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Strong Solids

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Abstract : The adjectives hard, harder and hardest are commonly used to describe strong solids and diamond is described by the superlative-hardest! Synthesis of strong solids is of far reaching technological importance in the areas of abrasives, reactors, space flight, turbine technology *etc* The quest for stronger materials leads scientists to understand the correlation between characteristics of interatomic interactions and macroscopic properties This will have implications in the pursuit of designing new and novel materials In this paper, the race for synthesizing a material which can dethrone diamond will be highlighted Results on some low Z compounds, nitrides, carbides and borides of transition metals, hypothesized to be harder than diamond will be described Efforts will be made to list down some important parameters that go into making a solid strong and then arrive at a possible ideal recipe for its synthesis

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1. Introduction

Synthesizing a material harder than diamond has become a passionate pursuit for several scientists. The race for the super hard material can be compared to a horse racing. Here, the theoreticians bet and the jockeys are experimentalists. In the end it is seen consistently that theoreticians decide to switch their bet on another material and experimentalists are taken for a ride. This report tries to trace the recent efforts in the race for synthesizing hard material and presents the status of the subject. In this process, the author also tries to come up with a possible recipe for synthesizing diamond like material, discussing the associated problems in executing such a recipe

Because of the importance of the subject, several reviews have appeared during the last couple of years [1–10]. In one of the papers, the author comments that "No material that is thermodynamically stable under ambient conditions and composed of light (small) atoms will have a hardness greater than that of diamond" [10]. Remarkably, Blank and his co workers have published a series of papers from 1998-2001 in which they claimed to have synthesized ultra hard fullerites starting from C_{60} as well as C_{70} [11–19]. The material was recovered after soaking at 13 GPa, 1773 K kept ~20 minutes. The authors also offer extensive scratch tests on diamond as proof. However, many scientists are skeptical about the scratch tests and many have chosen to ignore their claims. We will examine the reasons as to why Blank and his coworkers' claim of ultra hard fullerite has not received extensive acceptance in the scientific community However, there are several positive aspects of their work. They seem to have identified the crystal structures of the high pressure ultra hard phases of C_{60} and C_{70}. An US patent also has been issued in 2001 [19]. They have published in a refereed journal explaining with proof as to how the ultrahard fulleruite scratches diamond. However, there are several minus points in their claim. The ultra hard fullerite has not been reproduced yet by other scientists. Carrying out reliable Raman and XRD on such samples quantities is difficult task and may not be reliable. Electronic structure calculations do not support their claims [20]. Further, hardness estimates on small inhomogeneous and textured samples is difficult. Also, the nanoscale technique used for measuring the hardness has questionable reliability for measuring nearly similar hardness values. Then according to the principle of soft indenter under certain conditions, Cu can scratch MgO! [21]. Also, at high temperatures, c-BN can scratch diamond. Hence, the scratch test alone may not be sufficient to ascertain the hardness of a material.

In another report, Talyzin *et al* [22] have carried out investigations to confirm the claims of ultra hard fullerite. They have reported that samples of C_{60} treated at 13 GPa and 830 K for 20 minutes formed a hard phase. However the hardness is much lower than that of even c-BN (hardness ~60 GPa), where as the hardness of diamond (90-120 GPa). Hence it is not surprising to see that in a most recent review by Brazhkin *et al* [7], the phase diagram of fullerite doesn't even get mentioned. Therefore

It is prudent to conclude that the synthesis of ultrahard fullerites is yet to be confirmed and accepted by the scientific brethren.

More recently, Dubrovinskia *et al* [23] have reported aggregated diamond nanorods (ADNRs) which are harder than diamond. These results are yet to be confirmed and stand the test of time. Moreover, they are only different forms of the same parent materials *i.e.*, diamond.

Table 1 lists few hard materials and it can be noted that the number two position is still held by c-BN. The generally accepted convention which is followed for describing hard materials is that if the hardness is more than 40 GPa it is called super hard, and if it is more that 80–90 GPa, it is called ultrahard material.

Table 1. Gives the list of few of the best known hard, harder, and hardest materials. The table alos serves the purpose of defining the convention followed for classification of materials.

Material	K (GPa) Bulk modulus	G (GPa) Shear modulus	E (GPa) Youngs modulus	H (GPa) Hardness
Diamond	442–433	534–535	1142–1164	60–150
c-BN	369–382	409	973–840	46–80
w-BN	390	330	790	50–60
B_4C	200	201	474	30
Al_2O_3	246	160	403	20–27
B_6O	200–208	204		35

Convention · H_v Superhard > 40 GPa; ultrahard > 80–90 GPa.

Synthesis of strong solids is of tremendous technological importance in the area of abrasives, reactors, space flight, turbine technology *etc.* Surely, one can think of several improvisations on various technologies if suitable stronger material are available. More importantly, scientists are trying to understand the correlation between characteristics of interactions and microscopic properties. This will have implications in the pursuit of designing new and novel materials.

2. Strong solids of today

Before going further, it will be informative to look at the plethora of strong solids available to us today for various applications, and the type of bonding in them (Table 2). Firstly, we have covalent and ionic-covalent solids compounds formed by light elements from periods 2 and 3 of the periodic table, *e.g.*, Be, B, C, N, O, Al, Si, P; Al_2O_3 (corundum); SiO_2 (Stichovite), BeO, B_6O, C_3N_4, Si_3N_4, B-C-N, B-C-O, *etc.* Secondly, we have specific covalent substrates including various crystalline and disordered carbon modifications, diamond polycrystalline; carbon films; fullerite-C_{60}; BC8 phases of carbon *etc.* Thirdly, partially covalent compounds of transition metals with light elements such as borides, carbides, nitrides and oxides like Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W; WB_4, WB_2, and WB, high pressure phases of RuO_2, ZrO_2 and HfO_2.

Table 2. List of well known hard materials under three categories following Brazhkin *et al* [1].

Type of material	Examples
Covalent and ionic-covalent compounds formed by light elements from periods 2 and 3 of the periodic table.	Be, B, C, N, O, Al, Si, P -Al_2O_3 (corundum) -SiO_2 (Stichovite) -BeO, B_6O -C_3N_4, Si_3N_4, B-C-N and B-C-O
Specific covalent substances including various crystalline and disordered carbon modifications.	-diamond polycrystals -carbon films -fullerite-C_{60} -BC8 phases of carbon
Partially covalent compounds of transition metals with light elements such as borides, carbides and nitrides and oxides.	-WB_4, WB_2 and WB Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W, + B, C, N, O HP phases-RuO_2, ZrO_2 and HfO_2

3. Characterization of strong solids

Before discussing some of the important advanced materials presently under investigations world wide, we will try to examine the basic physical parameters useful in the characterization of strong solids. The elastic properties of a material are described by bulk, shear and Young's modulus and elastic stiffness coefficients (which are in turn dependent upon microscopic interatomic interaction. Young's modulus is the tensile strain *versus* tensile stress (E, GPa); shear modulus is the shear strain *versus* shear stress (G, GPa); bulk modulus is the change in volume *versus* pressure (K, GPa) Poisson's ratio is contraction strain/extension strain (*v*). Also, $E = 9KG/(3K+G)$ under homogeneous medium approximation. $B = (C_{11} + 2C_{12})/3$; $G = (C_{11} - C_{12} + 3C_{44})/5$ The mechanical properties are determined by the hardness, strength and yield stress (these are limiting stresses corresponding to failure or plastic flow respectively). The next step will be naturally to examine as to how these parameters can be determined experimentally under various situations we foresee, like, under pressure and temperature conditions. It will also be useful if techniques are developed or extended for calculation of these properties. The elastic stiffness coefficients C_{ij} can be experimentally determined under certain high pressure conditions for cubic, homogeneous single phases *e.g.*, Au, Ag, Mo, and Bi *etc.* [24]. The experiments and analysis both are complex for low symmetry, multiphase, heterogeneous solids. Therefore, when we are dealing with high pressure-high temperature synthesis experiments, it is mostly possible only to determine bulk modulus and hardness of the recovered samples. *Ab initio* LDA, GGA electronic structure calculations leading to determination of bulk modulus, *K*, total energy, structural stability, and elastic constants are carried out regularly. In addition, *ab initio* calculations are now extended to predict tensile and shear stress, ideal shear strength

etc. ABINIT phonon calculations are used to predict phonon instabilities, mode softening in the materials. However, the ability to predict new phases and novel compounds is yet to evolve.

In high pressure-high temperature synthesis experiments, hardness is used and continued to be used several confusions exists in its basic understanding. Hardness has no precise definition and no recognized unit. Hardness scale are not intercomparable easily. Several models are used to measure and quantify measured values. The measured values of hardness depends upon grain size, applied load, temperature, defects *etc.* In spite of all these confusions, hardness is very efficient and a very quick strength probe. Because of its acceptance by materials scientists, it is widely used to measure the strength of a given solid. Therefore, given the scenario, one has to then look for correlations between hardness and elastic properties.

The confusions in hardness values arise, because, while applying the load, the similarity law has to hold good (*i.e.*) the major part of the applied load. P_{cr} should be used for plastic flow (see Figure 1). For soft materials, P_{cr} should be less than 0.1 N. However, for hard materials P_{cr} should be ~10–100 N. Moreover, the nanoindentation loading curve (in the nanoindentation technique used widely) can be nonlinear in all its segments thereby preventing an unambiguous determination of hardness. Viewing all these important factors, it is clear that the ultrahardness values measured by nanoindentation technique has to be carefully examined before coming to any conclusion.
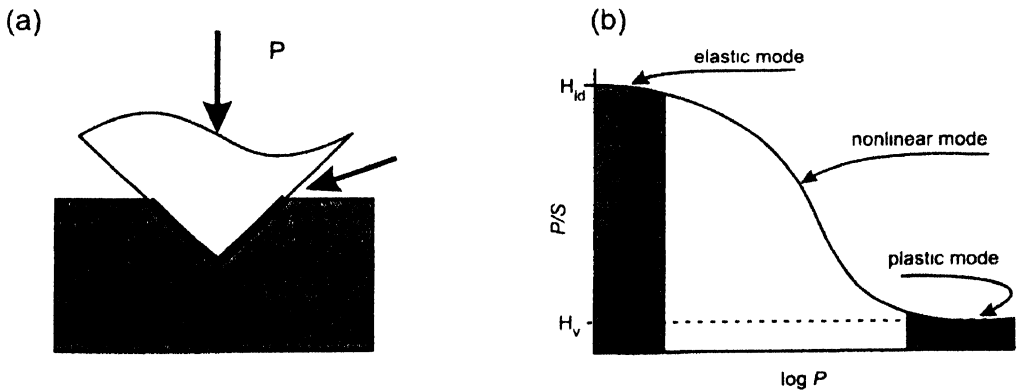

Figure 1. Measurement of hardness : Similarity law has to hold good. Reprinted figure with permission from [V V Brazhkin, A G Lyapin and R J Hemley "Harder than Diamond : dreams and reality", *Philosophical Magazine A*, Vol. 82 240-242 (2002)] © (2002) Taylor and Francis Ltd.

Now we shall see the correlation of various elastic properties with hardness. Firstly if we look at the bulk modulus and hardness, the dependence is not unequivocal and monotonic. For example, corundum (Al_2O_3) has a higher bulk modulus K than B_6O. However, Al_2O_3 is less hard. For C_3N_4 the calculated bulk modulus is higher than that of diamond. However, the shear modulus (G) of C_3N_4 is much lower than that of diamond, and hence C_3N_4 is less strong than diamond. It is therefore seen that

hardness values do not have good correlation with bulk modulus. This is supported well with experimental data (Figure 2).
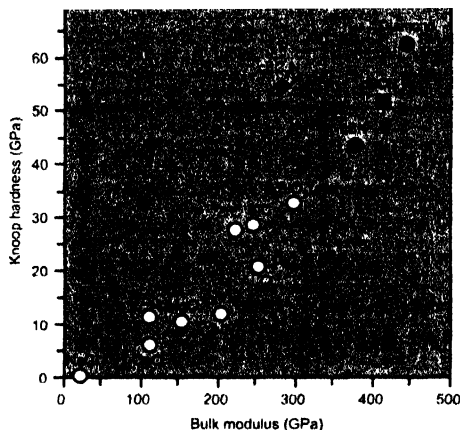

Figure 2. Bulk modulus *versus* hardness, the correlation is not good. Reprinted with permission from the *Annual Review of Materials Research*, **Volume 31** © 2001 by Annual Reviews www.annualreviews.org

Young's modulus correlates well with density ρ and shows a relatively linear relationship with hardness. If we look at the Figure 3, it is seen that we need a density of ~3.5 g/cc for achieving the hardness of diamond. This could be one reason as to why it is difficult to form ultrahard fullerites.

From the above relationships, it is clear that while comparing strength, it is the shear modulus which plays a dominant role. Remarkably it shows a monotonic variation with hardness (Figure 4). Therefore we should look for techniques to extract the shear
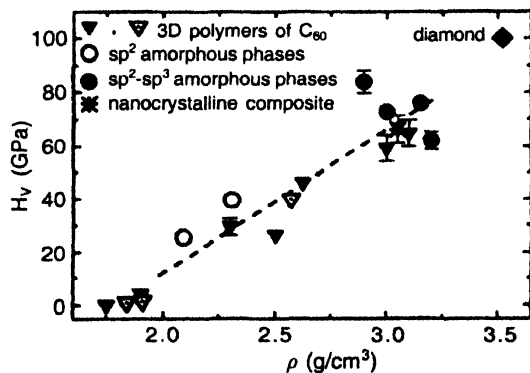

Figure 3. Young's modulus (density) *versus* hardness. Reprinted figure with permission from [V V Brazhkin, A G Lyapin and R J Hemley, "Harder than Diamond : dreams and reality", *Philosophical Magazine A*, **Vol. 82** 240-242 (2002). © (2002) Taylor and Francis Ltd.
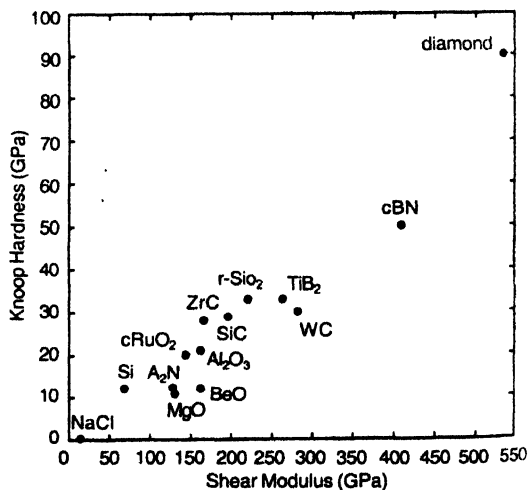

Figure 4. Shears modulus *versus* hardness. Reprinted with permission from the *Annual Review of Materials Research*, **Volume 31** © 2001 by Annual Reviews www.annualreviews.org

modulus from the high pressure experiments, as this parameter is a better indication of the strength of the solid

For an ideal strong solid, Hideal can be expressed as $Ecot(\varphi)/2(1 - \nu^2)$ For non-metals ν^2 is less than 1 and for standard pyramid indenter $cot(\psi) \sim 0.5$ Therefore H_{ideal} is equal to $E/4$ Ideal theoretical shear strength σ is $G/2\pi$ The ultimate shear strength of the solid depends upon E and G However, for real solids $H \sim (0.01-0.02)$ H_{ideal} due to the presence of dislocations, defects and structural phase transformations Hence any approach towards synthesizing a strong solid should be based on maximizing H and α.

In our approach to obtain ideal strength, we must look for correlations between physical properties and strength This can give clues as to which property needs modification in order to attain ideal strength There are several empirical relationships along with bulk modulus For ionic crystals, $K = Z_a Z_c / V$ (Z-anion and cation charges, V is specific volume per ionic pair) [25] For crystals with diamond structure, ($K = (1971 - 220\lambda)d^{-3.5}$) [26] In general K is proportional to ρ, the valence electron density We will now look at some archetypal hard material diamond and the reason why it is strongest material known to mankind Subsequently we will describe a few of those materials which were predicted to be stronger but proved otherwise after synthesis Finally, a possible recipe for synthesis of a hard material is discussed

Diamond

The various reasons attributed to the strength of diamond are (i) its high degree of covalency, (ii) large bond bending forces, (iii) low Poisson's ratio ~ 0.07, and (iv) $Z = 6$ (high coordination number) Also if we examine the total valence charge density along the bond in diamond, it is the most symmetric, purely covalent bond, in Figure 5 [27]
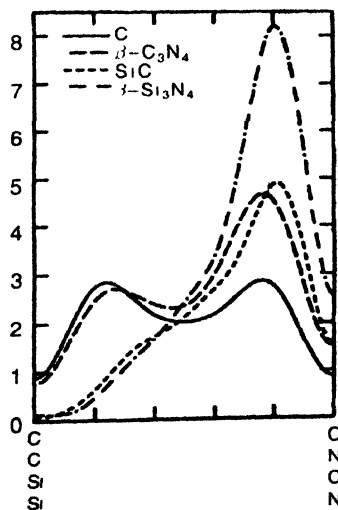

Figure 5. Total valence charge density along the bond length Reprinted figure with permission from [A Y Liu and M L Cohen *Phys Rev B* **41** 10727 (1990)] © (1990) American Physical Society

However, the other systems like Si-C, C-N have asymmetric distribution of valence charge density. It is therefore imperative that in order to mimic properties of diamond, one needs to obtain symmetric charge distribution along the bonds.

C_3N_4 Polymorphs :

Starting from the prediction by Liu and Cohen in the year 1990 [27] that C_3N_4 might turn out to be harder than diamond there has been tremendous experimental efforts to synthesis this compound but all in vain. Till date we do not have a well characterized bulk compound. A recent calculation has poured cold water over the fire by concluding that although C_3N_4 and diamond have similar bulk modulus the shear strength in C_3N_4 is anisotrpic and much lower than even c-BN [28,29]. Therefore it is now considered important to calculate the ideal strength (*i.e.*) the stress at which a perfect crystal becomes mechanically unstable that sets an upper bound for strength of the materials.

Si_3N_4 :

The compound Si_3N_4 has been a great disappointment as compared to the initial enthusiasm it created among the material scientists. The maximum hardness it shows is around 45 GPa, which is even lower than that of c-BN [6].

B-C-N Compounds :

Recently, the BC_2N compound has shown lot of promise as it is a good contender for in the race for ultrahard material [30]. The compound has been synthesized by multianvil presses, as well as laser heated diamond anvil cell. It has a bulk modulus of ~76 GPa. Subsequently, however, calculations of the tensile stress in these compounds are found to be highly anisotropic and much lower than that of even c-BN [31].

4. Concluding remarks : Recipe for future

These long drawn efforts to synthesize a material harder than diamond motivates one to draw up a recipe based on the experience/experiments so far. The first and the foremost requirement is that the average valence electron should be high (more than that of at least diamond). The material should have high symmetry tetrahedral network structure. It should have preferably covalent bond, short bond lengths, and isotropic bond strength. It should also have high coordination number greater than or equal to 6. However, unfortunately, high coordination also leads to increase in electron density and subsequent metallization. Also, there are lot of difficulties in achieving these specifications in binary and ternary systems. Poisson's ratio should be = 0–0.2. The hypothetical material should have strong anisotropy in electron density distribution along key directions and should have preferably ions with small cores.

All these conventional possibilities may or may not lead to the dream ultra hard material. The routes are laden with obvious difficulties which are difficult to

surmount. A certain amount of unconventional thinking in this direction is the need of the hour. Recently, experiments have tried to introduce shear in additional to the usual high pressure and high temperature in hexagonal BN, leading to enhanced strength of the resultant material. The other approach would be of course to look for strong solids with more useful applications rather than focusing on a material just harder than diamond material.

Acknowledgments

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