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The Search for New Super- and Ultrahard Materials: Go Nano!

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Super- ($H \geq 40$ GPa) and ultrahard ($H \geq 80$ GPa) nanostructured and nanocomposite thin films, which have been developed during the last two decades, are finding an increasing number of applications, such as wear-protective coatings on tools, hard and self-lubricant coatings for harsh and variable environment, for corrosion protection and others. Increasing interest receive materials with a high ratio of hardness to Young's modulus as mechanically adaptable coatings on machine parts, where their high compliance combined with high hardness reduce the wear. After a brief overview of the the recent search for new super- and ultrahard materialds I shall concentrate on the progress achieved in the understanding of the properties, preparation and industrial applications of hard and superhard nano-structured coatings on tools for machining (drilling, milling, turning), forming, stamping, injection moulding and the like.

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Intrinsically super- and ultrahard materials attain high hardness from their large intrinsic strength derived from strong covalent bonds and three-dimensional stable bond network, whereas extrinsically super- and ultrahard materials reach such hardness due to their nanostructure which impedes plastic deformation by dislocation activity (crystal plasticity) or another mechanism [1,2]. Thus, high values of elastic moduli do not gurantee high hardness. I shall briefly discuss examples of bulk materials with high elastic moduli but relatively low hardness (e.g. C_3N_4, $ReB2$) because upon shear strain they undergo electronic instability and structural transformation to softer phases with lower shear resistance [2,3]. The transformations to phases with lower plastic resistance are also the reason for the sluggish approach of the measured hardness to the correct, load-invariant value at a high load of several N [2]. In contrast, boron suboxide has relatively modest elastic moduli but high hardness because of a strong and stable three-dimensional bond network [4,5].

Such transformations and instabilites do not occur in the nc-TiN/a-Si_3N_4 and related nanocomposites where the interfacial regions are the carrier of the plastic flow [2,6], and the load-invariant hardness is achieved already at a relatively low load of 50-100 mN. The nanocomposites consist of 3-4 nm size TiN nanocrystals which are "glued" together by an about 1 monolayer thick SiNx interfacial layer, that is strengthened by valence charge transfer from the TiN nanocrystals. Ab initio density functional theory (DFT) calculation of the shear strength of the interfaces, Sachs averaging of randomly oriented nanocrystals, pressure enhancement of the flow stress and the constraint factor C, which is the relation between the hardness H and yield strength Y, $H \approx 2.8 \cdot Y$, explain why these materials can reach hardness larger than natural diamond [6] if correctly prepared and with low concentration of defects and impurities [7]. The validity of the constraint factor C ≈

2.8 for these materials has been recently discussed in Ref. [2] on the basis of slip-lines field model. It has been shown that the expanding cavity model, which has been advocated by some workers, is not appropriate because it contains only radial flow of the material, i.e. it describes only the behavior of materials which deform by densification (e.g. oxide glasses) or viscoelastic flow (e.g. polymers and elastomers).

The strenghtening by decreasing crystallite size (Hall-Petch mechanism) is usually followed by softening at a crystallite size below 10-15 nm ("the strongest size") due to increasing grain boundary shear ("inverse Hall-Petch") [8]. Such softening is however absent in the nanocomposites with strengthened interfacial SiNx layer. I shall show several other examples where remarkable strengthening has been achieved in nanostructured materials with low-energy interfaces, such as twins and stacking faults [2], and discuss the general aspects of such strengthening.

There are, however, many limitations to the preparation of superhard TmN/SiNx (Tm= transition metal nitride that forms stable and hard nitrides). It will be shown that oxygen impurities degrade the mechanical properties, and hinder the phase segregation and formation of a stable nanostructure [7], thus apparently increasing the "stability" of the Ti-Si-N solid solution and causing an extremly high density of defects, which have been reported in several recent papers (e.g. [9]). Another limitation is the choice of the correct TmN-Si3N4 (or more generally TmN/XY) system because not all decompose by the spinodal mechanism [7], which seems to be the necessary condition for the formation of superhard nanocomposites with a sharp, one monolayer thick interfacial layer, such as Si_3N_4-like in the TiN/Si_3N_4 nanocomposites.

The charge transfer to the SiNx interface induces oscillations of the valence charge density within the TiN which are damped with increasing distance from the SiNx interface, thus weakening the adjacent Ti-N

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bond and causing shear and decohesion to occur within the TiN nanocrystals but not in the SiN_x interface [10]. These calculations also explain why one monolayer of Si3N4 is the strongest configuration, and why the hardness decreases when it is two or more monlayers thick [11].

Non-linear finite element modelling, that accounts for pressure enhancement of elastic moduli and of flow stress, provides a deep insight into these materials and explains their unusual combination of mechanical properties [15].

The results of the theoretical studies by means of DFT [10] have been confirmed and extended by means of first-principles molecular dynamics studies of the TiN-SiN system [12] and for a variety of different TmN/XY heterostructures by Ivashchenko et al. [13,14]. A special attention has been devoted to the question of stability of different interfacial XY layers in nitride-based heterostructures. The future design of new superhard nanocomposite systems by first principles methods will be more efficient than the experimental approach.

The lecture will close with a brief overview of the present and future industrial applications [2,16].

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