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Nano works to get it harder

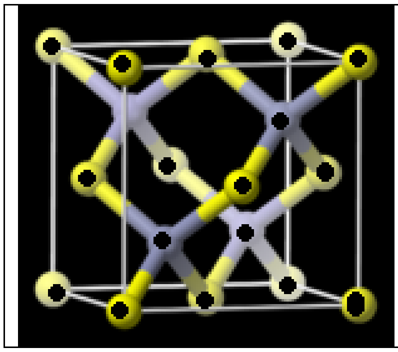
Diamond may yield place to a material that was long on its heels, says S.Ananthanarayanan

The diamond cutting tool has been the last word in hardness, for cutting and grinding other materials. China scientists Yongjun Tian, Bo Xu, Dongli Yu, Yanming Ma, Yanbin Wang, Yingbing Jiang, Wentao Hu, Chengchun Tang, Yufei Gao, Kun Luo, Zhisheng Zhao, Li-MinWang, Bin Wen, Julong He & Zhongyuan Liu (two of them in the US) have found a way to reduce the grain size of Boron Nitride to do better than diamond.

Crystals and hardness

The element, carbon, of which diamond is one form, owes its remarkable properties to its atomic structure. Atoms have between 1 and 8 electrons in their outermost electron shell. The cases of 2 electrons or 8 electrons in the outer shell are balanced and stable. Atoms that do not have this structure try, by combining with other atoms, to mutually borrow and lend electrons and get to these numbers. But among all elements the element carbon, and some others, have four outer shell electrons, which allows these elements to form links with 4 other atoms, which may be other carbon atoms. This allows a variety of compounds with carbon or other elements and also many geometric forms where an atom shares each of its outer electrons with similar atoms, to give both sharing atoms the stability of the ‘8 electron’ state.

Graphite is a form of carbon where carbon atoms form sheets of a honeycomb lattice, which sit on each other. The sheets can slide over each other and graphite is useful as a lubricant. But a different form of carbon, where the atoms take 3-dimensional, form of interpenetrating cubes, is diamond. This crystalline structure has the feature that it does not present ‘cleavage planes’, where the crystal could disintegrate, and it has tremendous strength, higher than that of other crystal forms. Diamond thus shows luster and strength, in contrast to charcoal, which is chemically the same thing, and for its hardness, diamond has extensive industrial use. But, as diamond is finally nothing by carbon, diamond is readily oxidized and cannot be used where there are high temperatures. This is a great limitation of it industrial use.

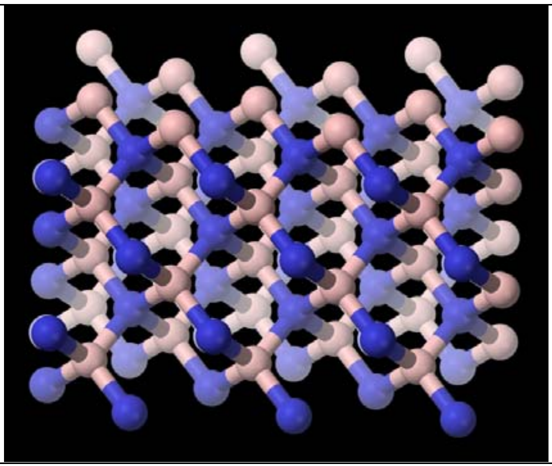


Another compound that forms this interpenetrating cubic form of crystal is ***Boron Nitride***, or a compound of boron and nitrogen. As boron and nitrogen have 3 and 5 outer shell electrons respectively, they form a stable molecule, but when the molecules form crystals, they form bonds with 4 neighbouring molecules, just like the carbon atom. There is thus the graphite-like form of layers that slide, which has use as a lubricant and also the cubic form, which is like diamond. This form, known as ***cBN***, also has very high hardness. And though hardness is not so high as that of diamond, the ***BN*** molecule is not affected by heat and for many industrial uses, ***cBN*** is able to replace diamond.

Increasing hardness

Materials are hard because component parts mesh together and resist shearing forces. It has been found that materials formed of smaller crystalites provide more irregularity and less smooth surfaces and thus lead to greater hardness. This kind of hardness is said to arise from ***grain boundary strengthening*** or ***Hall-Petch strengthening***, named after ***E O Hall*** of the University of Sheffield and ***N J Petch*** of the University of Leeds, who published groundbreaking discoveries during the 1960s. As it was found that the smaller grain size impeded movement of dislocations and hence increased the ***yield strength,*** methods have been sought to reduce grain size.

One of the methods has been through ***heat treatment***, which is to control the rate of solidification after plastic deformation by heat. Variations of this method include adding particles during the solidification from the melt, to act as nuclei, or inducing a very small fraction of the melt to solidify at a higher temperature, creating a huge number of miniscule seed crystals. As an equal number of crystallite are formed, the size of grain is stays low. Another aspect of grain boundary strengthening is that when the grain size is esceedingly small, this tends to facilitate rather than impede sliding and we have the ***reverse Hall-Petch effect***. .



In the case of cubic Boron Nitride (cBN), very small grain size has been attained by synthetic transformation of other crystal forms, like the graphite-like BN form. This method was first used for creating very hard steel, by rapid cooling or quenching of a form of steel known as ***austenite***. Austenite has a ***face-centred cubic*** structure and rapid cooling results in capture of carbon atoms. This results in the parent austenite getting transformed, while cooling, into the ***body-centred cubic*** form, known as ***martensite***, after ***Adolf Martens***, a German metallurgist who developed the technique in the 1860s.

Martensitic transformation of BN has resulted in cBN with grain size down to 14 nanometres and hardness, which is measured in units of pressure, of 85 billion atmospheres (or ***Giga Pascals – GPa)***). This hardness is still short of the hardness of over 100 Gpa in the case of synthetic diamond, with grain size of 10-30 nanometres.

Chinese transformation

The method the Chinese group has developed brings the grain size of cBN down to 3.8 nanomentres, and hardness of the order of 100 GPa, which is that of diamond. Going below the level of 14 nm, which is what has been achieved so far, is limited by the high-energy grain boundaries which promote crystal growth. Attaining 'twinning boundaries', or symmetric crystals which attach along matching surfaces, can reduce the boundeary energy and make for more stability. .The Chinese group started out with graphite-like sheets of BN, The BN precursor was subjected ***High Pressure and High Temperature (HPHT)*** treatment and the crystal structure was monitored using X Ray interference methods. At 15 GPa and above 1,000 ˚C, the BN material transformed into a translucent cubic phase, mixed with diamond-like structures. At1,600˚C, the material changed completely into ***transparent cBN***.

The reverse Hall-Petch effect, which reverses the increase of hardness with reducing grain size comes into action when the grain size is down to about 10-15 nm, in metals and alloys. cBN with twin domains that was produced by the China team, is seen to continue growing in hardness well below this limit. "***Our findings introduce a new strategy and direction in the quest for superhard materials***," say the authors in their paper published in the journal, ***Nature***.

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