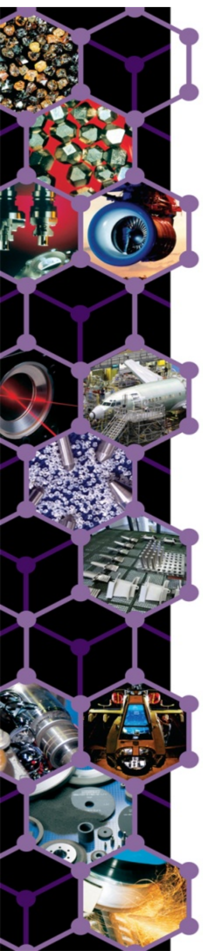

Crystallographic Defects and Mechanical Strength of Micron Size Monocrystalline Diamond

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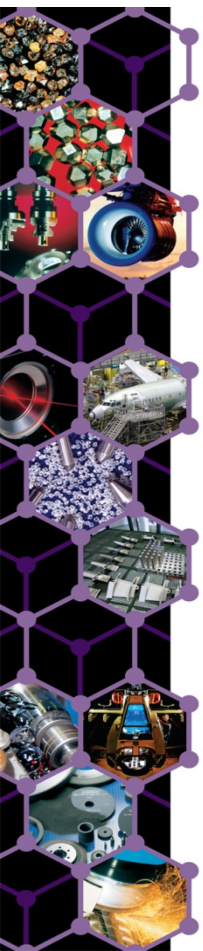
Outline

- ❖ Introduction
- ❖ Experimental Techniques
- ❖ Experimental Results
- ❖ Summary
- ❖ Conclusions

Crystallographic Defects of Diamond



- ***Crystallographic defects*** or ***crystal growth defects*** of diamond are the result of the nucleation and crystal growth processes that govern the catalytic high pressure-high temperature (HPHT) graphite to diamond transformation (so called diamond synthesis process)

- Crystallographic defects (substitutional or interstitial impurities, vacancies, dislocations, etc.), are sources of mechanical stresses, thus contributing to mechanical strength and fracture characteristics of monocrystalline diamond particles

Crystallographic Defects of Diamond

- The intrinsic properties of diamond crystals are determined by the particularities of the catalytic HP-HT synthesis process; mainly the nucleation & growth rates

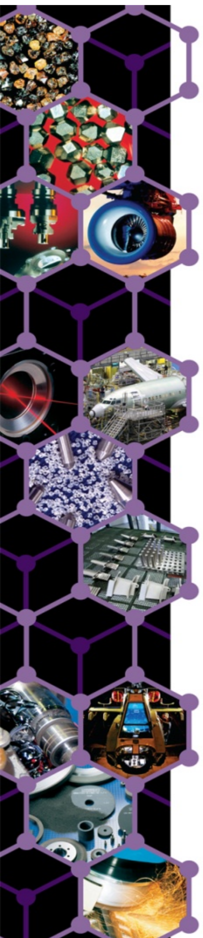
- For a given graphite-metal catalyst system the kinetics of the diamond synthesis process (nucleation & growth rates) is controlled via thermodynamic parameters pressure & temperature
  - Low nucleation & growth rates → diamond crystals with low level of crystal growth (CG) defects → high mechanical strength
  - High nucleation & growth rates → diamond crystals with high level of crystal growth (CG) defects → low mechanical strength

Micron Size Monocrystalline Diamond

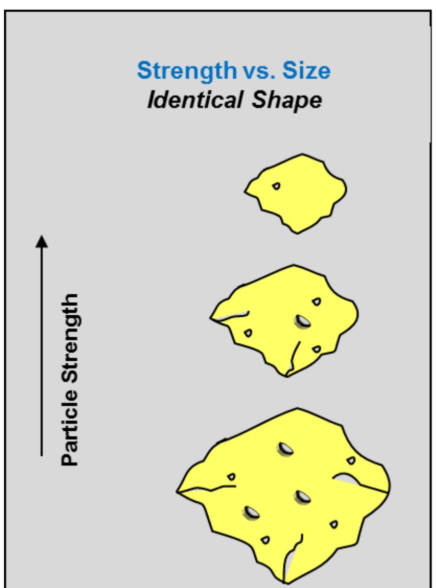
- Most micron size monocrystalline diamond powders are produced by size reduction (milling) of mesh size diamond powders (starting mesh diamond powder feed)

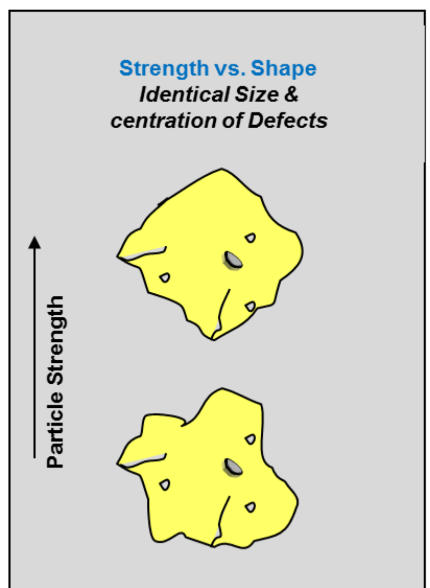
- Following the micronizing process (mechanical, chemical, and thermal process steps):
  - A large number of the ***initial crystal growth (CG) defects*** of the starting mesh diamond powder feed ***are released***
  - ***Some of the initial crystal growth (CG) defects of the starting mesh diamond powder feed are transmitted to the resultant micron size diamond powder as residual crystal growth (RCG) defects***

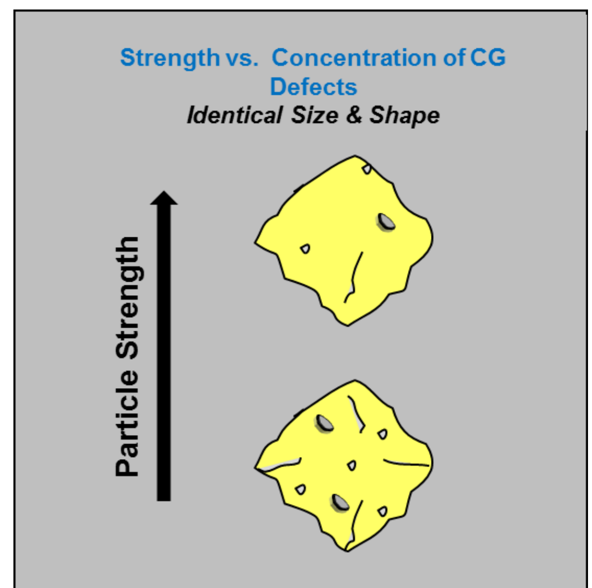
Mechanical Strength of Diamond



- Mechanical strength of diamond particle characterizes its ability to resist fracture under static or dynamic (impact) loading
- Mechanical strength of monocrystalline diamond particle is dependent upon particle size, particle shape and concentration of residual crystal growth (RCG) defects

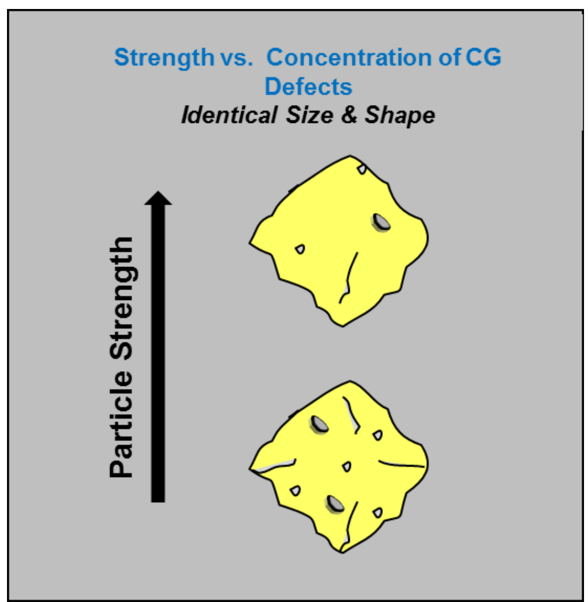






Micron Size Monocrystalline Diamond

- For a given size and shape, the mechanical strength of a micron size monocrystalline diamond particle is directly related to the concentration of residual crystal growth (RCG) defects:
  - Low concentration of RCG defects ⟶ High mechanical strength
  - High concentration of RCG defects ⟶ Low mechanical strength



DR-FTIR Spectroscopy

- The concentration of crystallographic defects of micron size monocrystalline diamond powders was gauged using the Diffuse Reflectance Fourier Transform Infrared (DR-FTIR) Spectroscopy

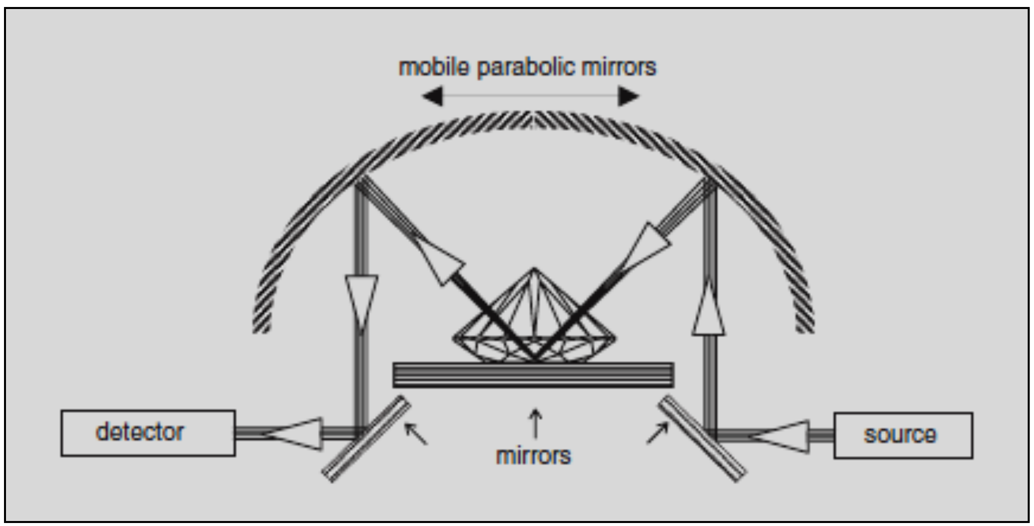


Fig. 1 – Schematic view of FTIR transmission spectroscopy with a diffuse reflectance accessory

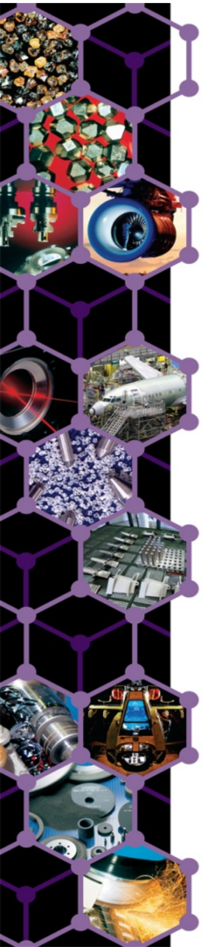
DR-FTIR Spectroscopy

- Diffuse reflectance FTIR is a technique well suited for analysis of powder samples that can give quantitative and qualitative information about the nature and level of impurities and crystalline defects

- FTIR transmittance is related to elastic light scattering due to crystallographic defects such as dislocations and grain boundaries

DR-FTIR Spectrum of Diamond

- 2670 to 1600 cm-1 represents transmittance from the C=C bonding
- 1400 to 1050 cm-1 contains peaks due to Nitrogen defects:
  - A centers, B centers, C centers (single substitutional N at 1130 & 1344 cm-1) and platelets



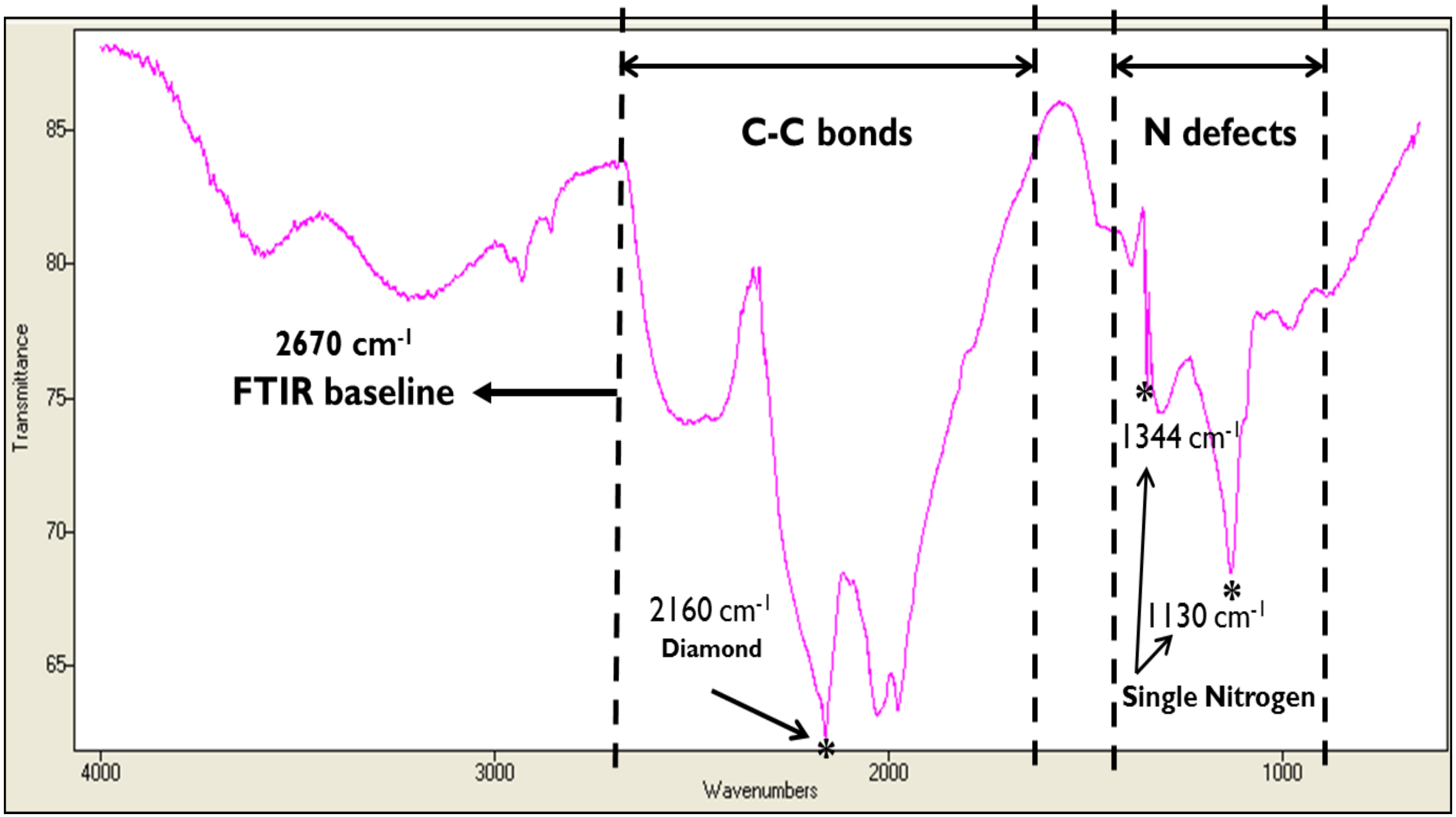


Fig. 2 – DR-FTIR spectrum of diamond

Experimental Results

❖ Different μ size diamond powder types sharing "identical" size

- 6-12 μm HQ-MB = High quality metal bond diamond
- 6-12 μm LQ-MB = Low quality metal bond diamond
- 6-12 μm RB = Resin bond diamond

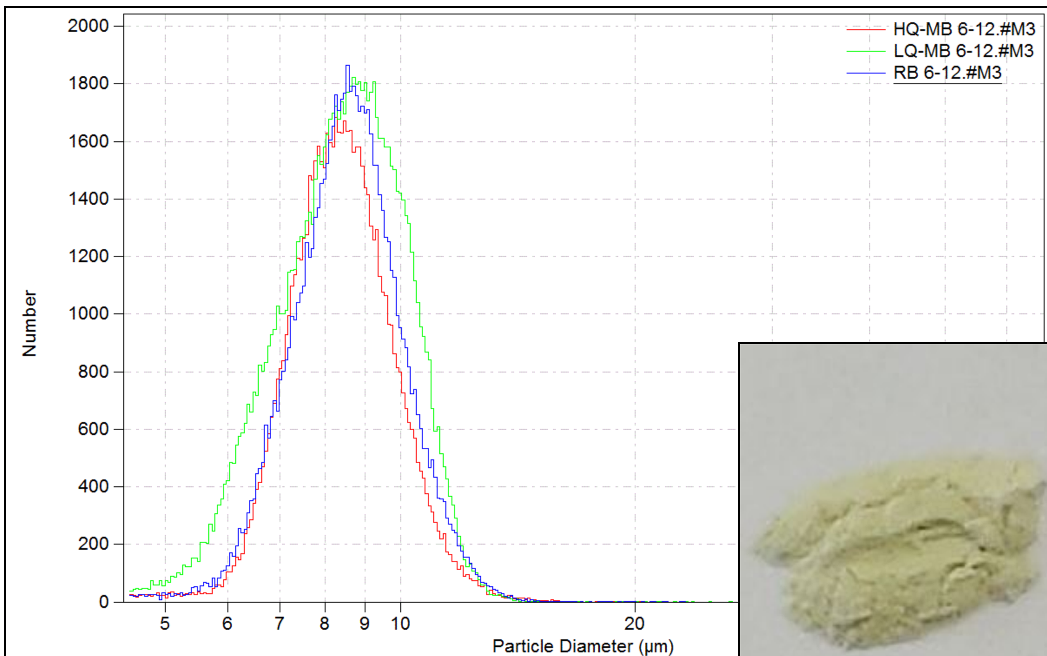


Fig. 4 – PSD overlay of diamond samples

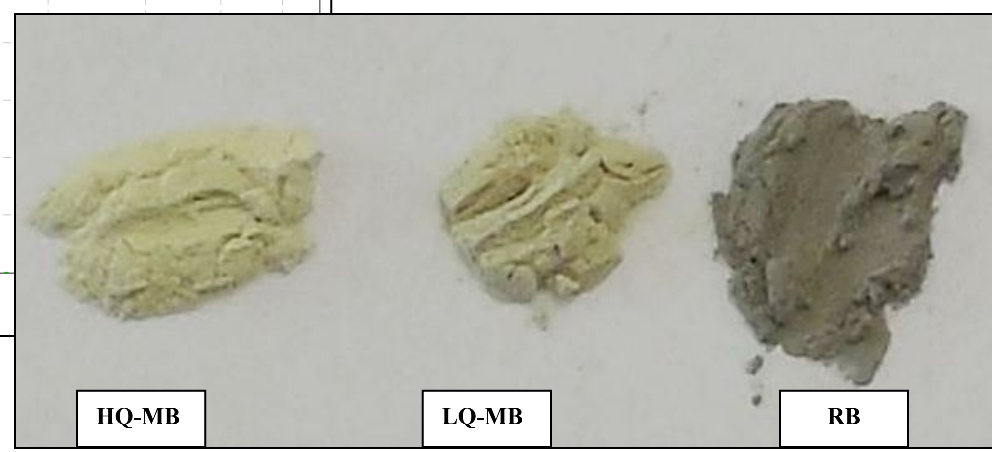


Fig. 3 – Images of diamond samples

Experimental Results

❖ FTIR baseline transmittance

- FTIR baseline transmittance mirrors the concentration of crystallographic defects (residual crystal growth defects) of micron size monocrystalline diamond powders – **the higher the concentration of crystallographic defects, the lower the baseline transmittance**

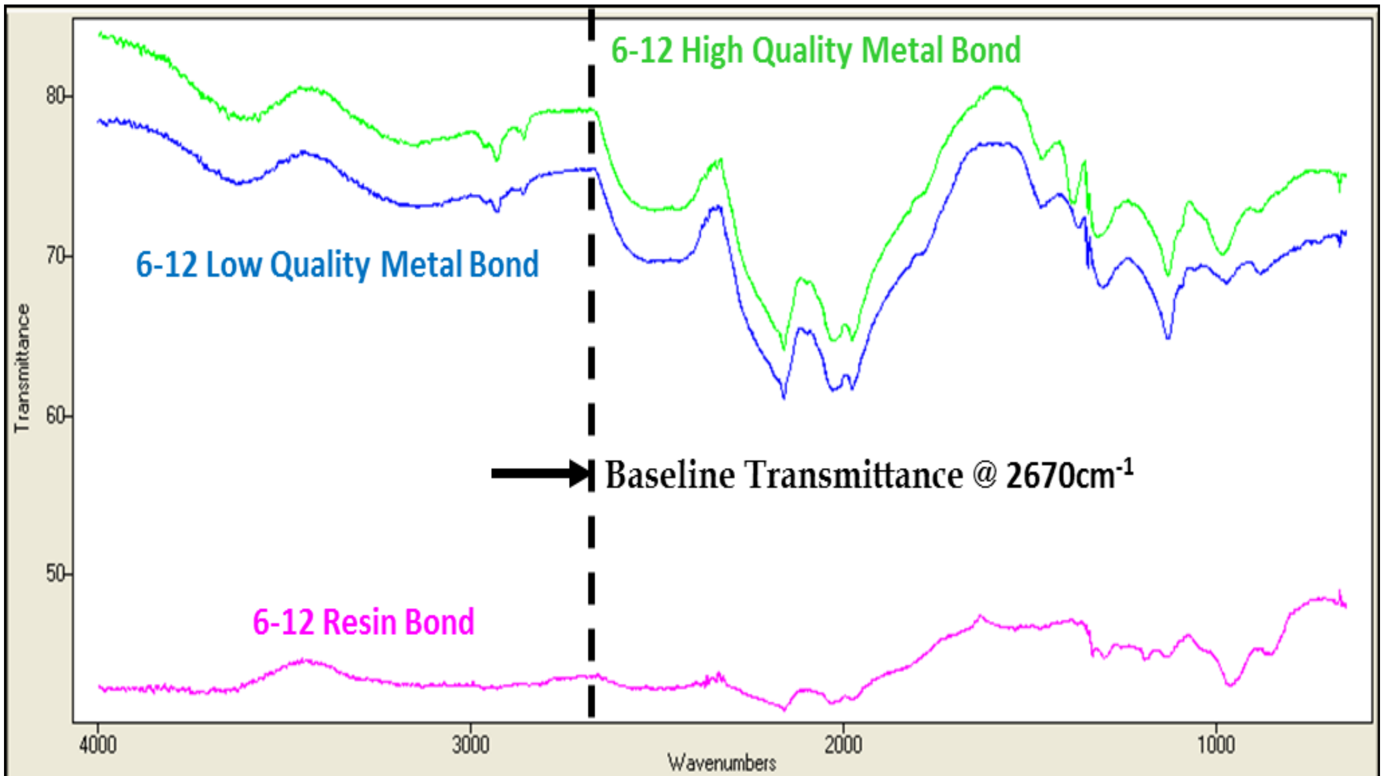


Fig. 5 – Overlay of FTIR baseline transmittance of 6-12 μm diamond samples

Crystallographic Defects & FTIR Baseline

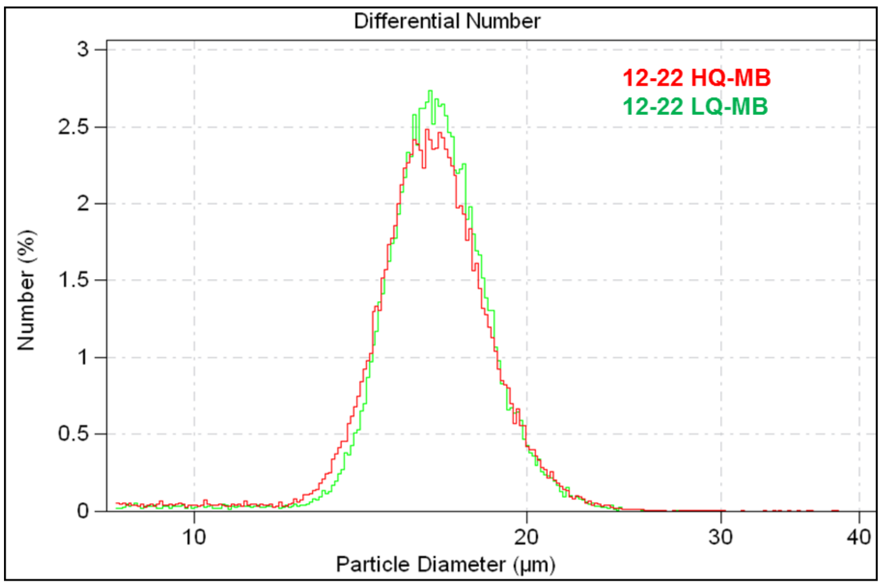
- RB diamond sample which possesses intrinsically high concentration of crystallographic defects, exhibits a much lower FTIR baseline transmittance compared to MB diamond samples

- MB diamond samples possess much lower concentration of crystallographic defects and, consequently, exhibit much higher FTIR baseline transmittance

- ***FTIR baseline transmittance represents a good measure for the concentration of crystallographic defects in micron size monocrystalline diamond powders***

Experimental Results

- Different quality μ size metal bond (MB) diamond powder sharing "identical" particle size & shape
  - 12-22 μm HQ-MB = high quality metal bond diamond
  - 12-22 μm LQ-MB = low quality metal bond diamond



Sample ID	Diameter on % (μm)			
	5%	50%	95%	99.9%
12-22 HQ-MB (#R0206)	13.57	16.41	19.9	25.35
12-22 LQ-MB (#11288)	14.04	16.54	19.78	24.33

Fig. 6 – PSD overlay

Particle Shape Data	11288 LQ-MB	R0206 HQ-MB
Total Particle Count	4884	4541
Average Aspect Ratio (Mean)	0.710	0.704
Number Particles with AR < 0.5	195	179
Number Particles with AR < 0.5 (%)	3.99%	3.94%
Particle Size Data Equivalent Spherical Diameter (ESD) - μm	**11288 LQ-MB**	**R0206 HQ-MB**
5%	12.94	12.79
50%	15.32	15.41
95%	18.55	19.70
99.9%	24.51	25.66
Max Particle	26.95	29.33

Table 1 – Particle shape & size data

Experimental Results

- FTIR spectroscopy results on different quality μ size metal bond (MB) diamond powder sharing "identical" particle size & shape

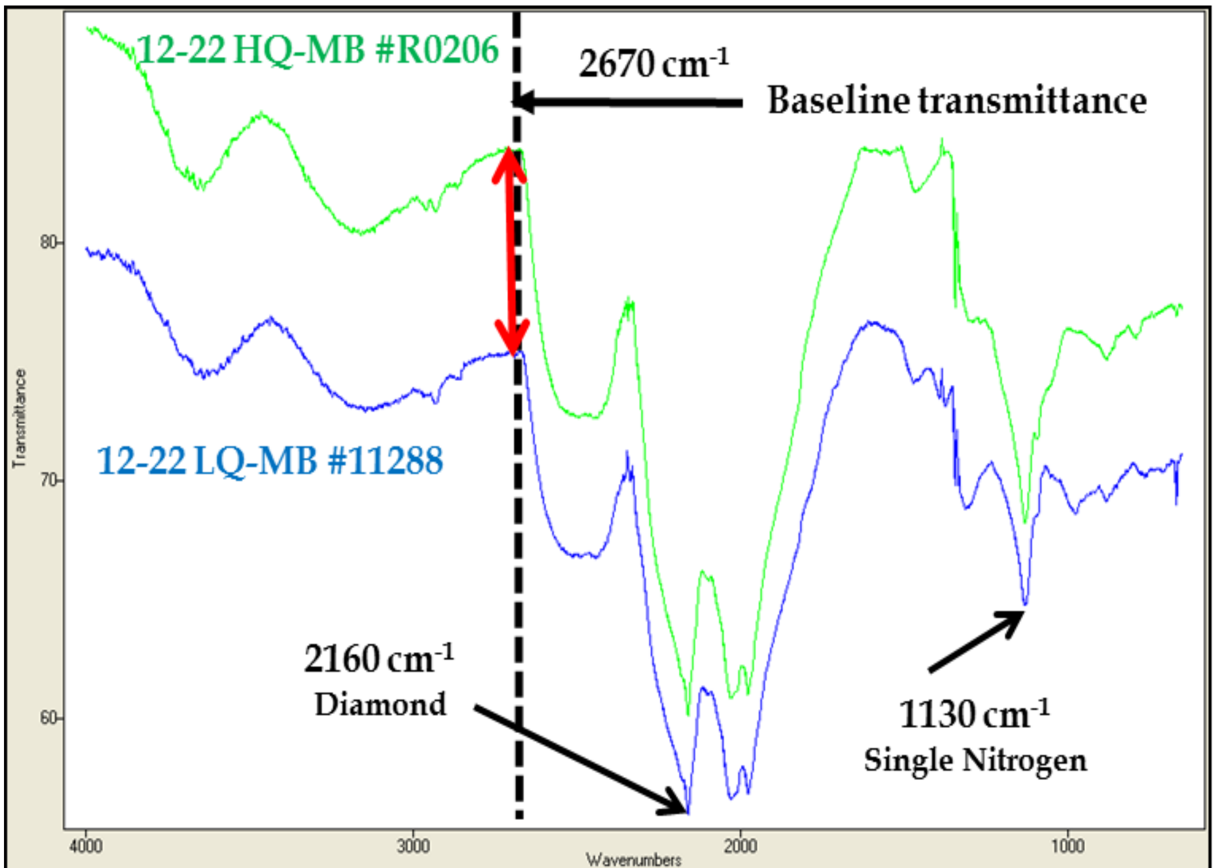
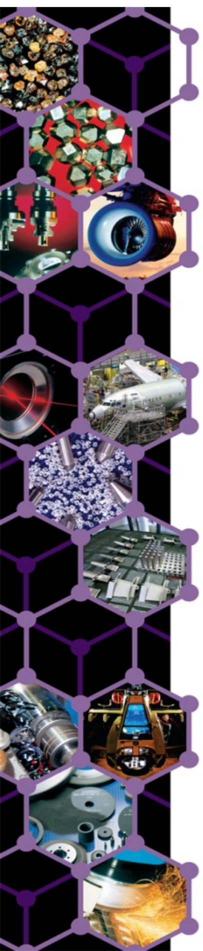


Fig. 7 – Overlay of FTIR spectra of 12-22 μm diamond samples

Substitutional Nitrogen Impurities in Synthetic Diamond

- Substitutional Nitrogen impurities in synthetic diamond (Type Ib)



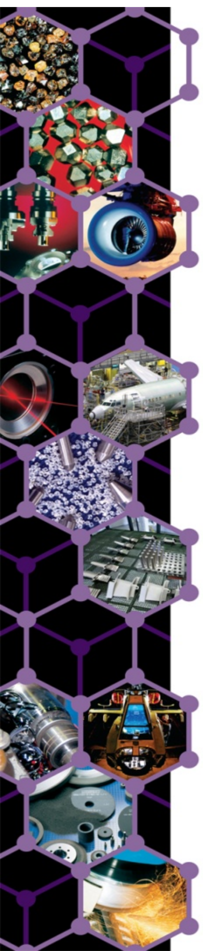
- It is known that the amount and defect type of substitutional nitrogen in synthetic diamond strongly influences crystal strength
- Generally, the concentration of the substitutional Nitrogen impurities in the type Ib diamond is proportional to the intensity of the band at 1130 cm−1
- The substitutional N defect (SND) concentration is calculated as the ratio of the percent transmission of the diamond peak (at 2160cm-1) and the single N defect peak (at 1130cm-1) as follows:

SND = (% transmission @ 2160 cm-1) / (% transmission @ 1130 cm-1)

Experimental Results

❖ FTIR baseline transmittance and substitutional Nitrogen defect

		Baseline Transmittance	Substitutional Nitrogen Defect
R0206	HQ-MB	83.88	0.881
11288	LQ-MB	75.40	0.864



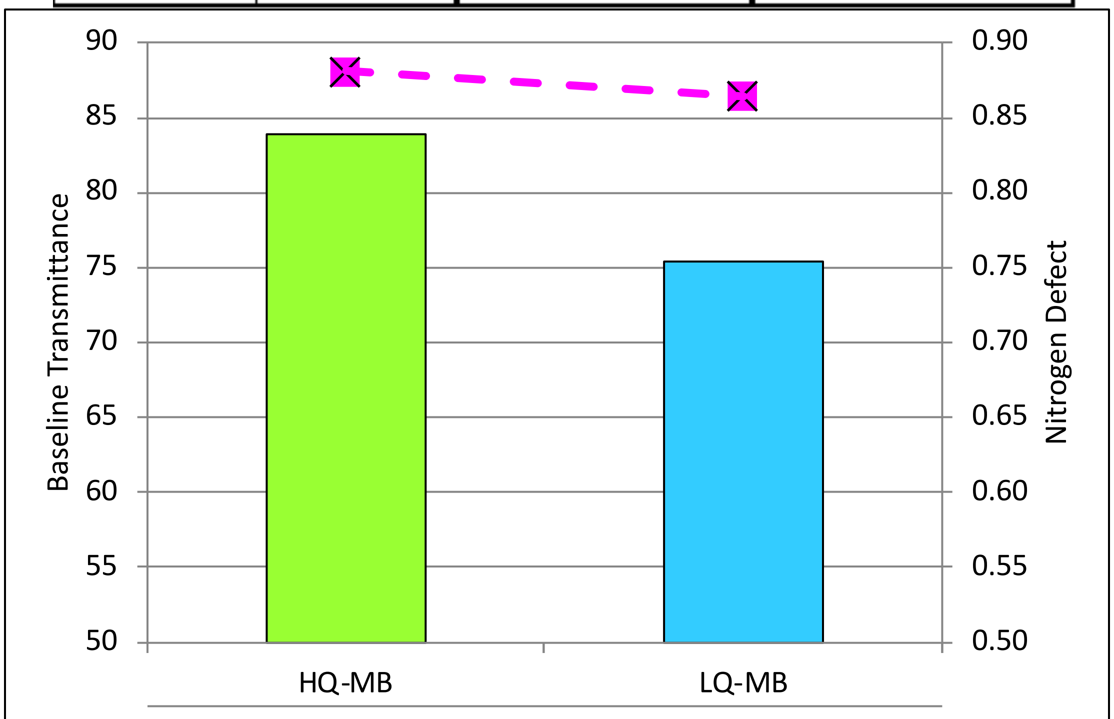


Fig. 8 – FTIR spectroscopy results of 12-22 μm diamond samples

Experimental Results

- Both 12-22 μm HQ-MB and LQ-MB diamond samples show similar concentration of the substitutional Nitrogen defect

- There is a noticeable difference between the baseline transmittance of the two diamond samples, with HQ-MB diamond exhibiting a higher baseline transmittance and therefore, lower concentration of crystallographic defects

Raman Spectroscopy

- ❖ Macro Raman spectroscopy to complement FTIR spectroscopy
  - ❖ The change in the Raman intensity may be caused by increase in the elastic (Rayleigh) scattering of light from crystallographic defects
  - ❖ More defects such as lattice dislocations would tend to elastically scatter more of the incident beam and reduce the inelastically scattered Stokes or anti-Stokes Raman scattering

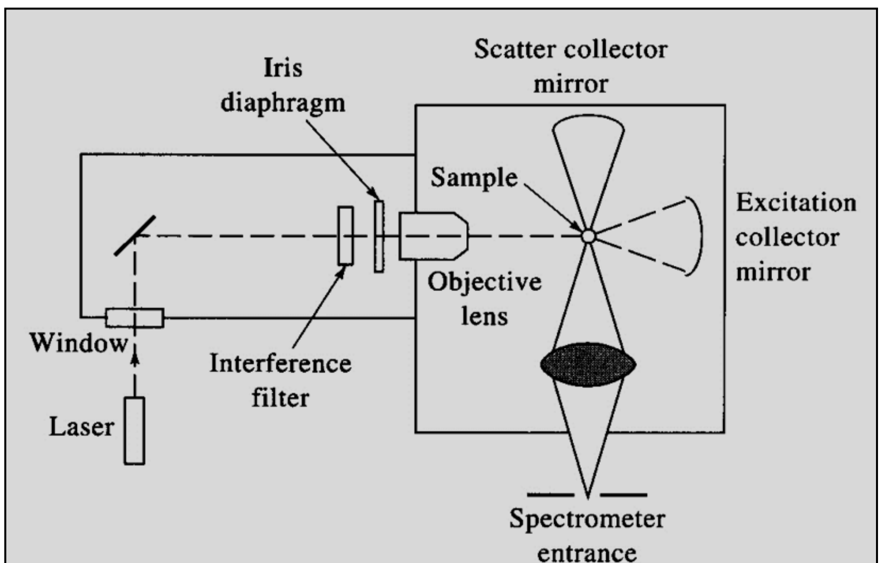
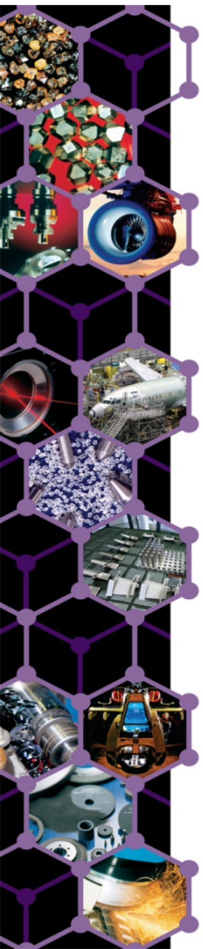


Fig. 9 – Schematic view of Raman spectroscopy

Raman Spectroscopy – Results

- Raman spectroscopy results on different quality µ size metal bond (MB) diamond powder sharing "identical" particle size & shape



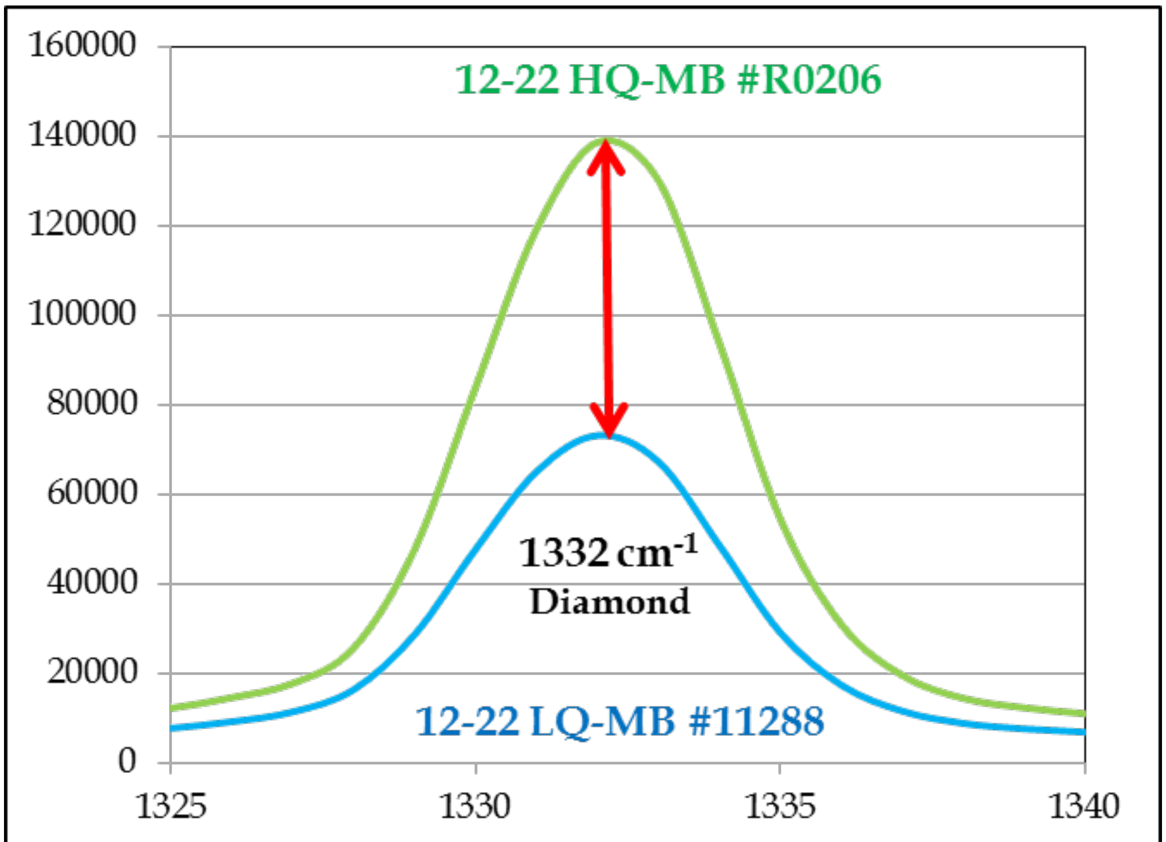


Fig. 10 – Overlay of the Raman diamond peak intensity of 12-22 µm diamond samples

FTIR & Raman Spectroscopy – Results

❖ Correlation between FTIR baseline transmittance & Raman diamond peak

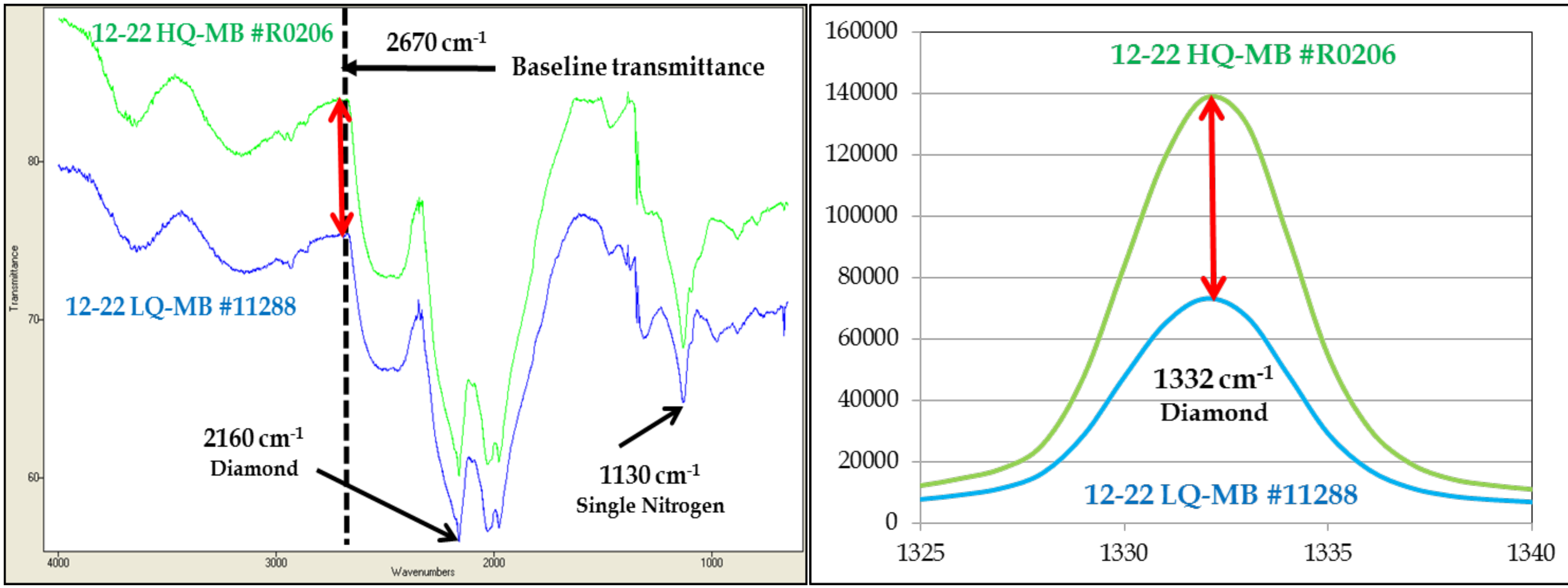


Fig. 11 – FTIR & Raman Spectroscopy results of 12-22 μm diamond samples

❖ ***The macro Raman spectroscopy results on same diamond powders (12-22 μm HQ-MB and 12-22 μm LQ-MB) show that the change in intensity of the diamond peak at 1332 cm-1, correlates well with FTIR base line transmittance***

Crushing Strength Testing of μ Size Diamond

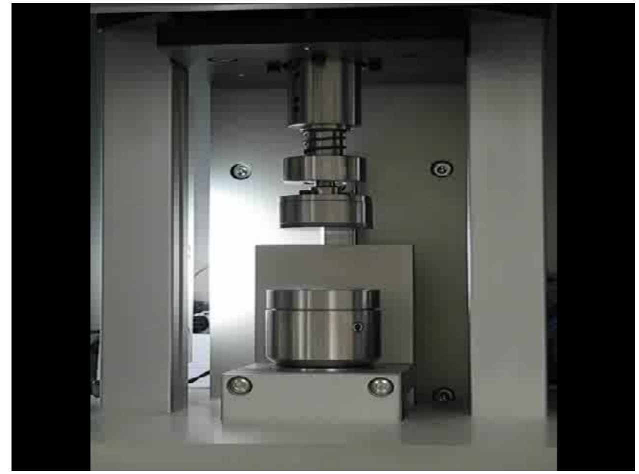


Fig. 12 – Crushing strength apparatus (US Patent 7,275,446)

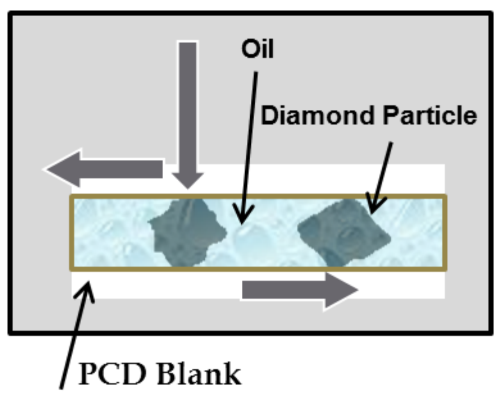


Fig. 13 – Schematic representation of the crushing strength testing

Crushing Strength Testing of μ Size Diamond

❖ Crushing Strength Index (CSI)

CSI = ROS/IOS x 100

IOS: initial number of on-size particles (50-95% of number distribution before crushing)
ROS: resulting number of on-size particles (50-95% of number distribution after crushing)

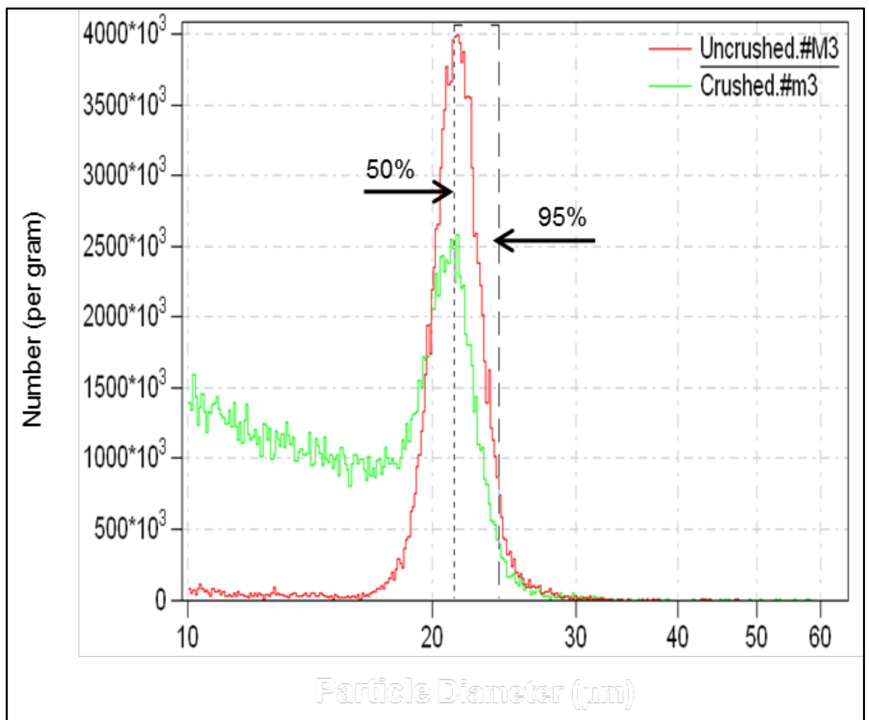


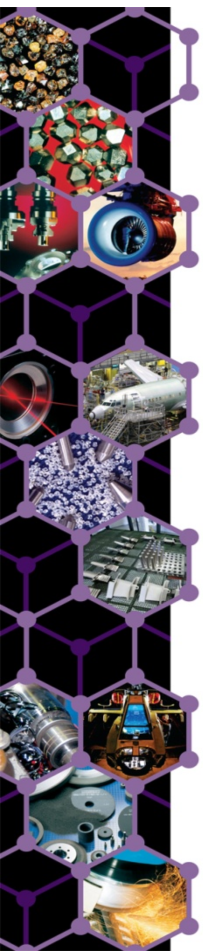
Fig. 14 –PSD overlay of uncrushed and crushed diamond powder (example)

Experimental Results

❖ CSI of different quality μ size metal bond (MB) diamond powder sharing "identical" particle size & shape

Diamond	12-22 HQ-MB & LQ-MB
Compression Force	20 lb.
RPM (piston & cup)	10
Time	10 sec.

Sample ID	Crushing Strength Index (CSI)				
	test #1	test #2	Test #3	average	std. dv.
12-22 HQ-MB	52.5%	60.8%	51.9%	55.0%	5.0%
12-22 LQ-MB	43.6%	41.3%	43.3%	42.7%	1.3%



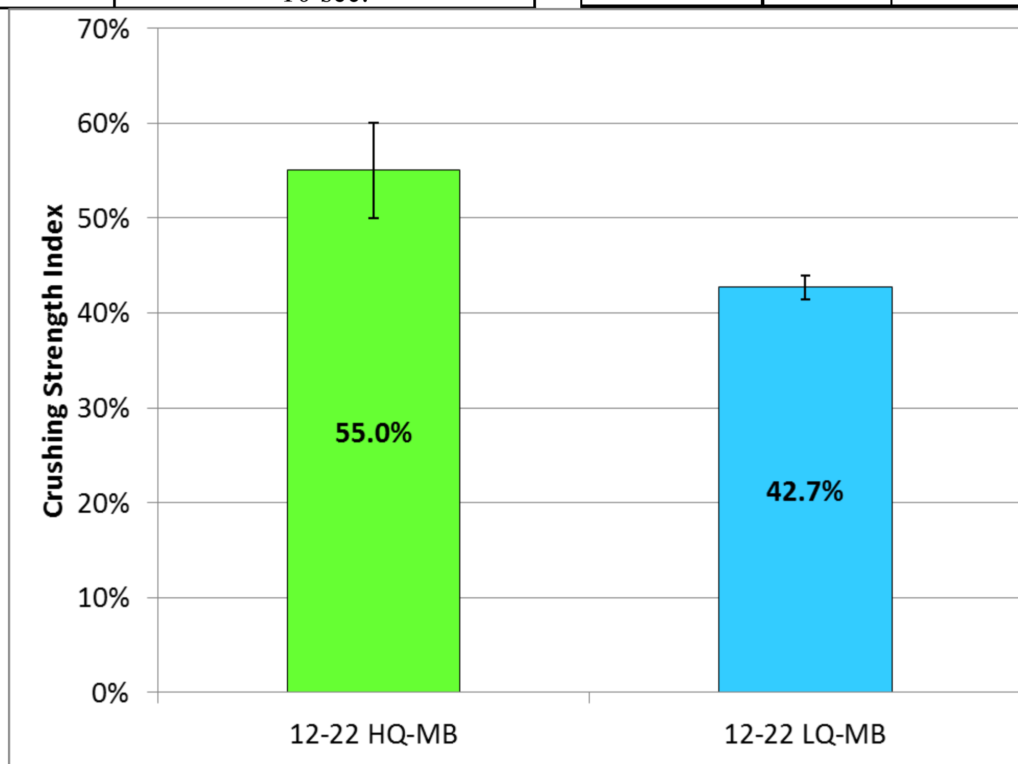


Fig. 15 – Crushing Strength Index (CSI) of 12-22 μm diamond samples

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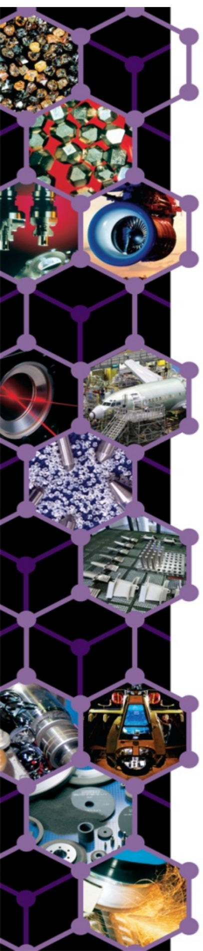
Experimental Results

- FTIR baseline transmittance & CSI of different quality μ size metal bond (MB) diamond powder sharing “identical” particle size & shape



		CSI	BT	SND
R0206	12-22 HQ-MB	55.0	83.88	0.881
11288	12-22 LQ-MB	42.7	75.40	0.864

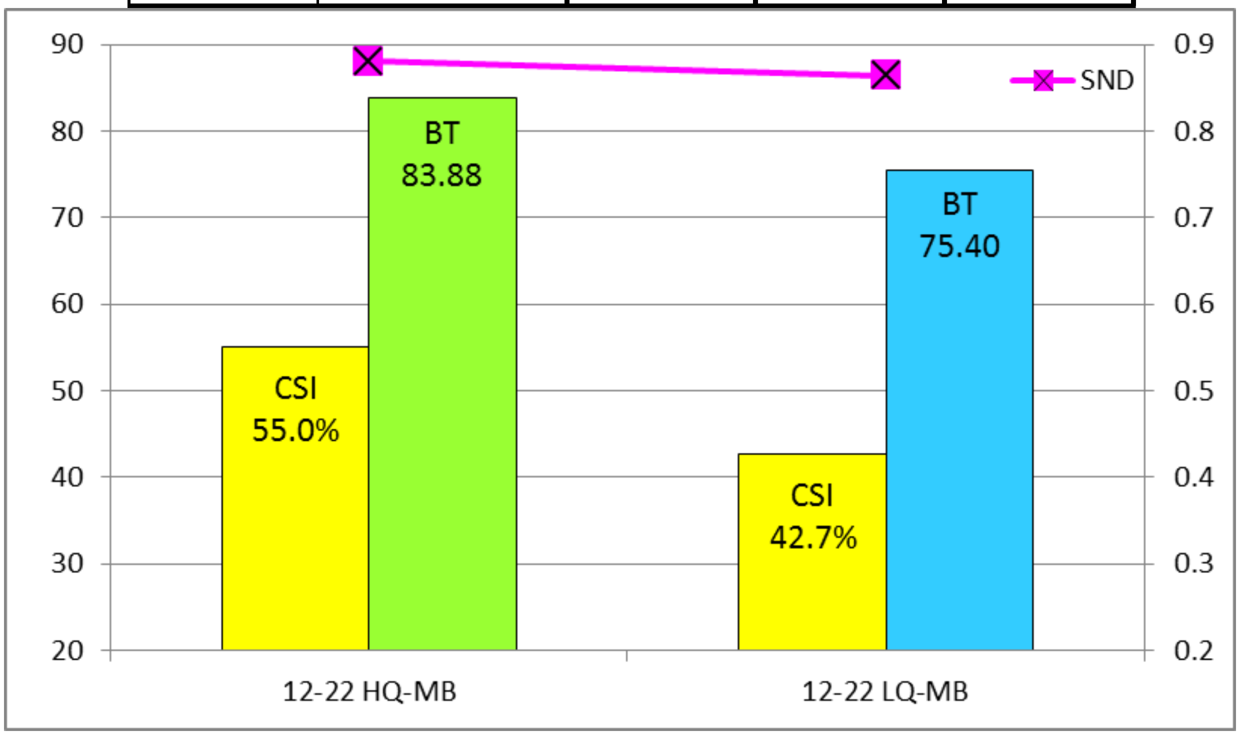


Fig. 16 – Correlation between FTIR baseline transmittance and crushing strength index (CSI) of 12-22 μm diamond samples

Experimental Results

- Experimental results established that the ***FTIR baseline transmittance represents a good measure of the concentration of crystallographic defects***, ***which*** (for a given particle shape and particle size distribution) ***is directly related to the mechanical strength of micron size monocrystalline diamond powders***
  - HQ-MB micron diamond powder exhibits higher FTIR baseline transmittance (BT), which indicates lower concentration of crystallographic defects. Mechanical strength expressed as crushing strength index (CSI) is higher
  - LQ-MB micron diamond powder exhibits lower FTIR baseline transmittance (BT), which indicates higher concentration of crystallographic defects. Mechanical strength expressed as crushing strength index (CSI) is lower

Experimental Results

❖ Different μ size diamond powder types sharing similar (?) size

Sample ID	Mesh size diamond powder feed type
30-40 μm RB1	Resin bond diamond
30-40 μm RB2	Resin bond diamond
30-40 μm RB3	Resin bond diamond
30-40 μm LQ1-MB	Low quality metal bond diamond
30-40 μm MQ1-MB	Medium quality metal bond diamond
30-40 μm HQ1-MB	High quality metal bond diamond
30-40 μm HQ2-MB	High quality metal bond diamond

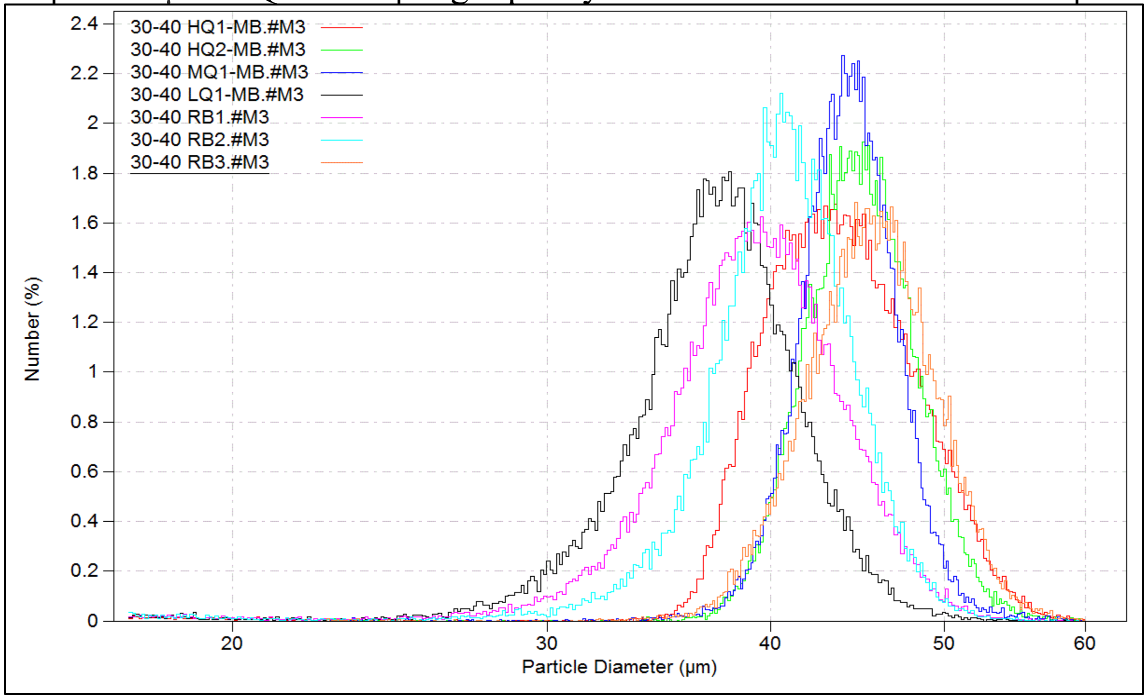


Fig. 17 – PSD overlay of 30-40 μm diamond samples

Experimental Results

❖ FTIR spectroscopy results on different μ size diamond powder types

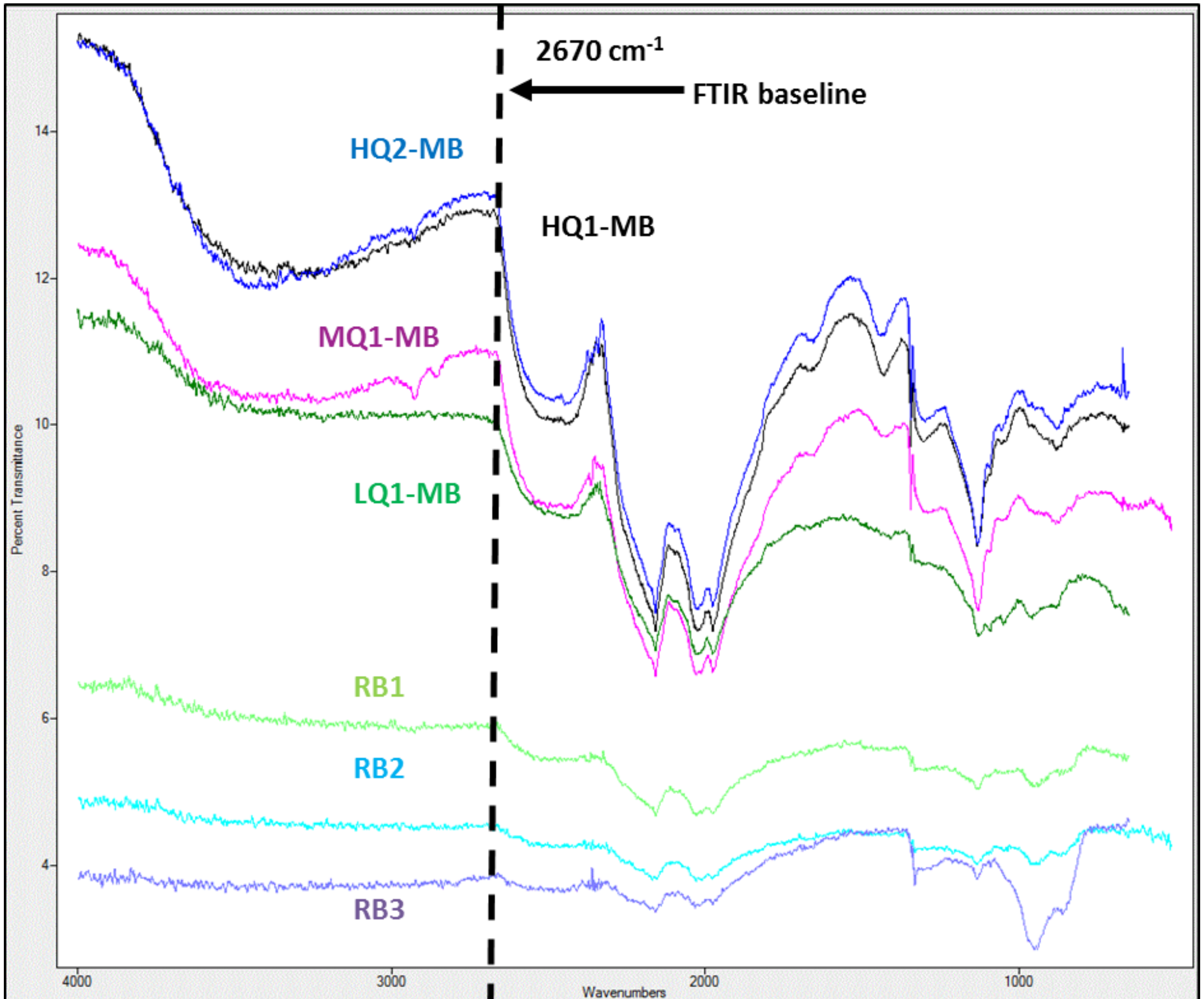
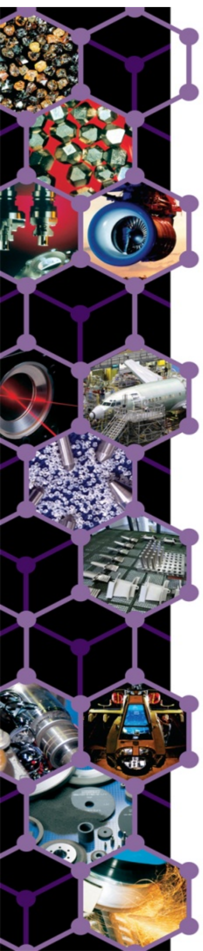
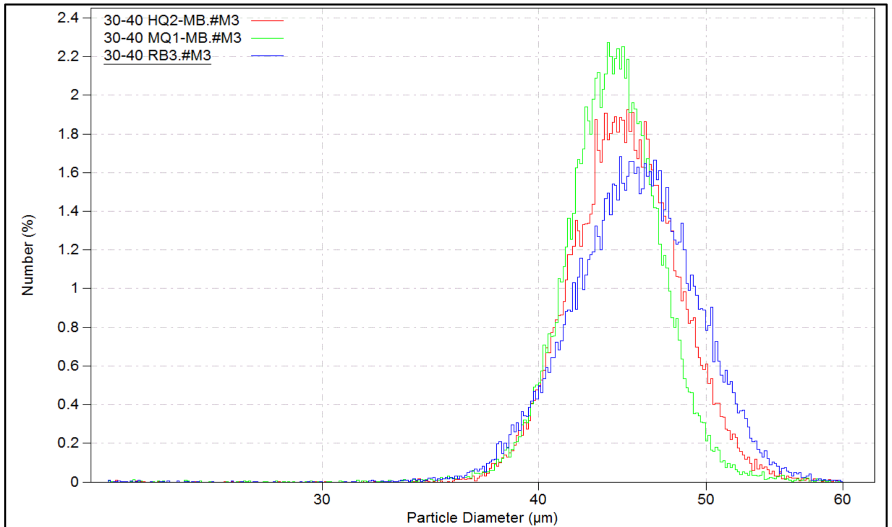


Fig. 18 – Overlay of FTIR spectra of 30-40 mm diamond samples

Experimental Results

- Different μ size diamond powder types sharing "similar" particle size & shape





Particle Shape Data	30-40 HQ2-MB	30-40 MQ1-MB	30-40 RB3
Total Particle Count	4677	4895	4761
Average Aspect Ratio (Mean)	0.724	0.711	0.718
Number Particles with AR < 0.5	139	153	141
Number Particles with AR < 0.5 (%)	2.97%	3.13%	2.96%
Particle Size Data Equivalent Spherical Diameter (ESD)	30-40 HQ2-MB	30-40 MQ1-MB	30-40 RB3
5%	34.88	33.75	33.86
50%	40.25	38.74	40.86
95%	46.21	44.973	49.07
99.9%	52.97	53.63	59.98
Max Particle	55.21	61.65	68.44

Fig. 19 – PSD overlay of 30-40 mm diamond samples

Experimental Results

❖ FTIR spectroscopy results on different μ size diamond powder types sharing "similar" particle size & shape

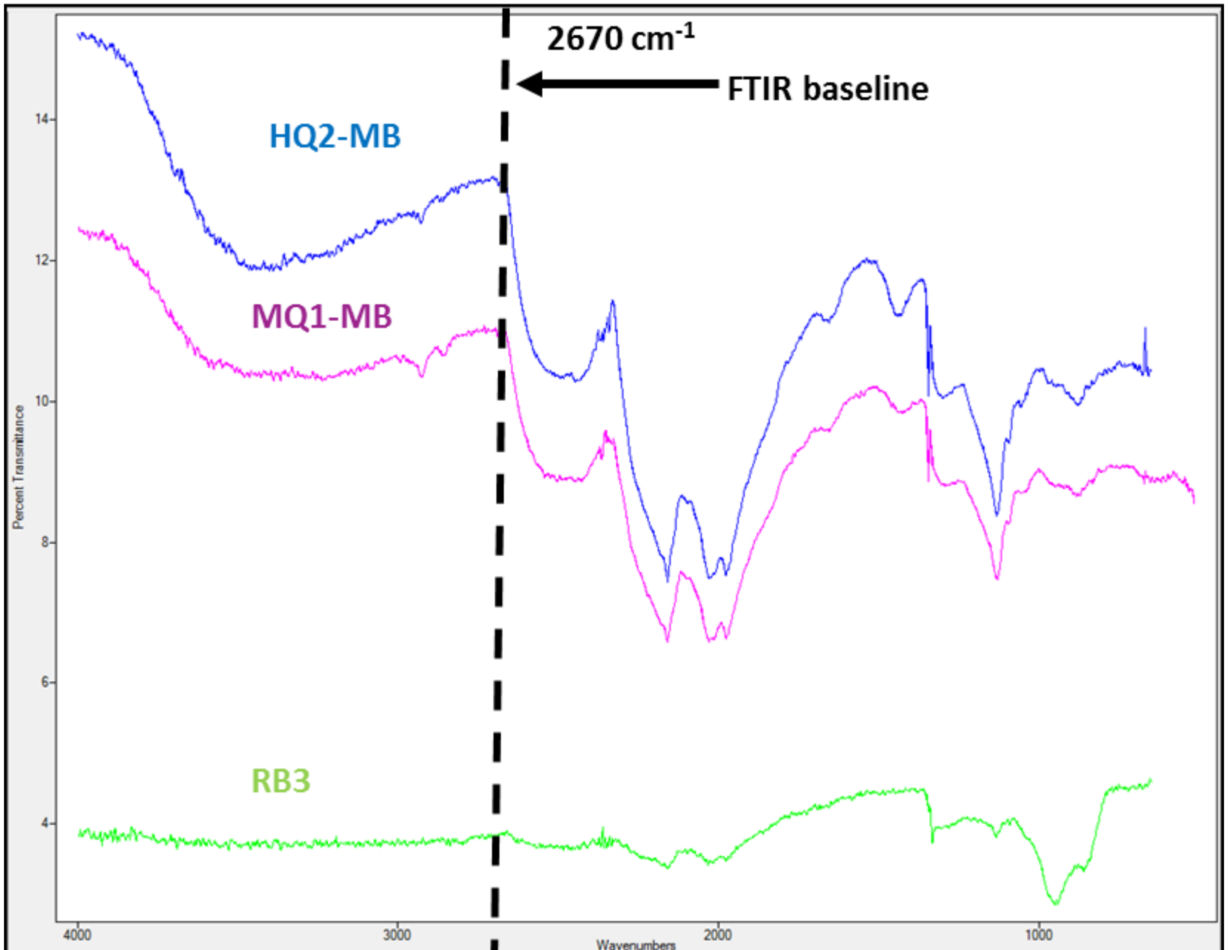


Fig. 20 – Overlay of FTIR spectra of 30-40 μm diamond samples

Experimental Results

❖ CSI of different μ size diamond powder types sharing "similar" particle size & shape

Diamond	30-40 RB3; MQ1-MB & HQ2-MB
Compression Force	10 lb.
RPM (piston & cup)	10
Time	20 sec.

Sample ID	CSI (%)				
	trial 1	trial 2	trial 3	Average	Std. Dev.
30-40 RB3	36.4	37.3	36.8	36.8%	0.5%
30-40 MQ1-MB	46.2	44.8	39.9	43.6%	3.3%
30-40 HQ1-MB	49.6	44.2	49.5	47.8%	3.1%

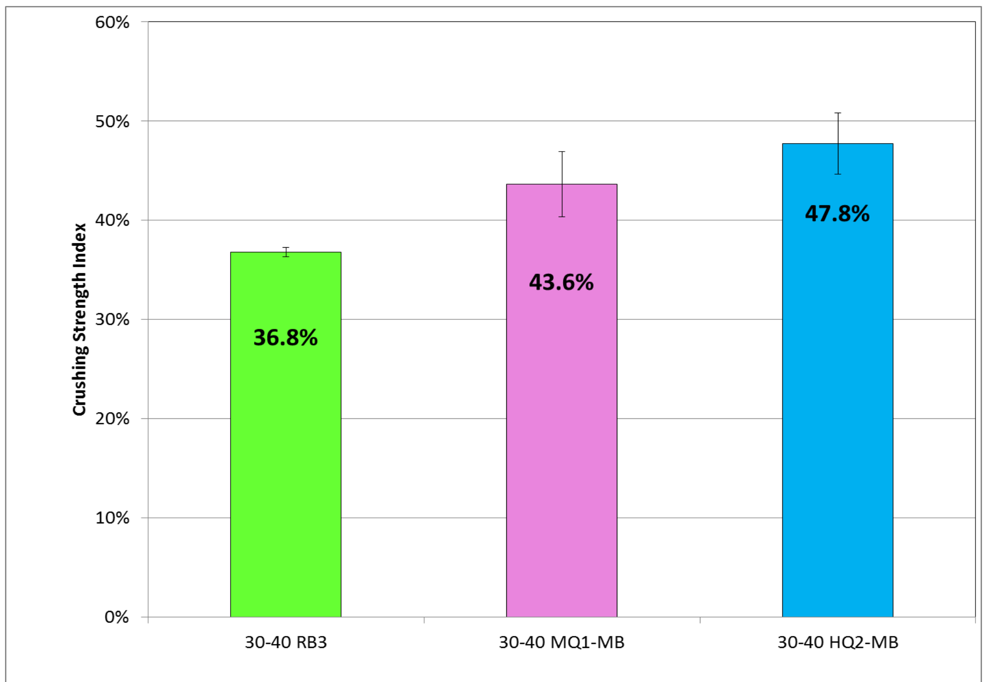


Fig. 20 – Crushing Strength Index (CSI) of 30-40 μm diamond samples

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Summary

- ***The objective of this work was to investigate the correlation, between the concentration of crystallographic defects of micron size monocrystalline diamond powders and their mechanical strength***

- Experimental results showed that ***the FTIR baseline transmittance of micron size monocrystalline diamond powders represents a good measure of the concentration of crystallographic defects*** (residual crystal growth defects) ***which*** (for a given particle shape and size distribution) ***is directly related to their mechanical strength***, expressed as crushing strength index (CSI)

Conclusions

- ***High quality metal bond micron diamond powder*** (produced from high quality mesh diamond powder feed), ***exhibits increased FTIR baseline transmittance***, which indicates ***low concentration of crystallographic defects*** and, consequently, ***high mechanical strength***
- ***Low quality metal bond micron diamond powder*** (produced from low quality mesh diamond powder feed), exhibits ***lower FTIR baseline transmittance*** which indicates ***higher concentration of crystallographic defects*** and, therefore ***lower mechanical strength***
- ***Resin bond micron diamond powder*** (produced from resin bond mesh diamond powder feed), exhibits ***lowest FTIR baseline transmittance***, which indicates ***highest concentration of crystallographic defects*** and, accordingly, ***lowest mechanical strength***

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Thank you!

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