Different Approaches to the Design of Superhard Materials and Coatings

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Intrinsically superhard materials attain high hardness from their large intrinsic strength, whereas extrinsically superhard materials reach such hardness due to their nanostructure [1]. Elastic moduli describe the reversible elastic deformation upon small strain close to equilibrium, whereas plastic deformation occurs at atomic level in shear upon a large strain where the electronic structure may undergo instability. Therefore many solids with a high value of elastic modulus undergo structural transformations to a softer phase. We shall show several recent examples of such materials. This softening is absent in the superhard nc-TmN/a-Si_3N_4 nanocomposites where the transition metal nitride nanocrystals deform only elastically, and the plasticity is carried by shear near the strong grain boundaries. I shall focus on the origin of hardness enhancement in the nc-TiN/a-Si_3N_4 nanocomposites: A combined ab initio DFT calculation of the shear strength of the interface, 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 shows that these materials can reach hardness of > 100 GPa, when correctly prepared and essentially free of defects [2]. The one monolayer thick SiN_x interface is strengthened by valence charge transfer, being stronger than bulk SiN_x. However, this charge transfer causes weakening of the Ti-N bonds near that interface thus limiting the achievable hardness [3]. Non-linear finite element modelling [4] explains the mechanical properties of these materials, and the validity of the Tabor's relation between hardness and yield strength, $H \approx 2.84 \cdot Y$ [5]. A brief discussion of the issue of the reproducibility of the high hardness, toughness and oxidation resistance will conclude the lecture.

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