consisting of two molybdenum parallel plates. It was found in both cases that diamond nucleation occurred primarily at the WC grain boundaries. Diamond particles nucleated mainly at the grain boundaries of the WC-Co substrates and continued to grow forming clusters, each of which consisted of nano-sized diamond grains. A continuous diamond film was formed after 30 min of BEG on the micrograin WC-Co substrate; whereas, the diamond clusters were isolated from one another in the coarse-grain substrate even after 30 min of BEG. Generally, both the average cluster size and the cluster densities increased with BEG time. However, the increase in both of these factors was higher for the micrograin WC-Co substrate. Because the MFP for the micrograin substrate was small, compared with the coarse-grain substrate, more diamond nucleation reactions are expected to occur at the network of WC grain boundaries. Finally, we have discussed, using equations, the possibilities of Co diffusion from the bulk of the micrograin and coarse-grain WC-Co substrates during BEG to explain our findings. It was observed from SEM studies that a greater number of Co drops appeared on the surface of the coarse-grain substrate than on the micrograin WC-Co substrate. This is proof that there is a greater degree of Co diffusion through coarse-grain WC-Co than through micrograin WC-Co substrates during CVD.

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References

1. Kenneth J.A. Brookes, *World Directory and Handbook of Hardmetals and Hard Materials,* 6th ed., International Carbide Data, Barnet, U.K., 1996
2. P.W. May, Diamond Thin Films: A 21st-Century Material, *Philos. Trans. R. Soc. London, Ser. A,* Vol 358, 2000, p 473
3. M.N. Ashfold, P.W. May, C.A. Rego, and N.M. Everitt, Film Diamond by Chemical Vapour Deposition Methods, *Chem. Soc. Rev.,* Vol 23, 1994
4. N. Ali, W. Ahmed, I.U. Hassan, and C.A. Rego, Deposition of Synthetic Diamond Films: PVD, CVD, and Multiplexed Lasers, *Surf. Eng.,* Vol 14 (No. 4), 1998, p 292
5. H. Chen, M.L. Nielsen, C.J. Gold, R.O. Dillon, J. DiGregorio, and T. Furtak, Growth of Diamond Films on Stainless Steel, *Thin Solid Films,* Vol 212, 1992, p 169
6. J.T. Huang, W.Y. Yeh, J. Hwang, and H. Chang, Bias Enhanced Nucleation and Bias Textured Growth of Diamond on Silicon(100) in Hot Filament Chemical Vapor Deposition, *Thin Solid Films,* Vol 315, 1998, p 35
7. H. Sein, W. Ahmed, I.U. Hassan, N. Ali, J. Gracio, and M.J. Jackson, Chemical Vapour Deposition of Microdrill Cutting Edges for Micro- and Nanotechnology Applications, *J. Mater. Sci.,* Vol 37, 2002, p 5057
8. H. Sein, W. Ahmed, M. Jackson, N. Ali, and J. Grácio, Stress Distribution in Diamond Films Grown on Cemented WC–Co Dental Burs Using Modified Hot-Filament CVD, *Surf. Coat. Technol.,* 163-164, 2003, p 196
9. H. Rajab, N. Ali, H. Sein, and W. Ahmed, What a Bur-gain! CVD Process Offers Economical High Quality Cutting Edge Tools for Teeth, *Mater. World,* Vol 8 (No. 11), 2000, p 17
10. E.J. Oles, A. Inspektor, and C.E. Bauer, The New Diamond-Coated Carbide Cutting Tools, *Diamond Relat. Mater.,* Vol 5, 1996, p 617
11. R. Haubner and A.K.B. Lux, Diamond Deposition on Hardmetal Substrates After Pre-Treatment with Boron or Sulfur Compounds, *Diamond Relat. Mater.,* Vol 11, 2002, p 555
12. J. Oakes, X.X. Pan, R. Haubner, and B. Lux, Chemical Vapour Deposition Diamond Coatings on Cemented Carbide Tools, *Surf. Coat. Technol.,* Vol 47, 1991, p 600
13. A.K. Mehlmann, A. Fayer, S. Dirnfeld, Y. Avigal, R. Porath, and A. Kochman, Nucleation and Growth of Diamond on

Cemented Carbides by Hot-Filament Chemical Vapor Deposition, *Diamond Relat. Mater.,* Vol 2, 1993, p 317

14. R.K. Singh, D.R. Gilbert, J. Fitz-Gerald, S. Harkness, and D.G. Lee, Engineered Interfaces for Adherent Diamond Coatings on Large Thermal-Expansion Coefficient Mismatched Substrates, *Science,* Vol 272, 1996, p 396
15. B. Zang and L. Zhou, Effect of Sandblasting on Adhesion Strength of Diamond Coatings, *Thin Solid Films,* Vol 307, 1997, p 21
16. M.A. Neto, Q.H. Fan, and E. Pereira, Free-Standing Diamond Films Grown on Cobalt Substrates, Vol 10, 2001, p 316
17. J.B. Donnet, D. Paulmier, H. Oulanti, and T. Le Huu, Diffusion of Cobalt in Diamond Films Synthesized by Flame Method, *Carbon,* Vol 42, 2004, p 2215
18. R. Haubner, A. Kopf, and B. Lux, Diamond Deposition on Hardmetal Substrates After Pre-Treatment with Boron or Sulfur Compounds, *Diamond Relat. Mater.,* Vol 11, 2002, p 555
19. I. Endler, A. Leonhardt, H.-J. Scheibe, and R. Born, Interlayers for Diamond Deposition on Tool Materials, *Diamond Relat. Mater.,* Vol 5, 1996, p 299
20. T. Sharda, T. Soga, T. Jimbo, and M. Umeno, Biased Enhanced Growth of Nanocrystalline Diamond Films by Microwave Plasma Chemical Vapor Deposition, *Diamond Relat. Mater.,* Vol 9, 2000, p 1331
21. T. Sharda, T. Soga, T. Jimbo, and M. Umeno, Growth of Nanocrystalline Diamond Films by Biased Enhanced Microwave Plasma Chemical Vapor Deposition, *Diamond Relat. Mater.,* Vol 10, 2001, p 1592
22. Buhlmann, E. Blank, R. Aubner, and B. Lux, Characterization of Ballas Diamond Depositions, *Diamond Relat. Mater.,* Vol 8, 1999, p 194
23. J.B.J.W. Hegeman, J.Th.M. De Hosson, and G. With, Grinding of WC-Co Hardmetals, *Wear,* Vol 248, 2001, p 187
24. R. Polini, P. D'Antonio, and E. Traversa, Diamond Nucleation From the Gas Phase Onto Cold-Worked Co-Cemented Tungsten Carbide, *Diamond Relat. Mater.,* Vol 12, 2003, p 340
25. B.S. Park, Y.J. Baik, R.K.R. Lee, K.Y. Eun, and D.H. Kim, Behaviour of Co Binder Phase During Diamond Deposition on WC-Co Substrate, *Diamond Relat. Mater.,* Vol 2, 1993, p 910
26. R. Polini, F. Le Normand, G. Marcheselli, and E. Traversa, Early Stages of Diamond-Film Formation on Cobalt-Cemented Tungsten Carbide, *J. Am. Ceram. Soc.,* Vol 82 (No. 6), 1999, p 1429
27. A.K. Mehlmann, S.F. Dirnfeld, and Y. Avigal, Investigation of Cobalt Behaviour During Diamond Deposition on Cemented Carbides, *Diamond Relat. Mater.,* Vol 3, 1994, p 805
28. P.G. Shewmon, *Diffusion in Solids,* McGraw-Hill Book Company, New York, 1963
29. E.E. Underwood, *Quantitative Stereology,* Addison Wesley, Reading, MA, 1970