



Review

Different approaches to superhard coatings and nanocomposites

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Abstract

Different approaches to the preparation of superhard coatings such as intrinsically superhard materials, coatings whose hardness is enhanced by energetic ion bombardment during deposition, and nanostructured superhard materials are discussed with the emphasis on the question of how to distinguish between the different mechanisms of hardness enhancement in thin coatings. We compare the thermal and long-term stability in air and some further properties of such coatings. The lack of success of some workers to reproduce the high value of hardness reported by Veprek et al. is explained in terms of inappropriate choice of the deposition conditions and/or impurities.

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1. Introduction

Superhard coatings with Vickers hardness of ≥ 40 GPa have attracted large attention because of the scientific curiosity of preparing materials with hardness in the range of diamond (70–90 GPa) and with respect to their industrial applications. Three different approaches towards the preparation of superhard materials should be distinguished [1]: (1) intrinsically superhard materials such as diamond, hydrogen-free “diamond-like carbon” (DLC), and cubic boron nitride (c-BN); (2) thin coatings where the hardness enhancement is due to a complex, synergistic effect of ion bombardment during their deposition by plasma chemical or physical vapor deposition (P CVD or PVD); and (3) nanostructured superhard coatings, such as heterostructures and nanocomposites. Diamond and polycrystalline c-BN prepared by high-temperature, high-pressure flux growth find important applications, whereas the applications of thin coatings prepared by P CVD and PVD remain limited [2]. Because these materials were discussed in a large number of reviews (see e.g. [2] and references therein), we shall concentrate on the extrinsically superhard materials prepared as several-micrometer-thick coatings. The emphasis will be on the hardness enhancement by energetic ion bombardment during the deposition in comparison with superhard, thermally highly stable nanocomposites. The discussion of heterostructures will be brief and limited to their hardening mechanism, which is fundamentally different from that of nanocomposites and coatings hardened by energetic ion bombardment.

The design of strong solids by the formation of the heterostructures was suggested by Koehler in 1970 [3]. It is based on hindering of the movement of dislocations by the formation of sharp interfaces between several nanometer thin epitaxial layers of materials with a large difference in elastic shear moduli. Already in his original paper, Koehler suggested that this mechanism of hardening remains valid also when one of the layers is amorphous. Later on, the concept was further extended to polycrystalline heterostructures. We refer to the excellent reviews of Barnett et al. for further details [4–6], emphasizing here only two important aspects: firstly, this mechanism applies only to crystal plasticity (i.e., dislocation activity), and secondly, atomically sharp interfaces are needed for this mechanism to work for superhard heterostructured coatings with hardness of ≥ 40 GPa (see [1,5] and references therein). Therefore, the deposition of such coatings requires a precise control of that interface by means of

shutters, and it is difficult to achieve in an industrial-like coating unit where “multilayers” with a diffuse interface rather than heterostructures are obtained. Although the multilayers bring improvement of the machining performance of coated tools [7], these coatings are distinct from the concept of heterostructures as formulated by Koehler because their interfaces are not sharp. The improved cutting performance is usually due to an improvement of their fracture toughness.

The hardness enhancement by energetic ion bombardment is due to a complex, synergistic effect involving a decrease of crystallite size, densification of the grain boundaries, formation of Frenkel pairs and other point defects, and built-in biaxial compressive stress. Depending on the crystallite size in the given material, these effects may hinder the dislocation activity.

Dislocation activity is absent in the superhard, thermally highly stable nanocomposites that consist of a few-nanometer small crystallites of a hard transition metal nitride (or carbide, boride, . . .) “glued” together by about one-monolayer-thin layer of nonmetallic, covalent nitride such as Si_3N_4 , BN (or in the case of carbides by excess carbon, CN_x , and others [1]). These coatings, when correctly prepared [1,8–10], possess an unusual combination of mechanical properties, such as a high hardness of 40 to 100 GPa, high elastic recovery of 80% to 94%, elastic strain limit of $>10\%$, and high tensile strength of 10 to ≥ 40 GPa that is approaching the ideal strength of flow-free materials [10,11]. Moreover, the nanostructure and the concomitant superhardness (measured at room temperature after each annealing step) remain stable up to ≥ 1100 °C [12].

Unfortunately, these nanocomposites were in the past often confused with ordinary hard coatings in which the superhardness is achieved by energetic ion bombardment during their deposition. Therefore, we shall devote the next section to the question of how to distinguish these two different mechanisms of hardness enhancement. The emphasis will be on the thermal stability and dependence of the hardness on the composition, which show a different behavior for the two different mechanisms of hardness enhancement. It will be shown that the hardening by energetic ion bombardment yields coatings with low thermal stability. Therefore, we expect that such superhard coatings will be only of a limited industrial use.

Recently, some researchers doubted our published data on the high hardness and suggested that our measurements were incorrect (see, e.g. [13] and reply in [14]). The question of correct measurements of the hardness of

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