LIMITS TO THE PREPARATION AND CHARACTERIZATION OF SUPERHARD NANOCOMPOSITES

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In the introduction, we shall briefly discuss the different approaches to the preparation of new superhard materials with emphasis on nano-structured ones, where with decreasing crystallite size below about 10-15 nm the "Hall-Petch strengthening" is changing to softening due to grain boundary (G.B.) shear. When the G.B. shear is reduced by the formation of a strong interfacial layer, such as Si_3N_4-like monolayer connecting 3-4 nm large nanocrystals of a hard transition metal nitride (e.g. TiN), hardness enhancement by a factor of more than 5 can be achieved as compared to TiN. In the case of the nc-TiN/a-Si_3N_4/$TiSi_2$ quasi-ternary system, hardness of 80 to > 100 GPa is possible because the $TiSi_2$ getters the minor oxygen impurities, which otherwise weaken the Si_3N_4-like layer. However, because $TiSi_2$ prepared below 850°C forms metastable, low-density phases which do not resist the stress within the G.B., these coatings degrade within several months or a year. The hardness of the quasi-binary nanocomposites nc-TiN/a-Si_3N_4 is long-term stable, but they require much higher purity because of the absence of the $TiSi_2$ "getter" [1]. The possibility to achieve in these system hardness in excess of 100 GPa has been clarified in our recent theoretical papers (see [1,2] and references therein).

There is a continuing discussion about the reliability of the very high hardness reported by us for the nc-TiN/a-Si_3N_4 and nc-TiN/a-Si_3N_4/$TiSi_2$ nanocomposites. I shall show that the recent claims of Fischer-Cripps et al. [3], that our measurements of the very high hardness were incorrect, is based on their incorrect fitting of indentation curves and selective citation. Original SEM micrographs confirm our reported high hardness of 80 to >100 GPa. The lecture will concentrate on the discussion of the deposition conditions needed for achieving such high hardness, which is combined with high elastic limit to fracture and with high oxidation resistance at elevated temperatures. We shall demonstrate that oxygen impurities of few 1000 ppm (0.1 at.%) strongly degrade the mechanical properties (see [1] and references therein). The recent results have shown that the impurities also hinder the segregation of the TiN and Si_3N_4 phases and the formation of stable nanostructure, thus apparently stabilizing the Ti-Si-N solid solution [1b]. At an impurity level of about 0.8 at.% of oxygen, the temperature needed for the "recrystallization" of the solid solution approaches 1000°C. Because the Si-O bond is the strongest one in the system and SiO is volatile at temperature of more than 900°C, silicon is lost from the films and the formation of the nanocomposites becomes impossible. Therefore, for any further progress in the basic materials science we need to reduce the oxygen impurities in the coatings below 100 ppm. Our earlier experimental results suggest that with O-impurity in the range of few 10 ppm hardness above 80 GPa should be possible to achieve in the stable quasi-binary nc-TiN/a-Si_3N_4 system. Finally, we shall show examples of coatings with impurities (O, H, C) of 700-1000 ppm which have been deposited in large-scale industrial coating unit [4], and discuss the possibilities of their further improvement.

[1] a) S. Veprek et al., Thin Solid Films 476 (2005) 1; b) S. Veprek, J. Nanosci. Nanotechnol. 11 (2011) 14.
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[3] A.C. Fischer-Cripps et al., Philos. Mag. 2012 in press; and various press releases.
[4] M. Jilek et al. SHM ltd. www.shm-cz.cz