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Sintered Diamond Compacts with a Cobalt Binder

Abstract. *Diamond powder can be successfully cemented with cobalt. At 62 kilobars the sintering occurs over the temperature range from 1570° to 1610°C. The maximum microhardness of the compact (> 3000 kilograms per square millimeter on the Knoop scale) is obtained with a mixture of 20 percent cobalt (by volume) and a diamond particle size of 1 to 5 micrometers.*

Recently Stromberg and Stephens (*1*) and Hall (*2*) have reported the synthesis of a polycrystalline diamond compact, carbonado, at high pressures and temperatures. We have discovered a method for sintering diamond powder (also at high pressures and temperatures) in which cobalt is used as a binder, analogous to its role in cemented tungsten carbide. In comparison with synthetic carbonado (*1, 2*), it appears that this new material is easier to make and can be made in larger, more nearly uniform specimens. It is harder than cemented tungsten carbide and thus may be a useful replacement in many scientific and industrial applications. We describe here the sintering conditions used and some of the properties of the cemented compacts obtained.

The starting materials were commercially available diamond powder of either 0- to 2-μm, 1- to 5-μm, or 10- to 20-μm size and cobalt powder of 0- to 5-μm size and 99.9+ percent purity. The powders were dried, weighed, and mixed and then packed into tantalum containers for sintering. Pressure was generated in a piston-cylinder apparatus with appropriate modifications to allow us to work in the 60- to 65-kb range (*3*). The samples were heated by means of an internal graphite heater, and the temperature was monitored with a Pt–Pt (10 percent Rh) thermocouple. The electromotive force of the thermocouple was corrected for the effect of pressure (*4*), and the correction corresponded to an addition of 15°C to the temperature values obtained directly from the standard tables.

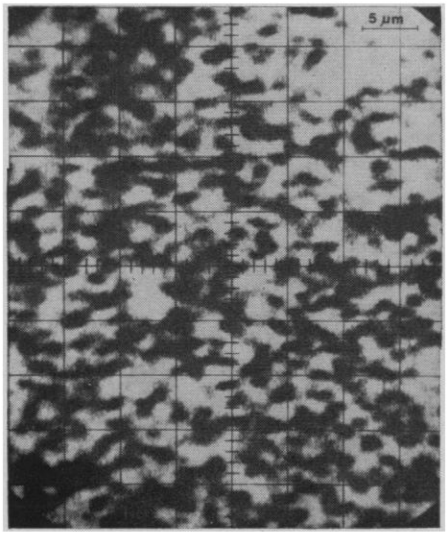

Fig. 1. Electron microprobe photograph of a sample containing 20 percent cobalt (by volume) and 1- to 5-μm diamond grains. The darker areas are cobalt, and the lighter ones are diamond.

We chose 62 kb as a convenient pressure at which to work and then determined experimentally the temperature range in which the sintering occurred. Samples had to be heated above the cobalt-diamond eutectic temperature, but not so high as to graphitize the diamonds. At 62 ± 1 kb the samples showed partial graphitization when heated above 1610° ± 10°C. This temperature is well below 1700°C, which is the diamond-graphite equilibrium temperature at 62 kb reported by Bundy *et al.* (*5*) and calculated by Berman (*6*). Recently Haygarth (*7*) has used a piston-cylinder apparatus similar to ours to determine a diamond-graphite equilibrium point at 51.8 ± 0.2 kb and 1335°C. Using this point and Berman's slope (*6*) of 30.4°C/kb, one can calculate an equilibrium temperature of 1645°C at 62 kb, which is much closer to the value that we find. Both Stromberg and Stephens (*1*) and Hall (*2*) report work on the sintering of diamonds at higher temperatures and at pressures close to those used in our study, but, since no cobalt was present in either case to dissolve and reprecipitate the metastable diamonds as stable graphite, higher temperatures could be used. Below 1570° ± 10°C, which is apparently the cobalt-diamond eutectic temperature at 62 kb, no strong compacts were formed.

Therefore, 1590°C and 62 kb were chosen as the sintering conditions. The samples were maintained at these conditions for about 20 minutes and were then cooled to room temperature in about an hour. As the samples were cooling, the pressure was slowly released in order to minimize the residual strains in the product but care was taken so that the samples were always kept within the diamond stability region.

The sintered samples were grayish, metallic-looking, slightly ferromagnetic cylinders, ~ 6.3 mm in diameter and 2.5 to 9.0 mm long. Their properties were determined by x-ray diffraction, scanning electron microscope, electron microprobe, density, and Knoop microhardness measurements.

The microhardness results are shown in Table 1 for various sintered samples.

The values are averages for indentations over one or more polished cross sections of a given sample. The relatively large deviations are a result of the difficulty associated with measuring the small indentations. The indentations were made with a force of 2 kg and were about 100 μm in length. Since the grain size of the samples is much smaller than 100 μm, these values are believed to reflect the hardness of the compact and not the hardness of the diamonds only. For comparison, the Knoop microhardness of diamond is 7000 kg/mm^2 (*8*), cubic boron nitride has a value of 3800 kg/mm^2 (*9*), and cemented tungsten carbide has a value which varies from 1400 to 1800 kg/mm^2 (*8*), with the value depending on the amount of cobalt binder present. We tested two samples of cemented tungsten carbide and the results are also shown in Table 1.

Table 1. Knoop microhardness of various samples. The amounts of the cobalt and nickel binders are percentages ± 1 percent (by volume).

Starting mixture	Knoop microhardness (kg/mm^2)
Cobalt (20%), diamond (1 to 5 μm)	3000 ± 300
Cobalt (20%), diamond (1 to 5 μm)	2900 ± 300
Cobalt (20%), diamond (0 to 2 μm)	2900 ± 300
Cobalt (20%), diamond (1 to 5 μm, 60%), graphite (20%)	2800 ± 400
Cobalt (20%), diamond (10 to 20 μm)	2700 ± 100
Cobalt (25%), diamond (10 to 20 μm)	2200 ± 200
Cobalt (16%), diamond (1 to 5 μm)	2100 ± 200
Cobalt (12%), diamond (1 to 5 μm)	1600 ± 100
Nickel (20%), diamond (1 to 5 μm)	2200 ± 200
Tungsten carbide, cobalt (15%)	1700 ± 50
Tungsten carbide, cobalt (20%)	1500 ± 50

The samples containing 20 percent cobalt (by volume) could be polished on fine-grained diamond wheels to a good metallic luster. Microscopic examination showed no signs of any diamond particles torn from the matrix during polishing. One could see the polished surfaces of the individual diamond grains, an indication that they were indeed bound by the cobalt. Other indications of the strength of the material included the fact that the polished surfaces could not be scratched with a tungsten carbide scribe and also that the Knoop diamond indenter required replacement after about 20 indentations into these surfaces.

Examination with the electron microprobe and scanning electron microscope showed that the diamond particles were well distributed in the cobalt matrix and that some diamond grain growth had occurred. A microprobe photograph of a sample containing 20 percent cobalt and a 1- to 5-μm diamond powder is shown in Fig. 1. There were some diamond grains with diameters as large as 6 to 8 μm in the samples in which the starting diamond powder was in the 1- to 5-μm size range. Also many diamond grains appeared to be fused together into clusters. These results suggest that the cobalt cleans the diamond surfaces of any adsorbed gases that might prohibit or retard grain growth or fusion, thereby making unnecessary the surface cleaning and degassing procedures described by Stromberg and Stephens (*1*). The grain growth very likely occurs when some of the diamond particles dissolve in the cobalt and then reprecipitate on other grains, an indication that the molten cobalt wets the diamond surfaces.

As can be seen from Table 1, the optimum amount of cobalt for "cementing" the diamond powder is 20 ($\pm$ 1) percent (by volume). Microscopic examination of samples with less cobalt content showed that regions of unwet diamond particles existed even after sintering for 2 hours. This result indicates that 20 percent cobalt is needed to wet all of the diamond surfaces. Samples with more than 20 percent cobalt are softer. An attempt to substitute nickel for cobalt under identical sintering conditions also led to a somewhat softer material.

If diamond particles of sizes 1 to 5 μm and 0 to 2 μm are used, the compacts are harder than those that result from the use of the 10- to 20-μm particles. In one experiment we replaced about one quarter of the 1- to 5-μm diamond powder with graphite powder and it was entirely converted to diamond under the sintering conditions, with the result that there was a large and nonuniform increase in the diamond grain size. It appears that more graphite can easily be substituted for diamond but that the resulting compacts may be a little softer as a result of the larger and less uniform diamond grain size.

The x-ray diffraction patterns of the samples with cobalt showed, besides diamond, the presence of only face-centered cubic or β-cobalt which is stable above 450°C at atmospheric pressure (*10*). No hexagonal close-packed or α-Co reflections were present. The density of each sample was found to be at least 90 percent of the theoretical density, and most samples had densities greater than 99 percent of the theoretical density.

In order to determine how well our new material would perform as a cutting tool and as a truer for grinding wheels, we carried out the following test. We weighed both our compact and a silicon carbide, resin-bonded grinding wheel and used the compact to turn off some silicon carbide from the grinding wheel. We then reweighed both and determined a ratio of the weight losses. For a comparison, we also tested a commercial diamond truer and a piece of tungsten carbide under identical conditions. The weight-loss ratios for the diamond truer, our compacts with 20 percent Co and 1- to 5-μm diamond powder, and tungsten carbide (10 percent Co) were 18,000:1, 9,500:1, and 1.5:1, respectively. Since the compacts with 20 percent cobalt (by volume) contain only $\sim$ 60 percent diamond (by weight), the compacts perform about 85 percent as well as pure diamond on the basis of a weight for weight of diamond.

In summary, we have synthesized a promising new material which should have commercial possibilities, for example, as a cutting tool or as a truer for grinding wheels. The procedure for its production is relatively simple and is economically feasible since inexpensive diamond dust together with graphite may be used as starting materials.

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Salt Extraction of Soluble HL-A Antigens

Abstract. *Extraction of cultured human lymphoid cells with hypertonic salt solutions (3 molar potassium chloride) resulted in high recoveries of membrane-associated histocompatibility (HL-A) antigens in soluble form with potent activity and marked immunologic specificity. The active principle was purified by preparative acrylamide-gel electrophoresis. Application of the hypertonic salt extraction method is now yielding sufficient HL-A antigen to begin the elucidation of the molecular basis of transplantation individuality.*

The elucidation of the HL-A locus, which governs the major histocompatibility factors in human transplantation, stimulated a search for effective methods of solubilizing the corresponding cell membrane antigens (*1*). Soluble HL-A antigens have a number of applications: (i) for the pretreatment of graft recipients to deceive their immunologic system into accepting foreign tissues, as has been shown for animal systems; (ii) for production and standardization of potent monospecific tissue-typing alloantiserums; and (iii) for clarification of the relation between the HL-A locus and its gene products (*2*).

Several unique aspects make the solubilization of HL-A antigens now amenable to attack. (i) Hosts develop reactivity against foreign transplantation antigens resulting in an array of specific alloantiserums; (ii) HL-A determinants can be rapidly and sensitively detected by their ability to inhibit the cytotoxic reactions of these serums; and (iii) human lymphoblastic cell lines, derived from the peripheral lymphocytes of a normal donor and perpetuated in tissue culture, provide abundant source material with greater amounts of antigen per cell than any other tissue. Thus, there has been a demand for a solubilization method which most effectively utilizes the cell lines to obtain potent inhibitors of specific HL-A alloantiserums.

Exposure to sonic energy is a successful technique for solubilization of transplantation antigens from a variety of cell sources (*3*). Soluble human histocompatibility antigens, obtained by exposure of cells from several cultured lines to low frequency sound, inhibited the cytotoxic reactions of 21 specific alloantiserums in a pattern consistent with the phenotype of the cell line donor (*4*). Although this technique provided as good a yield as any described method (*2*), greater recoveries were necessary to obtain enough antigen for biologic and chemical characterization.

Initial experiments revealed that hypertonic salt extraction with 3*M* KCl alone, or in conjunction with sonication, efficiently solubilized HL-A antigens from cultured lymphoblasts (*5*). We now report the method, yields, and specific activities of soluble HL-A antigens extracted with 3*M* KCl and purified by preparative, discontinuous polyacrylamide electrophoresis.

Table 1. Solubilization of HL-A antigens from cultured lymphoid cells (RPMI 1788).

Sample	HL-A2 (ID$_{50}$ units)*		HL-A7 (ID$_{50}$ units)*		HL-A2 specificity ratio†	Recovery (%)‡	
	Per milligram	Per 10^9 cells	Per milligram	Per 10^9 cells		HL-A2	HL-A7
1	25,000	450,000	9,000	162,000	70	37	29
2	33,000	462,000	5,500	170,500	75	38	31
3	20,000	620,000	5,500	165,000	70	51	30
4	40,000	920,000	11,000	341,000	100	85	64

* The reciprocal of the soluble protein antigen which inhibits cytotoxic antiserums TO 11.30 (anti-HL-A2) and Cutten (anti-HL-A7) at zero cytotoxic units to 50 percent. † Ratio of the concentration of antigen required to inhibit an indifferent antiserum compared to that required for a homologous antiserum. ‡ The percentage of recovery is equal to (AD$_{50}$/CE$_{50}$) × 100.

The source materials were cell line RPMI 1788, derived from the peripheral lymphocytes of a normal donor and propogated in culture for 2 years (*6*), and cell line WI-L2 initiated from a spleen which had been removed from a patient with hereditary spherocytic anemia, and perpetuated in culture for 3 years (*7*). Absorption typing, and the direct cytotoxic reactions of 21 specific alloantiserums were used to establish the phenotype of the peripheral lymphocytes of the RPMI 1788 donor (*4*). The phenotype of the RPMI 1788 cultured cells, as determined by absorption and by fluorochromasia techniques (*8*), was identical to that of the donor's peripheral lymphocytes. On the other hand, the WI-L2 phenotype, as ascertained by testing the cultured cells with the absorption and fluorochromasia techniques, could not be confirmed with the donor's peripheral lymphocytes since he was unavailable.

Up to 50×10^9 dispersed, cultured human lymphoid cells were suspended in phosphate-buffered saline containing 3*M* KCl, *p*H 7.4 (20 ml of solvent per 10^9 cells) and gently agitated for 16 hours at 4°C on an Eberbach shaker; they were then centrifuged at 163,000*g* (average) for 1 hour (maximum, 235,000*g*). During dialysis (24 hours) against three changes of 200 volumes of saline, a gelatinous material formed, which comprised 18 percent of the ultracentrifugal supernatant and contained primarily DNA. This gelatinous fraction was removed by centrifugation at 1500*g* for 20 minutes; DNA could not be detected in this supernatant (1500*g*) either by the diphenylamine test of a hot trichloroacetic acid extract (*9*), or by radioactivity labeling experiments. For example, the antigen which was contained in the 1500*g* supernatant was from two generations of cultured WI-L2 lymphoid cells that had been uniformly labeled with [2-^{14}C]thymidine (New England Nuclear, 50 mc/mmole; 0.1 μc per 5×10^5 cells); this antigen contained less than 1 percent of the total labeled DNA.

Experiments to determine optimum conditions revealed that 3*M* KCl extracted more antigen than either 0.3*M*