Superhard Alloys: A Review of Empirical Modeling and Computational Strategies

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\textbf{Abstract.} Superhard alloys has gained major research interest in recent past as it represents an effort to create man made alloys with hardness on par with the hardest substance available to us i.e. a naturally occurring diamond. They are virtually incompressible solids with high electron density and high bond covalency. Present paper aims to review the empirical methods and computational techniques developed by employing them using published literature, in order to attain a better understanding of complexities involved in synthesis of such compounds as a first step towards developing a new superhard metallurgical composition with similar mechanical attributes.

\textbf{Keywords:} Superhard alloys, Ultrahard alloys, Computational Metallurgy, Numerical Modelling, Metallurgy Guided ML, High Entropy Alloys, Quaternary Carbides.

\section{1. Introduction}

The ability to resist deformation under loading is defined as “hardness”. This is often measured using indentation depth under specific load which is then used to evaluate material performance against standardized scales like Mohr’s, Brinell, Rockwell and Vickers\textsuperscript{[1][2][3]}. If the measured value on Vickers scale in above 40 GPA or 80 GPA, then elements or alloys with such property are said to exhibit Super hardness or Ultra hardness respectively. Besides high hardness they are generally chemically inert with good compressional strength, high bulk modulus and melting point\textsuperscript{[4][5]}. Such Materials have a wide range of applications in fields like automotive, oil and gas, aviation, defence, space exploration etc\textsuperscript{[6][7]}. In 20th century a number of experiments were carried out aiming to design and synthesis super hard materials for industrial applications, which resulted in two famous compounds namely diamond \textsuperscript{[8]}, cubic boron nitride (c-BN) and zinc blended boron nitride (zb-BN)\textsuperscript{[9]}. It is estimated that about 3000 million carats are produced every year as they are predominantly used as super abrasives\textsuperscript{[10]}. The superhard diamond is not a very good abrasive material, as it is not suitable for high speed machining and forms iron carbides when used to machine ferrous alloys making c-BN as only alternative which has only half the hardness of that of a diamond due to which recent research has seen a rise in search of materials other than carbon allotropes which are chemically and thermally stable with many focussed on achieving it using nano crystalline tweaking\textsuperscript{[11]}.

\section{2. Current Research Trends}

High hardness values are a contribution of three dimensional network formed by buse elements of the alloy which is generally made up of short and long covalent bonds. The rigidity of these bonds are crucial for hardness values. For example graphite has layered hexagonal structure called graphene along crystallographic direction ‘c’ with weak van der Waals forces resulting in a very soft material whereas graphene bond energies are equal to that of diamond rendering it as one of the toughest materials\textsuperscript{[12]}, from which on can infer that composition, crystal structure along with pressure - temperature phases are important parameters in design of super hard materials. As carbon and boron are two hardest periodic elements know to us most of the super and ultra-hard materials developed using compounds wherein they are present in different phases\textsuperscript{[13]}. A number of carbon allotropes have been experimented using such ab initio approach \textsuperscript{[14]}, predicting phases such as monoclinic M-carbon\textsuperscript{[15]}. Similarly the rich phases of boron promise a large family of superhard compounds\textsuperscript{[16]}. Systems such as boron carbide B\textsubscript{4}C and boron superoxide B\textsubscript{2}O with \(α\)- rhombohedral boron (\(α\)-B\textsubscript{12}) present high hardness along with chemical...
inertness, wear resistance and melting point[17]. Recently boron superoxide system with $\beta$-orthorhombic boron has been predicted which exhibits hardness values higher than $\alpha$-B$_6$O[18]. A number of such hypothetical systems like tetragonal B$_4$CO$_4$. Metastable B$_6$C$_2$O$_5$& B$_6$CO$_3$ have been predicted with high hardness values[19]. Transition metal borides like WB$_4$ [20]and ReB$_2$ [21] have been considered as potential super hard material but their high reported values have been criticised[22]. Nitrides formed by reacting metals with nitrogen gas like Re$_2$ (N$_2$)(N$_2$) and similar compounds[23] in extreme pressure and temperature conditions is a promising approach but the high price is an inconvenience. Clathrates like polymerised partially decomposed fullerenes are superhard[24], similar polymerization is observed in carbon nano tubes[25]. Besides extreme hardness tetrahedral clathrate structures suggest existence of carbon clathrate framework which are not only harder than diamond but also present other properties like super conductivity. Recently predicted C$_3$B$_3$ clathrate structure that can host Sr atom is one such example[26]. Figure 1 presents an illustration in research trends of Hard, Superhard & Ultrahard Materials [27].

Figure 1: Hard, Superhard & Ultrahard Materials

However a major part of research is focussed on borides, carbides and nitrides of transitional metals like Rhenium [28]. Molybdenum[29], Chromium[30], Tungsten[31][32]Etc. Compounds like TiN[33] and WC[34] with hardness of 22 and 30 GPA respectively are already widely used in many industries. However these transitional metal complexes present a unique challenge as it is difficult to evaluate their compositions and crystal structure using regular experimental techniques like X-ray diffraction for which new methods to predict crystal structure have been developed and used to predict novel super hard materials.[35][36]. One such scenario where the super hardness of rhenium boride was predicted to be ~48 GPa but was later was refuted[37]. Sum of the transitional metals Carbides and Nitrides being perused as the potential Superhard material are presented in figure 2[38].

Figure 2: Transition Metal Carbides and Nitrides.
3. Empirical Modeling

Predicting mechanical properties using crystal structure is one of common approaches used in quest of novel super hard materials and a number of different techniques have been developed for the same[39][40]. A number of empirical models have been proposed which use crystal structures, compositions and material physical properties as an input to predict the hardness, like in the Chen model assumes that indentation size and dimensions are related to shear and bulk modulus[41] whereas Lyakhov-Oganov model uses crystal structure and chemical compositions[42] but it is often preferred to compare the model predictions with experimental data for no one model can accurately predict for all types of material combinations and phases.

3.1. Thermodynamic Phase Change

Besides the empirical methods the general strategies of predicting new chemical systems with superhard properties can be distinguished into two methodologies which are dependent on phases formed under high pressure conditions. (I) phase change under high pressure like in case of graphite to diamond conversion, (II) phase change induced densification of heterogeneous complexes under high pressure. A third approach has also gained great interest in recent times, it focuses on structural rearrangement at nano scale in systems made of unusual compositions of multiple elements under high pressure. An example of case (I) is orthorhombic γ-B_{28} discovered in 2008 has changed our understanding of allotropies of boron and its ability to form new phases under high pressure[43]. Till 2008 only three phases of known 16 phases of boron namely α-B_{12} rhombohedral at low temperature, β-B_{106} rhombohedral at high temperature and low pressure and t-B_{192} tetragonal at high temperature and high pressure were considered as promising systems [44][45]. With predicted hardness above 50GPA this discovery has renewed interest in different metastable phases of boron recently a nonicosahedral β-B allotrope of boron have been identified to format 2100 K and 115 GPA[46].

As per literature Case (II), where in phase change leads to densification can be achieved either by pressurising preformed low density complexes to induce phase change in turn densification (d-BC₃) or initiating chemical reaction at high pressure which causes estimated densification (B₁₁N₂). In practice these two approaches are mutually inclusive and can occur in same compound (c-BC₂N). With near diamond like structure d-BC₃ is synthesised by dissolving boron in carbon under controlled conditions of temperature and pressure in order to avoid initiation of any phase change and then using high pressure to convert the unusual stoichiometric solution in to boron ‘diamond’ with an estimated hardness of 70GPA[47]. The in-situ study of B-BN system made the discovery of rhombohedral sub nitride B₁₃N₂. With a unit cell structure similar to BC₄ it exhibits super hardness with hardness value of 41 GPA. Unlike boron carbide it is thermodynamically stable and at 5GPA it melts to form a eutectic solution and at further high pressures it form boron rich phases namely rhombohedral B₁₅N₂ and tetragonal B₅₀N₂. At further increase of pressure the B₅₀N₂ decomposes tetragonal t-B₃₂ and B₁₃N₂ [48][49]. With hardness of 76GPA cubic BC₂Nfills the gap between cubic boron nitride and diamond and is synthesised by phase transition of (BN)₀.₄₈C₀.₅₂ at high pressures. A macroscopic sample have been produced using a large-volume multi-anvil apparatus with a 5000-ton press at Bayerisches Geoinstitut. The super cell has a combination of high density phase C-B-N layers like in graphite and non-dense layers distributed across the structure leading to formation of zb-BC₂N phase contributing to high resistance to deformation under uniaxial loading[50].

3.2. Nano Structures and Hall Petch Effect

In later half of nineteenth century a phenomenon was proposed claiming significant increase in hardness of polycrystalline materials when there microstructure was made of nano sized grains and was called ‘Hall Petch Effect’ which has again gained popularity as the search of superhard material shifted its focus towards high pressure induced nanostructuration[51]. A simplified way to explain this effect is through dislocation pile-up because in polycrystalline material the grain boundaries act as barriers to crystal dislocation. Under applied stress, the more mismatch in the grain layout would mean more energy required to change the dislocation direction and move in to adjacent grain. Hence as the grain size is
decreased the number of grain boundaries per unit volume increases and also rises the number of dislocations occurring in an instance which are piling up against each other which causes an increase in energy required to overcome them. This means more stress is needed to be applied to overcome these dislocations in finely grained material in comparison to coarsely grained one thus making it harder\cite{52}\cite{53}. This relation between yield strength and grain size is defined by Hall-Petch as  

$$\sigma = \sigma_0 + \frac{k}{d^2}$$

However this equation is observed to be inaccurate as grain size decrease beyond a critical diameter (around 10nm) where in a decrease in hardness is observed causing ‘Inverse Hall Petch Effect’\cite{54}\cite{55}. 

This inverse effect is not completely understood yet it is understood that at critical grain size the dislocation controlled plasticity shifts towards grain boundary controlled plasticity where in sliding and grain boundary diffusion become prominent causing a reduction in hardness. A new generalised equation has been proposed considering these factors 

$$\sigma = \sigma_0 + \frac{k}{d^2} + k_1 + \frac{B_0}{d} + Bd^3$$

Where in $k_1$ and $B_0$ are constants and $B$ is obtained using strain vs temperature data terms represent diffusion controlled dislocation mechanism. For large grain sizes first terms are dominant and for extremely small grain sizes the last three terms are important to explain inverse effects. Another issue observed in nano structures is as one increases the temperature due to grain growth the size is no longer in nano scale. This phenomenon is well observed in ‘nano scaled diamond’ and ‘nano c-BN’. It has been observed that this can be easily overcome by maintaining the quality of starting material and controlling the temperature and pressure during synthesis process.

4. Computational Metallurgy

Two new approaches namely in situ and ab initio have gained immense popularity in recent years Advances in X-Ray diffraction along with improved optical and tomographic techniques and Synchrotron radiation sources for studying extreme conditions have propelled the in situ studies whereas next generation artificial intelligence and machine learning engines have pushed the ab initio beyond the frontiers of regular methodologies used in turn paving way for new generation of superhard materials in form of high entropy transition metal carbides\cite{56}\cite{57}.

4.1. In Situ and Ab Initio approaches

As observed by many it is not always possible to study superhard material using experimental techniques like X-ray diffraction studies alone, a hybrid approach of first principle equation for predicting mechanical properties from crystallography validated using experimental data is needed for better prediction is needed. A number of superhard materials are formed due to metastable phases at ambient pressures and temperatures and there synthesis requires controlled smooth transition monitored using constant feedback. Numerous microscopic models use parameters such as crystal geometry, atomic proximity and connectivity, valence electron density, electronegativity are available to predict hardness value\cite{58}. Such crystal structure prediction based algorithms have gained prominence in predicting new superhard composition of elements in recent years. Modified versions of first principle equations have been proposed by many which can used to optimise the hardness of such predicted crystal structures\cite{59}\cite{60}. A major drawback in such a system is that most of these models predict very high hardness values for structures with non-interacting forces like van der Waals forces which are needed for holding three dimensional shape of compound, this is overcome by models such as CALYPSO and UPEX which chemical graph theory to identify atomic bonds\cite{61}\cite{62}. We can estimate hardness using elastic, bulk and shear moduli but such a macroscopic approach are not employed to predict potential material compositions as it is very expensive to calculate these properties using first principle methods hence instead they are used to evaluate only promising set of permutations which are predicted from initial search settings\cite{63}\cite{64}\cite{65}\cite{66}.
4.2. Numerical Modelling

A number of models have been proposed to explain the phenomena of plastic deformation due to applied load using microscopic crystallographic concepts such as slip and twinning of grain structures.

4.2.1. Taylors Model

It is based on the assumption that the deformation field of all the grains in the specimen under load is equal disregarding the shape and size of grains in local neighbourhood also does not consider kinematic coupling where in the rotation of a grain due to external loading effects rotation of grains around it. It calculates the total deformation using slip, twinning and lattice distortion in given crystal system using power law based Cauchy stress equations and Taylor’s assumptions [67].

4.2.2. Viscoplastic Self Consistent Model (VPSC)

Similar to Taylor model it also doesn’t consider the shape and rotational effects of neighbouring grains under external loading but allows individual strain response for each grain in the system and their difference is dependent on stiffness between grain and surrounding homogenous media calculated relatively. It averages the microscopic behaviour of grains uniformly to match the overall macroscopic loading. In VPSC, each grain does not interact with its neighbouring grain instead its interaction is with entire aggregate treated as a unit equivalent medium [68].

4.2.3. Crystal Plasticity Finite Element Model (CPFEM)

It also considers geometric distortions caused due applied load. The change in shape and rotation are calculated and because of this feature it can predict material failure more accurately than the Taylor’s and VPSC models. Where they are able to predict failure due to textural effects, CPFEM has potential to evaluate localised deformations as direct interaction with neighbouring grains is considered and accordingly calibrated while calculating the final state of given specimen under load as illustrated in figure 3[69].

Using such approaches a number of material databases coupled with Machine Learning models have been developed which can predict a whole range of elemental combinations along with their properties like supercritical temperature, melting point, electronic bands, elastic properties for unary, binary, ternary, quaternary and quinary materials. Databases such as Open Quantum Materials Database (OQMD)[70], Automatic Phonon Library (APL), Automatic Gibbs Library (AGL), Automatic Elastic Library (AEL) containing vibrational properties, thermal and thermo-mechanical properties such as entropy, enthalpy, bulk and shear modulus along with Search API’s(Application Program Interface) like RESTful and AFLUX[71] allow AFLLOW[72], CALYPSO, CALPHAD, UPEX, XtalOpt[73], RandSpg[74] and other similar algorithms to access more than 2 million entries for estimation in a single run which have predicted compounds such as R3m-BC2N, Pnnm-CN, cubic BC3,Cr7C2, Cr7C3,Cr23C6, 

![Figure 3: Crystal Plasticity Finite Element Methods](image-url)
CrB, CrB₂, CrB₄, Cr₂B, Cr₃B₄, Cr₅B₃, Pmmn WB₅, Re₀.₅W₀.₅C and ReWC₀.₈ which exhibit superhard property\[75\][76][77].

Further using optimisation techniques such as Mendelealian Chemical Spacing, Energy Filtering and Pareto Technique combined systems like BₓCᵧ, BₓOᵧ, CₓNₓ, CₓCᵧ, ReₓBᵧ, WₓBᵧ, SiₓCᵧ, WₓCᵧ, AlₓOᵧ, TiₓCᵧ, SiₓNᵧ, TiₓNᵧ, BeₓOᵧ, RuₓOᵧ, OsₓOᵧ, RhₓBᵧ, IrₓBᵧ, OsₓBᵧ and RuₓBᵧ which have been long argued to possess high hardness values were found to be true, further promising systems such as MoₓBᵧ, BₓPₓ, VₓBᵧ, FeₓBᵧ, MnₓBᵧ, MnₓHᵧ, (Hfₓ₂₅Ta₀₂₅Zr₀₂₅Nb₀₂₅)ₓₐ₋₉ₚₓCₓ, (Cr₀₂Nb₀₂Ti₀₂V₀₂W₀₂)ₓ₋₉ₚₓCₓ, (Zr₀₂Hf₀₂Mo₀₂Ta₀₂W₀₂)ₓ₋₉ₚₓCₓ were predicted\[78\][79][80]. This kind of behaviour of material can be easily represented using Ashby Map of Fracture Toughness vs. Yield Strength as illustrated figure 4[81].

![Figure 4: Ashby Map of Fracture Toughness vs. Yield Strength.](image)

5. Summary

Super hard alloys like any other super material were developed as a solution for drawbacks in existing compounds and are constrained by the expensive and complex synthesis methodologies. During early stages of this quest major focus was on structures similar to that of diamond, which is the hardest known material available to us. As part of which a range of new allotropes of boron and nitrogen with potential of bonding capabilities similar to carbon were identified. With recent advances in modern experimental techniques, both at micro and macro level along with miniaturization of computational resources have opened a range of new compositions of elements utilizing in situ and ab initio techniques. A majority of these are built on the foundation of the idea that the hardness value is correlated to indentation dimensions which is in turn effected by the physical and chemical properties such as grain size, shape, valency, affinity, thermodynamic phases etc. Computational models such as VPSC, CPFEM coupled with normalisation algorithm like particle optimisation along with AI and ML models driven by AGL, AEL and other similar open databases has an ability to scan two million entries in a single run generating a plethora of potential configurations. The only short coming of such an approach is that it is based on published literature and the data isn't as accurate as it is believed to be, proved as in case of inverse Hall Petch recently established. Also all the models published either generalise or let user control the parameters while evaluating the values thus effecting the final solution. From current review we understand that a combination of CPFEM with CALYPSO is a popular method of proposing new type of super hard materials especially while considering transitional metal based complexes. This new advancement in metallurgical studies is not yet fully understood and needs more resourceful systems for further research.
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