

The following 8 pages copied from H. Tracy Hall's Scientific Journal shows the beginnings of an intensive experimental effort to develop marketable Sintered Diamond (PCD) products. The experimental record ultimately filled 200 or so pages.

SINTERED DIAMOND

17 May 1968 H.J. Hall - Run #1

a graphite tube (grade A GSR) ~~2 1/4~~ " 3/16" O.D. by ~.020" thick wall by ~ 1/4" L with ~.040" thick x 3/16" D graphite end disks was packed with Allied Chem Co. Diamond Powder (explosively formed variety). No end disks .010" thk, hard steel current rings. GR voltage control on, vars 140/160 setting (2.50 open ckt volts); 8000 psi oil.

15 sec	330 a	x	2.15 v	
30	350		2.14	
60	360		2.13	= 766w.
3 1/2 min	353		2.14	= 755
7	"		"	
9	"		"	

Exam: Diamond powder was "sintered" into a compact mass of moderate strength. Its fracture is conchoidal. It

is jet black in color. Temp. was ~1900°C.

Run #2/17 May 1968 - same as #1 above except natural diamond powder used (Michael Werdiger, Inc. 1-5 micron grade #3)

vars 140/160; 8000 psi oil

15 sec	200 a	x	2.30 v	= 460w
30	190	x	"	
60	180	x	"	
~2 min	" burnout "			

Exam: poor elect contact at one end. Pyrophyllite was whitered at this end but not at the other. at this ^{hot} end an excellent diamond compact was made. It readily

scratches cemented tungsten carbide

Run #3/17 May 1968 - Cell arrangement like #1/6 May 1968 except current disks are .005" thick. Natural diamond powder again. 8000 psi oil, 140/160 vars.

15 sec	380 amp	x	2.12 v	
30	400		2.10	= 840w
60	"		"	
120	395		"	830w

Exam: Good quality, "sintered" diamond compact obtained.

It is white in color and

reminds me of some of the polycrystalline, hard BN I have made.

Try higher Temp., or longer time for still better product. Diamond cleaves freely from graphite cylinder. No adhesion.

"sintered" diamond
(Allied Chemical)
~1900°C

"sintered" diamond
natural diam. powder.

sintered diamond
natural
~2100°C

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17 May 1968 H. Tracy Hall Run #4 - Same as

no. 3 today but higher temp. Variacs set at 150/190 (open

circuit volts = 2.70. oil P = 8000 psi

5 sec	~280 amp	x ~2.4 volt	= 674 watt
15	410	2.31	946
30	460	2.25	1032
60	475	2.24	1065
90	"	"	"
120	480	2.23	~2750°C 1070 off

Exam: Too hot. Diamond was destroyed and turned into a black, soft, graphite-like substance. It stuck to graphite cylinder.

Sintered natural diamond powder ~ 2750°C

Run #5/17 May HTH - Same as #3 Today. Var: 150/120 (open ckt v. = 2.60

5 sec	310 a	2.28 v	= 707 W
15	370 a	2.23 v	826
30	385	2.22	855
60	395	2.21	875 W
90	392	2.21	868 W
120	395	2.21	875 723 W

Exam: Diamond has turned black. It is quite well sintered. It did not adhere to graphite tube. It scratches glass in a "soft" sort of way. I think it is partially converted to graphite. Did not stick to graphite cyl

Sintered Diamond natural ~ 2230°C

Run #6/17 May HTH Same as #3 today. Var 140/200 (open ckt volts = 2.55)

8000 psi oil

5 sec	390 a	x 2.16 v	= 842 W
15	375	x 2.18	= 816
30	372	2.19	= 815 W
60	368	"	806
90	"	"	"
120	"	"	"
180	370	2.18	806 off

Exam: Dense, hard, white compact formed with a little (~15%) black material formed on one side (|| to cyl axis) where heating tube was thin &

Sintered Diamond natural ~ 2040°C

hence hotter than thicker portions of the tube. The compact readily scratches glass, but ~~not~~ scratches carbonyl with difficulty. Material ~~does~~ did not adhere to graphite

FIXED NITROGEN ON FARMLAND FORMED IN PLACE

20 May 1968. I have been wondering if it would be economical to "fix" nitrogen of the air "in situ" (so to speak) on farm land by spark discharge just behind a cultivator blade that parts the ~~low~~ soil (soil being pulled by a tractor) and then allows the soil to quickly enfold the oxides of nitrogen formed by the spark discharge as the cultivator blade moves along. This idea may be quite practical and also patentable. HTH

Artificial Diamond

20 May 1968 H. Tracy Hall. Run #1 Same as #3/17 May 1968 17

except a thin disk of NaN_3 placed at one end of the compacted, natural diamond powder (1-5 micron) cylinder.

It is hoped that the NaN_3 will provide nitrogen which hopefully, will improve the "sintered diamond" product. 8000 psi oil; variances set at $\underline{140/160}$. Exam: A moderate

15 sec	370 a	x	2.14 v	=	
30	375	x	2.13	=	800w
60	380		2.12		
90	372		2.13		
120	370		2.13	=	790W+off

strong cylinder of white "sintered" diamond was made

near the ~~the~~ NaN_3 end the cylinder was grayish-tan color and was weaker than the opposite end of the diamond cylinder. The graphite plug adjacent to the NaN_3 is a very shiny black color. The NaN_3 did not improve the product.

sintered diamond, natural NaN_3 added. $\sim 2010^\circ\text{C}$

21 May 1968 H. Tracy Hall - Run #1 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ decomposes when heated at atmospheric pressure to give N_2 , H_2O , & Cr_2O_3

This run is like the run above (on this page) except a little $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was used instead of NaN_3 . oil P=8000psi; var 140,

5 sec	370 a	x	2.13 v	=	789W
15	385		2.11		
30	390		2.11		
60	385		2.11		
90	375		2.12		
120	372		2.12	=	789W
150	368		2.12		
180	"		"		

Exam: $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was replaced with a black, crystalline substance. The diamond powder near the $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ did not cement together. The other

end of the diamond powder, however, did form a moderately strong compact. The black crystalline substance may be new.

sintered diamond, natural $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ added. $\sim 2000^\circ\text{C}$

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21 May 1968 H. J. Hall Run #2 - Cell arrangement

is the same as run #1/6 May 1968. Sample is $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

oil P = 8000 psi ; variacs set at 140/160 (2.50v open ckt.)

 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

5 sec	380 a	2.11 v	= $\frac{800}{765}$ W
15	387	2.11	
30	390	2.10	
60	387	2.10	
120	380	2.11	800 w
180	378	2.11	off

Exam: Same black, crystalline material made as in run #1 today. Parts of sample had a greenish tinge

22 May 1968 H J Hall - Run #1 same as # 3/17 May 1968

Natural diamond powder - 8000 psi , Var 140/160

5 sec	200 A	2.30 v	= 460 W
15	220 A	2.27	500
45 30	385 A	2.10 v	810
1 min	398	2.09	832 W ~ 2080°C
2	390	2.09	815
4	385	2.09	805
8	"	2.08	800 ~ 2030°C
12 min	385	2.07	796 ← off abruptly

Exam: A dense, hard "sintered" diamond compact weighing .068 g (.34 carat) was made. It readily scratches WC. I think its wearing qualities may not be as good as I would like. A portion of the sample on one side turned black. (The central hole was off center & consequently the thinner wall on one side made the temperature higher there.)

23 May 1968 H J Hall - 3/8" cubic anvil placed in press (200 ton cubic)

A = steel current ring 5/16" O.D.
x 7/32" ID x 3/32" L.

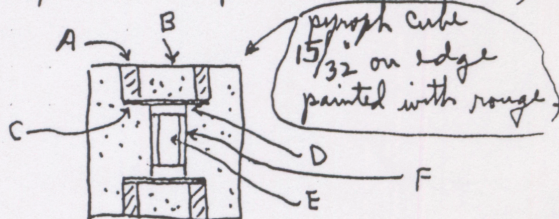
B = pyrophyllite cyl 7/32" D x 3/32" L

C = Mo disk 5/16" D x .005" thick

D = AGSR graphite disk 1/32" thk x .155" D

E = sample

F = AGSR graphite cyl. .155" OD x 5/32" L x .100" ID



Sample for this run is diamond powder (1-5 μ Michael Wardiger)

oil P = ~~8000~~ 6000 psi ≈ 85 lb (if III-V Bi trans = 88 lb)

time	var	volts	amps	watts
1 min	70/120	1.10	200	220
2	85/120	1.31	245	321
4	95/120	1.45	275	390
5	105/120	current fell at this setting		
6-7	"	1.61	265	427
8	7	current started to rise - shut off power		

~ 970°C

~ 970°C only

sintered diamond powder

"sintered" diamond

85 lb

23 May 1968 H. Tracy Hall - Run #1 cont'd

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Exam: The sample has turned ~~gray~~^{gray}-black in color as though the temperature was too high. The current had started to rise rather rapidly at 8 minutes time and probably was an indication that "graphitization" of the diamond powder was taking place. However, the pyrophyllite "whitening" was small and from this, I would not have judged the temperature to have been high enough for graphitization.

The product is moderately strong and scratches carbonyl.

From previous runs I would estimate a various setting of 150/120 (743 watts; 322 amps x 2.30 volts) to give

a temp of $\sim 2200^{\circ}\text{C}$. at 85 kb it "should" take about 2200°C to graphitize diamond. I'm certain that

I was nowhere near this temperature^{in today's run #1.}. What's going on?

Could it be possible that there is a ~~pressure~~ region where increasing pressure lowers the temperature required for graphitization of diamond? The diamond cylinder split, on opening the cell, into two equal length cylinders and graphitization was high on the circular surfaces where the break occurred. ← Perhaps this was just

intrusion of graphite cylinder. - I just had a thought. The starting material (diamond powder) is ^{quite} rather gray in color.

Perhaps it has not sintered at all in this run. It whitens up on sintering & then darkens again on graphitization.

23 May 1968 H. Tracy Hall. Run #2. same as #1 today

oil P = 6000 (~ 85 lb). Variables set at 140/120

5 sec	360a x	2.1V	755
15	370	2.07	
30	375	2.07	= 776W
1 min	375	2.07	
2 "	377	2.06	
3 "	378	2.06	778W

Exam: SUCCESS !!!

0.16 carat (.0325 g.) of tough, strong (holds sharp cutting edge) "self-bonded" or "sintered" diamond was made!

It was heated in conc. $H_2SO_4 - KNO_3$ solution for $\frac{1}{2}$ hr. This removed a graphite skin but apparently did not affect the diamond cylinder. This material is much superior to anything previously made. It scratches cemented tungsten carbide (8% Co - WC) with extreme ease, leaving a clean cut trough without dulling the diamond cutting edge. The making of this material is an important development! The process should be patentable and the use of "self-bonded" or sintered diamond powder will soon be within a few years spread throughout the world! It will now be possible to make diamond "shapes" and relatively large components of pure self-bonded diamond. There will be a multitude of uses for this material. This material should have a value near \$20⁰⁰ per carat. This makes it a product of immediate practical value. The profit margin for making this should be higher than for manufacturing diamond grit.

SUCCESS !!!

~ 1870°

~ 1870° C

± off abruptly

self-bonded diamond powder

Artificial Diamond

Run #2/23 May H. Tracy Hall - Same as #1 today except

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Pt-Pt 10% Rh thermocouple (.010" diam wires) inserted in center of sample to get an idea of the temperature.

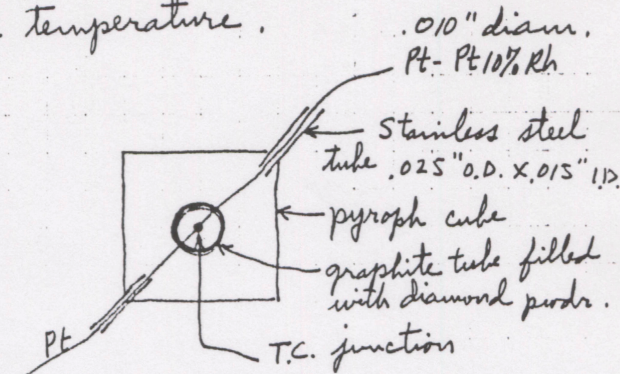
3/32" on edge pyrophyllite cube

painted with Fe₂O₃

6000 psi oil (~ 85 lb if Pi)

III-V trans is taken as 88 kbar.

Room temp = 24.2°C (ref junction)



time	variacs	volts across sample	x amps through sample	= watts	T.C. mv. reading	corr mv. (mv. temp. added)	Temp °C
0 min	5/120	-	-	-	.15	.29	50°C
	36/120	.65	x 100	= 65	.856	1.00	148
	50/120	.84	140	118	1.69	1.83	247
	-	1.00	170	170	2.67	2.81	354
7 min	72/120	1.15	200	230	3.90	4.04	482
	82/120	1.30	230	299	5.57	5.71	647
10 min	92/120	1.44	260	374	7.67	7.81	753 843
	101/120	1.54	280	430	9.31	9.45	990
	105/120	1.65	300	495	11.12	11.26	1140
	118/120	1.75	320	560	13.15	13.29	1313
	125/120	1.85	340	629	15.24	15.38	1487
	129/120	1.90	350	665	16.28	16.42	1576
	135/120	1.98	360	713	17.35	17.49	1667
20 min	140/120	-	-	-	17.14	erratic & falling	
21	"	2.06	360	740	16.85	and falling with time	
22	off				~ 1750°C		

mv. readings taken with Rubicon potentiometer. Temperature given has not been corrected for any pressure effect.

Exam: after run: T.C. had reacted with graphite tube to form a little diamond. A "sintered" diamond product was obtained but it was not bonded as well as run # 2 today. Sample appeared to have not been quite as hot as in run # 2. I think the T.C. carries away some heat. also max wattage above is not quite as high as in run # 2 today

"Self-Bonded Diamond Powder" Temp. calib.

Temperature calibration data from
run #3/23 May 1968 previous page

$\frac{7}{32}$ " cube ; $\frac{3}{8}$ " anvils ; 6000 psi oil
(150 tons of thrust) = 85 kb (if Bi 3-5 trans = 88 kb)

See p. 18 (run #1/23 May) for
heater-sample tube
dimensions etc.

