The Role of Diamond Surface and Intrinsic Contaminates on Sintering of Polycrystalline Diamond Compacts (PDC)

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Abstract

High pressure/high temperature sintering of polycrystalline diamond compacts (PDC) is sensitive to impurities in the diamond feedstock, both surface and intrinsic. Diamond powders subjected to the ultra-high pressure sintering environment break down and fracture, exposing new surface area. Thus intrinsic contaminants are exposed as surface contaminants to the sintering environment as a function of pressure. The surface contaminants of three diamond feedstocks were measured after exposing the material to increasingly higher pressure up to the diamond stable region. Two of the samples exhibited a three fold increase in the cumulative addition of contaminant material as pressure was increased. The third sample added very little contaminants to the sintering environment. The control of contamination material presented to the in-situ reaction environment may be fundamental in maintaining a reliable production system for sensitive diamond sintering processes.

Introduction: Sintering of polycrystalline diamond requires heat, ultra-high pressure, and the use of a catalytic/solvent metal system that allows the sintering process to proceed at an economically viable rate[1,2]. The source of the catalytic/solvent metal may be provided by direct addition to the feedstock diamond material to enhance sintering[3] or by an in-situ process in which a substrate material is placed in such a condition that the catalytic/solvent metal is able to flow or sweep from the substrate through the interstitial spacing of the feedstock diamond material and thus sinter the adjoining diamond crystals.

Ultra-high pressure is also a necessary condition for sintering of diamond to be successful. In order for the catalytic/solvent metal to be effective a temperature must be reached in which carbon may dissolve and re-precipitate. These temperatures are usually in excess of 1200ºC. For temperatures at which the catalytic/solvent systems become active, the diamond at near atmospheric pressure is susceptible to significant degradation by graphitization. To keep the diamond from graphitizing the pressure is increased to approximately 70 Kbar. At this state the diamond is stable in the sp^3 configuration and sintering may proceed without the concern of significant degradation the diamond feedstock material.

As a consequence of having to use ultra-high pressure to keep the diamond feedstock stable at high temperature, significant numbers of defects may nucleate and transition into the propagation phase in the form of deep cracks where they may arrest or continue their growth resulting in complete structural failure of the diamond crystal. This

structural failure of the diamond crystal, or crushing as it is commonly referred to, results in the production of new surface area with the accompanying exposure of intrinsic material heretofore encapsulated in the diamond crystal proper. This study was undertaken not to elucidate the effect of the newly exposed surface area on sintering mechanisms but to investigate the amount of additional material presented to the sintering environment as a function of applied pressure for multi-sourced equivalent feedstock material.

Experimental: Three different feedstock samples were selected for this study. Each set of samples was exposed to the same pressure loadings. The samples were encapsulated in identical assemblies and run up to the target pressure with no addition of heat and immediately brought back to ambient pressure. The sample assemblies were then dismantled and the diamond feedstock material captured and placed into glass vials. Samples for surface chemistry analysis were sent to DataChem labs of Salt Lake City, Utah, for leaching of surface materials and determination of concentration. Specific elements analyzed for were Al, Ag, B, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Th, Ti, W, V, Zn, Zr. The method applied to leach surface materials was test method 3050B (EPA). Particle size distribution (PSD) was determined using a Micromeritics® Elzone® 5380 PSD analyzer. Samples were suspended in an isopropyl alcohol solution and agitated by ultrasound.

Results: As shown in Figures 1-3 the fracturing of the diamond feedstock proceeded until the pressure reached approximately 37 Kbar where the material is observed to maintain a fairly stable count/surface area ratio indicating that gross amounts of crystal crushing had reached steady state values.

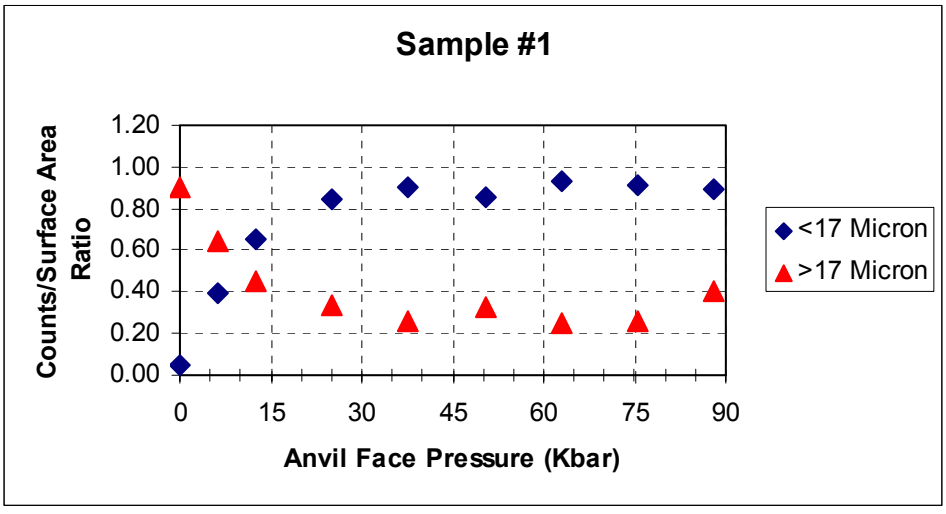

Figure 1 Sample#1 Crushing curve.

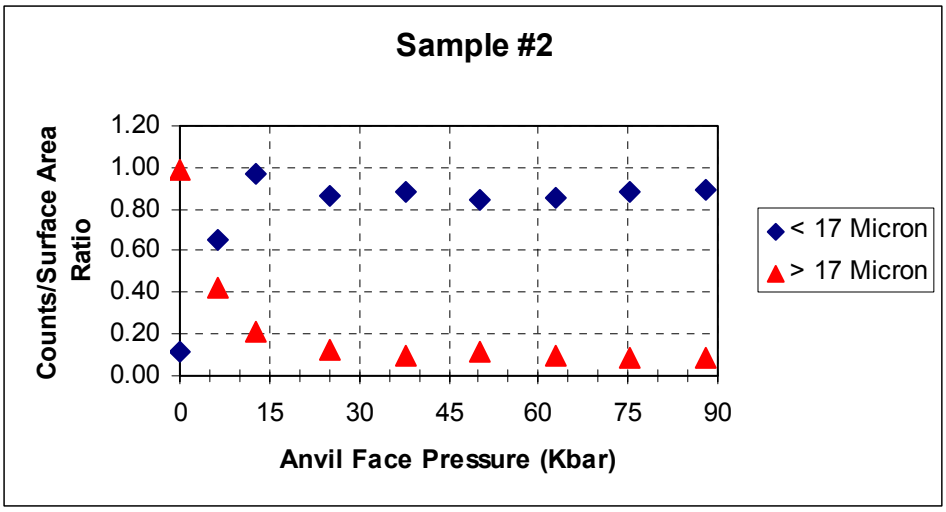

Figure 2 Sample #2 Crushing curve.

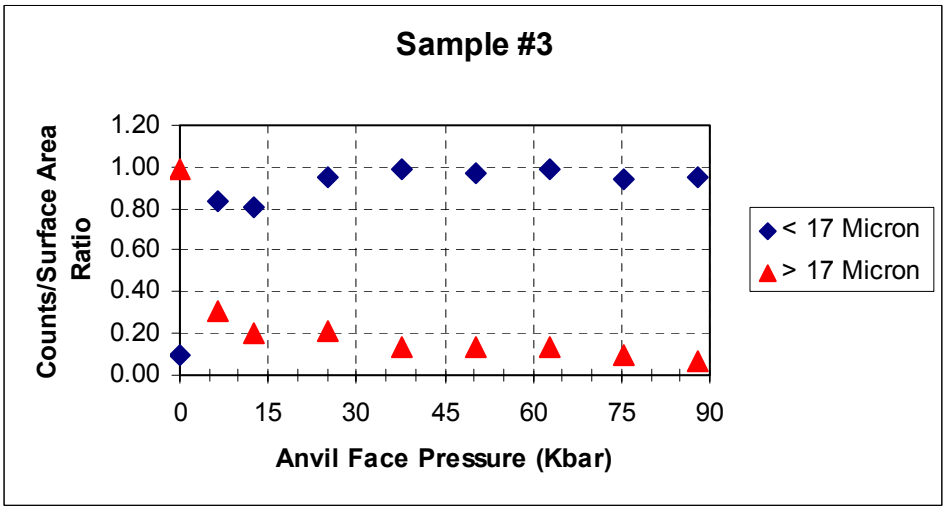

Figure 3 Sample #3 Crushing curve.

From the chemical analysis it was noted that calcium (Ca) was present in inconsistent amounts, some values rather large. The source of the calcium is still unknown. Tungsten (W) was also screened for but the substrate material used for crushing the samples contained a substantial amount of tungsten and this may have introduced some uncertainty into the numbers for this element. In calculating totals these two elements were neglected. The group of elements comprising the top eight concentration levels is shown in table 1.

Table 1 Eight elements with highest concentration.

Boron	Chromium	Cobalt	Iron
Manganese	Nickel	Silicon	Sodium

Comparisons including and excluding Ca and W in the summation were calculated. The relative influence of these eight elements with respect to the total element count is shown in table 2.

Table 2 Summation and ratio values (ppm).

Sample #	1			2			3		
Pressure (Kbar)	0	6.3	37	0	6.3	37	0	6.3	37
Σ	86	316	469	178	110	113	128	225	515
No Ca W Σ	60	269	416	93	79	87	89	217	431
8 Elem/Σ	66%	83%	81%	47%	62%	77%	63%	94%	81%
8 El/Σ No Ca W	95%	98%	92%	89%	87%	100%	90%	98%	97%
8 El Σ	57	264	381	83	68	87	80	212	418

The cumulative surface element content for the three samples are shown in Figure 4. The values for the catalytic/solvent metals for each sample are shown in Figure 5.

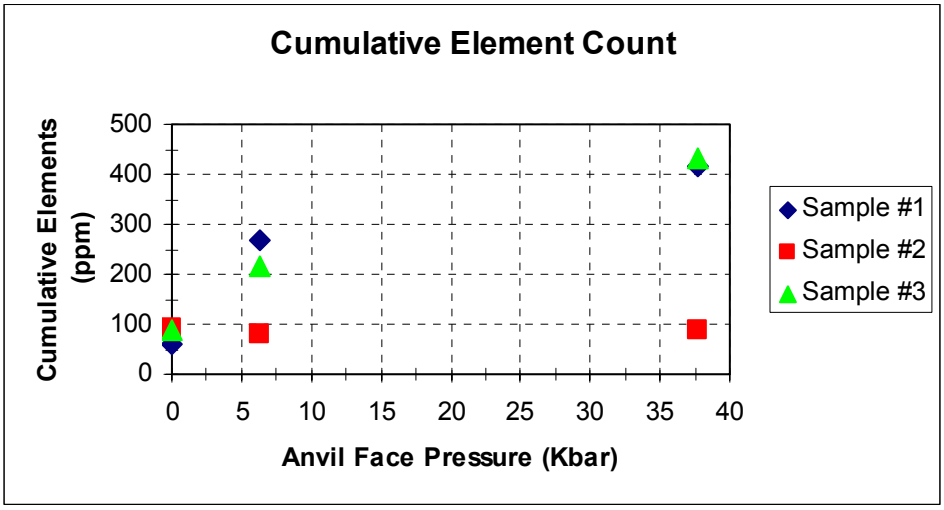

Figure 4 Cumulative surface element count.

Discussion: The motivation for this study was the interest in what materials are presented to the sintering environment as new surface area is created due to pressure/crushing and in what amounts. As shown in Figures 1-3 the introduction of new surface area is observed to increase up to approximately 37 Kbar at which point a steady state condition is reached.

The pressure regions of interest were the as received material (0 Kbar), an intermediate point (6.3 Kbar), and when production of new surface area had stabilized (37 Kbar). As illustrated in Figure 4 the concentration of surface contaminants for the as received material is very nearly equivalent for all three samples. For a specification that called out a surface content level reflecting the highest observed amount for the as received material all three sample would be deemed to be acceptable.

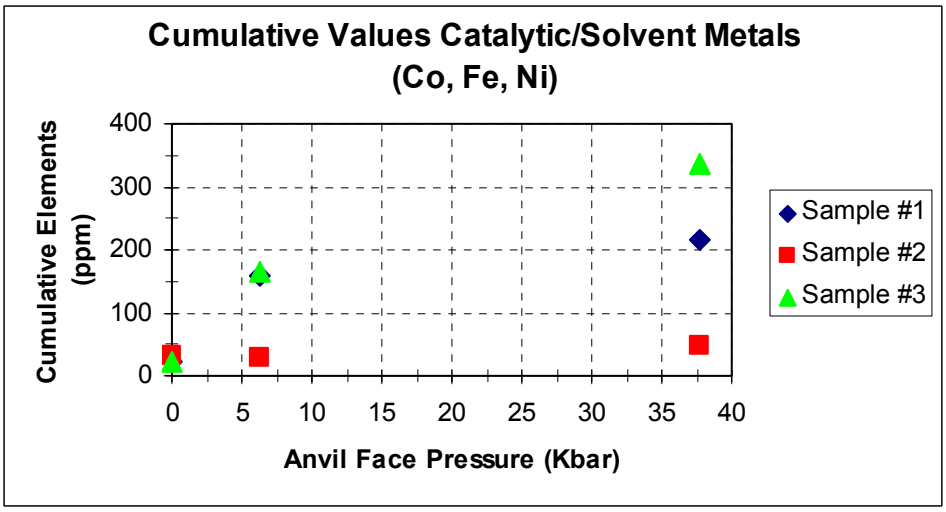

Figure 5 Cumulative Catalytic/Solvent Concentration.

As the pressure/crushing is increased samples one and three are observed to present increased amounts of what was heretofore intrinsic material to the sintering environment whereas sample number two exhibits a more constant behavior. It is observed from Figures 1-3 that there is no gross discrepancy among the three samples in the amount of crushing and subsequent generation of new surface area. This would indicate that the increase in material being detected is due to increased internal material being exposed concurrent with the new surface area.

With continued increase in pressure/crushing it is observed from Figure 4 that samples one and three continue to expose intrinsic material concomitant with the generation of new surface area. This behavior is not observed for sample two in that the indicated element levels remain nearly constant with an increase in surface area. From this it may be surmised that sample two, with regards to the amount of intrinsic elements, is different from samples one and three.

As was stated earlier twenty-three elements were screened for. Analysis is costly and time consuming. A group of eight elements were selected and evaluated as to their contribution to the total amount of material added to the environment. In table 2 the relative amounts of the eight elements are evaluated. For samples one and three these eight elements comprise 90% or more of the material introduced on crushing. For sample two the eight elements comprise 87% or more of the material introduced on crushing. Limiting the screening to these eight elements covers the materials of concern and also reduces the cost and time requirement.

Also of interest was the amount of catalytic/solvent elements introduced to the sintering environment upon high pressure/crushing. In Figure 5 samples one and three are observed to exhibit large increases in the amount of catalytic/solvent material introduced to the sintering environment upon crushing. This behavior is not observed for sample two. Although all three samples were considered to be very similar this study would appear to indicate that there are some significant differences that require consideration as to their impact on process control. When applying various methodologies to enhance the diamond performance such as large embedded diamond crystals,[4] layered or transition layer technology,[5,6] or attempting to impart thermal

stability,[7,8,9] material being presented to the sintering environment by the high pressure treatment of the feedstock diamond may have deleterious effects on these enhancements if not accounted for in the design phase.

Conclusion: Having an awareness of the performance characteristics of feedstock materials assists the engineer in developing specification criteria to promote consistency in processing. In this study it has been observed that three similar feedstock materials when processed bring to the sintering environment varying amounts of material. The composition of a feedstock material may not necessarily be the leading concern when compared with the consistency of the material. With processes that are sensitive to minor differences or changes in feedstock material, multi-vendor dependence dictates diligence in understanding the fundamental characteristics of each supplied material and the possible variance introduced to a given process.

References:

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