Search for New Ultrahard Materials: Go Nano!

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Intrinsically super- ($H \cong 40 - 70$ GPa) and ultrahard ($H \geq 70$ GPa) materials attain high hardness through their large intrinsic strength, whereas extrinsically super- and ultrahard materials reach such hardness through their nanostructure. The recent search for intrinsically super- and ultrahard materials has concentrated on those with high elastic moduli. However, elastic moduli describe only the reversible, infinitesimal elastic deformation close to equilibrium, whereas plastic deformation occurs in shear at large strains at the atomic level, where the electronic structure may undergo instability. We shall show several examples of materials with high values of zero-pressure elastic moduli but relatively low hardness due to such instabilities. Such softening is absent in the superhard nc-TmN/a-Si_3N_4 nanocomposites (Tm = Ti, W, V, $(Al_{1-x}Ti_x)N$, $(Al_{1-x}Cr_x)N$ …) in which 3-4 nm size TmN nanocrystals are "glued" together by about 1 monolayer thick SiN_x interface. A combined ab initio DFT calculation of the shear strength of such interfaces, Sachs averaging of the shear resistance of the interfaces of randomly oriented nanocrystals, pressure enhancement of the flow stress and Tabor's relation between the hardness *H* and yield strength *Y* explains why these materials can reach hardness significantly larger than diamond, when correctly prepared and essentially free of defects [1]. The one monolayer (1 ML) thick SiN_x interface is strengthened by valence charge transfer, being stronger than bulk SiN_x. However, this weakens the Ti-N bonds adjacent to the interface layer [2], with weakening increasing with increasing thickness of the SiN_x interface, explaining why 1 ML is the strongest. Non-linear finite element modelling [3] explains the unusual combination of mechanical properties of these materials, and provides evidence for the validity of the Tabor's relation between hardness and yield strength, $H \approx 2.84 \cdot Y$ [4].

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