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Toward hard yet tough ceramic coatings

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ABSTRACT

Over the past decades, hard and super hard ceramic coatings have been developed and widely used in various industrial applications. Meanwhile, an increasing number of studies have realized that the toughness is just as crucial, if not more, than hardness especially for ceramic coatings. However, hardness and toughness do not go naturally hand in hand. In other words, hard coatings usually are brittle and less durable while toughened coatings are of lower strength. For practical engineering applications, it is more desirable to have coatings with high hardness without sacrificing toughness too much. In this article, a review is presented on continuous progress to realize hard-yet-tough ceramic coatings from an angle of hardening as well as toughening.

Contents

1. Introduction

Ceramic coatings have been widely used in various engineering systems, for instance, protecting structural materials in harsh environment, prolonging life of manufacturing tools by improving wear/corrosion resistance and enhancing efficiency in energy storage and/or conversion. However, a low toughness limits the use of ceramic coatings. The most typical example is the sudden failure of machining tools with hard ($H > 20$ GPa) or super-hard coatings ($H > 40$ GPa) when they are in contact with large foreign impact [1]. To solve this problem, a number of works have been put forth to understand the origin of cracks in hard or super-hard coatings [2–5]. Many toughening methods have been developed to obtain coatings of both improved hardness and toughness [6,7]. In this article, we reviewed the academic journey targeting hard-yet-tough ceramic coatings in the past decades.

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2. Toward hard-yet-tough ceramic coatings

The foremost feature of a machining tool is high hardness. Hardness is the resistance of a material against plastic deformation. Experimentally, hardness is measured using a stiff and hard indenter. In most cases, the indenter is a diamond pyramid or cone of a given shape, which is pressed into the surface of the material with a given load P. After the load is removed, the remnant contact area A can be observed with a microscope. The load P over this contact area P / A is referred to as the indentation hardness H or, H = P / A. Nowadays, an automatic load–depth-sensing indentation instrument automates this process and the hardness is determined from analysis of the loading–unloading curve (i.e. Oliver–Pharr method [8]). It should be emphasized that the hardness values measured using indentation are sensitive to a number of factors: indenter geometry, tip rounding, indentation size effect and substrate condition in terms of surface roughness, surface oxidation and surface piling-up/sinking-in [9]. Toughness, on the other hand, measures the resistance to crack propagation or energy consumed to fracture a pre-cracked sample. If the fracture is abrupt (i.e., little plastic deformation) the material is referred to as brittle. If the fracture requires considerable plastic work and is accompanied with steady drop in stress before complete separation, the material is ductile, in other words, tough. To evaluate the toughness, a stress intensity factor K_{IC} (with a unit of MPa $m^{1/2}$) is generally used and can be readily determined according to ASTM standards [10,11]. The subscript "IC" stands for the mode I crack opening, where the crack opens under a normal tensile stress perpendicular to the plane of the crack. Over a long history in the development of fracture mechanics theory, many other fracture parameters, in terms of energy release rate, J-integral and crack-tip opening displacement/angle, are also important in experimental evaluation of toughness. The values of these parameters are technically influenced by factors, for instance, loading-rate, crack-tip constraint, fracture instability and environmental temperature [12].

An ideal coating would be hard yet sustaining a sudden impact without catastrophic failure. That is why hard-yet-tough ceramic coating has been the focal point of research for the last few decades. Needless to say, fabricating such a coating is difficult because of the natural conflict between hardness and toughness, or an increase of hardness usually goes at an expense of toughness. Fig. 1 shows the typical dilemma in hard ceramic coatings [6] and the engineer's dream ("hard yet tough"). To realize a "hard yet tough" ceramic coating, one needs to consider ways toward both hardening and toughening.

2.1. Ways toward hardening of ceramic coatings

Hardness is defined as the resistance of a material to plastic deformation. For coarse-grained ceramics, plastic deformation occurs predominantly through dislocation. Under this circumstance, increasing the resistance to the dislocation movement is the essence of hardening. However for fine-grained ceramics (e.g. ceramics with grain size less than 10 nm or amorphous phase), deformation by grain boundary microcracking and sliding (i.e. quasi-plasticity) is the major cause of strength decline [13]. As of yet, the evolution of cracking can be observed using advanced transmission electron microscopy (TEM) [14]. Currently, several major strengthening mechanisms are active in hardening ceramic coatings: (i) grain size refinement, (ii) grain boundary reinforcement, (iii) solid solution hardening, (iv) multilayer hardening and (v) ion bombardment/stressing hardening. It should be mentioned that some of the above hardening mechanisms are not applicable to amorphous coating systems, for instance, diamond like carbon (DLC), which is an important coating for industrial application due to its intrinsically high hardness. Hardening of DLC lies on the proper doping of foreign elements (e.g. Si, B, N, W, Mo, Ti and Ni), microstructural optimization (i.e. gradient or multilayer) and good control of hybridized carbon bond ratio (i.e. sp^3/sp^2). Limited by the length of the article, it is recommended to follow other related review papers or book chapters to better understand the mechanisms involved [15,16].

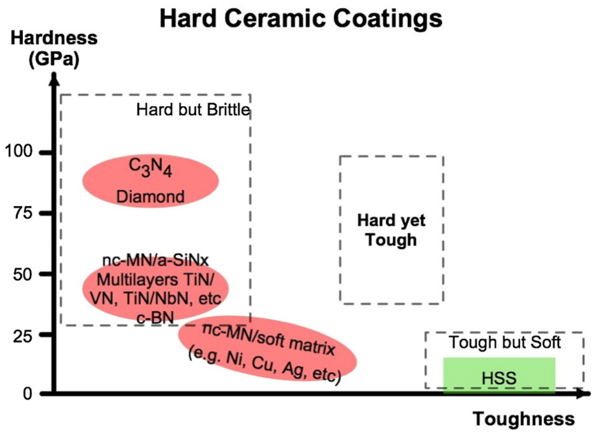

Fig. 1. Schematic of the current status of hard ceramic coatings. Re-plot from [6].

2.1.1. Hardening via grain size refinement

The dominant mechanism of plastic deformation of a crystalline material is the generation and motion of dislocations. Under an applied stress, existing dislocations and dislocations nucleated mostly from Frank–Read sources will move through the crystal structure until a grain boundary is encountered, where the large atomic mismatch between different grains creates a repulsive stress field to oppose continued dislocation movement. As more and more dislocations propagate to this boundary, a "pile-up" occurs. These dislocations will generate repulsive stress fields, countering the energy barrier to cross the boundary. As the energy barrier is overcome finally, dislocations move across the boundary, leading to a further deformation in the material. Decrease of grain size, however, decreases the amount of possible pile-ups at the boundary but increases the threshold of applied stress to move a dislocation across a grain boundary, thus increases strength. Theoretically, the stress needed for generation and motion of dislocations increases in inverse proportion to the distance of the pinning points in the dislocation network, and the strength increases with decreasing crystallite size are well governed by the Hall–Petch relation [17,18]

$$H = H_0 + kd^{-1/2}$$

where H_0 is the intrinsic hardness, d is the grain size and k is a constant parameter for a given material.

2.1.2. Hardening via grain boundary reinforcement

The Hall–Petch effect governs the coarse-grained materials (i.e. grain size d > ca. 30 nm). However, as the grain size is decreased down to the order of a few tens of or even a few nanometers, this rule ceases to function perfectly. Many researchers have reported an abnormal behavior and correlated it to an inverse or reverse Hall–Petch effect. As seen in Fig. 2, a maximum hardness is achieved when d is close to ca. 10 nm [4]. It is suggested that the traditional view of dislocation-driven plasticity in polycrystalline materials needs to be revisited and the way of achieving further hardening needs to be reconsidered. Several factors such as grain boundary sliding, creep diffusion, triple junctions, and impurities could contribute to reverse Hall–Petch effect. Among them, the grain boundary sliding via a certain accommodation mechanism is considered the most primary cause. When grain sizes are below a critical value (i.e. d < ca. 10 nm [19]), nanocrystallites contain a large fraction of atoms at interfaces. In this case, pile-up of the dislocations against grain boundaries are hardly expected to occur since the size of a Frank–Read source is smaller than the grain size. With a phenomenological mesoscopic model, Hahn et al. have predicted a critical grain size at which the grain boundary sliding becomes dominant [20,21].

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