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Current status of hard coating research

Min Ge, Jianbo Zhu, Rui Zhang, Chongyang Wang

Tianjin University of Technology and Education, Tianjin, 300222, China

Abstract: The emergence of hard coatings has improved tool productivity and service life and reduced machining costs while ensuring machining quality. In order to meet the development needs of difficult-to-machine materials and cutting processes, coating materials have been continuously developed and updated in terms of composition and structure, and the composition has developed from simple binary coatings (such as CrN, TiN) and ternary coatings (such as AlCrN, TiAlN, TiC) to multi-coatings, nanocomposite coatings and high-entropy alloy coatings, and the structure has changed from single-layer to multi-layer direction.

Keywords: Hard coating; Multi-coating; Nanocomposite coating; High-entropy alloy coating.

1. Introduction

In recent years, China has made remarkable achievements in the field of machining through continuous innovation, and cutting tools, as the "teeth" of machining, play an irreplaceable role in improving the technology level of manufacturing. The deposition of coating on the surface of the tool ensures the cutting quality and improves the productivity, to a certain extent, blocks the diffusion of elements between the workpiece and the tool, inhibits the chemical reaction between them, reduces the friction loss in the cutting process, and effectively alleviates the accumulation of chip tumors on the workpiece. Compared with traditional tools, coated tools show better advantages in terms of tool applicability and cutting accuracy, so it is of great significance to the development of manufacturing industry to continuously improve the design system and performance of tool coatings [1].

2. Binary and multiple coatings

With the continuous development of industry, surface treatment technology has been widely used in machining as an important way to improve the durability of components, tools and machine parts. In the past few decades, interest in transition metal nitride films has grown rapidly, and metal nitride coatings such as titanium nitride (TiN), chromium nitride (CrN), and zirconium nitride (ZrN) were the most widely used early binary coatings due to their excellent hardness and friction properties. Among these different metal nitrides, the TiN coating prepared by PVD technology belongs to the NaCl-type crystal structure, which has high hardness (2100-2300 HV), excellent lubricity, and good ductility [2] and is suitable for low-speed cutting fields. Especially in the cutting process, it can reduce the friction coefficient between the tool and workpiece, reduce cutting heat, and prevent the chip tumor from causing wear to the tool. However, during dry cutting machining, when the temperature is higher than 500 °C, TiN coating will oxidize rapidly and generate loose TiO_2, leading to deterioration of the mechanical properties of the coating. Compared with TiN, the hardness of CrN coating can reach 19 GPa, which has higher toughness and bond strength. The Cr element in the coating can easily react with oxygen to form a dense oxide film on the surface, which can protect and insulate the inner part of the coating, but the oxidation resistance temperature of CrN coating only reaches 700 °C, which is far below the melting point of steel and cannot be used as a protective coating for steel materials.

In more and more applications, the mechanical and frictional properties of binary transition metal nitride cannot meet the requirements, so there is an urgent need to design and develop a new hard coating to improve this situation. In order to further improve the hardness and anti-wear properties of CrN films, the method of alloying it with another metal element to form a ternary hard composite film was explored. crAlN coatings are obtained by adding Al elements to CrN, and the addition of Al elements induces the generation of Al_2O_3 protective film on the surface, which prevents oxygen from continuing to react with the interior of the coating and has a thermal and chemical barrier effect. wang et al [3] prepared CrAlN composite coatings with different Al contents by magnetron sputtering technique, and the CrAlN coating has a unique amorphous/crystalline nanocomposite structure compared with the CrN film, and also exhibits a relatively small grain size and dense structure, with a hardness of 33.4 GPa and excellent wear resistance. Ternary TiAlN coated tools show better cutting performance than binary TiN coated tools, especially under high speed cutting conditions, TiAlN coating can significantly reduce tool wear and friction and have longer service life.

3. New nanostructured coatings

The field of modern machining presents a trend of high speed, high precision, green and environmental protection. Traditional tool materials are difficult to adapt to the development requirements. The demand for mechanical properties of industrial components drives the development of nanostructured materials. The new nanostructured coating has attracted many researchers in recent years because of its “high hardness, strong toughness, low friction, self-lubrication”and other characteristics. As one of the new nanostructured coatings, PVD nanostructured coating is developing in the direction of nano-composite coating and nano-layer coating.

3.1. Nano-composite coating

A coating composed of two or more phases with different structures or compositions is called nanocomposite coating, which has a net-like crystal structure, and the structure consists of interfacial phase and basic phase, where the interfacial phase wrapping the basic phase is a common structure of nanocomposite coating[4]. As shown in Figure 1. Nanocomposite coatings are divided into three major categories[5]: (1)crystalline/amorphous composite coatings,such as nc-ZrN/a-Si_3N_4, nc-TiN/a-Si_3N_4, etc; (2)crystalline/metallic composite coatings, such as nc-ZrN/Ti, nc-ZrN/Cu, etc; (3)crystalline/crystalline composite coatings, such as nc-MeN/nc-C_3N_4, nc-TiCN/nc-TiNbCN, etc. The most widely used nanocomposite coatings, adding Si and B to the conventional hard coating nitrides (CrN, TiN, CrAlN), form a three-dimensional mesh structure of nc-MeN/a-Si3N4 or nc-MeB2/a-BN, in which the amorphous phase is wrapped around the nanocrystals and cannot form dislocations, and it is difficult to slip between grain boundaries, which inhibits the growth of grains The smaller grain size improves the hardness and toughness of the coating[6], reduces the oxygen diffusion rate, and retards crack generation. Therefore, the coating technology and application can reach a higher level, and these materials have also attracted widespread attention due to their excellent mechanical properties and thermal stability. nanocomposite coatings can be applied in extreme environments such as high temperature and corrosion in addition to their use under normal conditions, and given the variety of excellent properties, nanocomposite coated coatings are potential candidates for surface modification and extension of workpiece life. Chang et al[7] deposited three coating materials, CrAlSiN, TiAlSiN and TiAlN, on the tool respectively and found that: the first two have better cutting performance as well as red-hardness compared to the latter. Zhang Jiaojiao et al [8] studied the Zr-B-N coating, and with the increase of ZrB_2 target power, the coating appeared as a composite structure with amorphous a-BN wrapped with nanograins and enhanced wear ability.

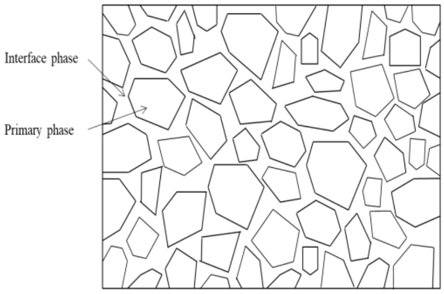

Figure 1. Schematic diagram of nanocomposite coating

3.2. Multilayer coating

Multilayer coating is a coating system formed by repeated deposition of two or more layers of materials with different properties as alternate layers. Compared with single-layer structural coatings, multilayer coatings combine the performance advantages of each layer and make up for the defects of single-layer coatings in mechanical, friction and other usage properties. The mechanical properties and morphology of multilayer coatings are closely related to the modulation period and modulation ratio. The modulation period is, as the name implies, the thickness of the coating deposited in one cycle, and the thickness ratio of each layer in the modulation period is called modulation ratio. With the use of hard coatings in the cutting field, single-layer coatings are more brittle under harsh conditions such as corrosiveness, resulting in poor adhesion and crack resistance of the coating to the substrate, causing serious damage to the workpiece and reducing the reliability of the engineering structure. To meet the machining requirements and obtain long-life hard coatings, Shuai et al [9] found that the latter exhibited higher plasticity, toughness and crack resistance by comparing TiAlN single-layer and Ti/TiAlN multilayer coatings, and the Ti layer in the multilayer coating enhanced the film/substrate bond through coordinated deformation, which further hindered crack expansion.

3.3. High entropy alloy coatings

In 1993, Professor Greer of Cambridge University, UK, proposed the "chaos principle" in Nature, which caused a sensation in the materials industry. It was pointed out in the paper that when there are more elements in an alloy, the more chaotic the internal structure will be, and the easier it is to form amorphous alloys. The concept of high entropy alloy (HEA) was first proposed by Yeh et al [10] in the early twenty-first century. Unlike previous alloys, high entropy alloys contain a variety of metals without embrittlement and are a new alloy material. To extend the range of alloy design, HE alloys may contain major elements with atomic fractions of each major element ranging from 5% to 35% (As shown in Figure 2), and extensive experiments have produced many alloy systems with simple crystal structures and extraordinary properties. Based on the experience with conventional alloys, more intermetallic compounds or other complex phases were expected to form in polyalloy systems. However, the phases obtained in all studied high-entropy alloys are also quite simple, and their high mixed entropy enhances the phase stability of the solid solution and drives the alloy to form simple solid solutions [11].

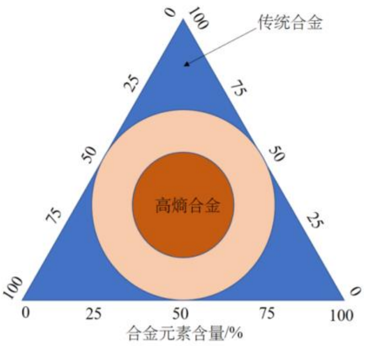

Figure 2. Schematic diagram of elemental content of high entropy alloys

The most important feature of high-entropy alloys is the high entropy value, and entropy can reflect the degree of chaos in the alloy system; the more chaotic the system is, the higher the entropy value, and the more orderly the entropy value is, the lower the entropy value. Following Boltzmann's (Boltzmann) hypothesis on the relationship between entropy and system complexity [12], the molar entropy change (coordination entropy) ΔS_{conf} in the formation of a solid solution from n elements with equal molar fractions can be calculated according to the following equation.

$$\Delta S_{conf} = -kIn\omega = -R\left(\frac{1}{n}In\frac{1}{n}+\frac{1}{n}In\frac{1}{n}+\cdots\frac{1}{n}In\frac{1}{n}\right) = RIn\frac{1}{n} = RIn \tag{1}$$

where k is the Boltzmann constant, ω is the system chaos, and R is the gas constant: 8.314 J/(K · mol). The entropy values ΔS_{conf} are 1.10 R、1.79 R、 2.20 R and 2.57 R when the main elements of equal molar fraction are taken as 3、6、9 and 13, respectively, and the higher the number of elements, the higher the entropy value and the entropy growth rate gradually decreases. In fact, considering the effects of vibration, electron and torque randomness, the mixed entropy variation of the equal molar fraction alloy is higher than the calculated value.

The composition of the high-entropy alloy is complex, and the equimolar concentration of each component gives the alloy a crystal structure, strengthening mechanism, high-temperature resistance, and corrosion resistance that are different from those of conventional alloys. Researchers have summarized four core effects: thermodynamic-high entropy effect, structural-lattice distortion effect, kinetic-slow diffusion effect, and characteristic-cocktail effect.

(1) High entropy effect: Because the high entropy alloy contains a variety of primary elements, the mixed entropy generated during the formation of solid solution is higher, far exceeding the entropy value of conventional alloys, increasing the system chaos, reducing the Gibbs (Gibbs) free energy for the formation of solid solution phases, and making it easier to form simple solid solution phases hcp, fcc, and bcc structures, especially at high temperatures where the high entropy effect is more significant. Taking the as-cast $CuCoNiCrAl_xFe$ alloy system [10] as an example, only simple face-centered cubic structures existed in the alloy when the aluminum content increased from 0 to 0.5, and body-centered cubic structures appeared when the aluminum content exceeded 0.8, and even then only two structural simple solid solution phases, bcc and fcc, were identified. Zhang et al [13] pointed out that multi-principal element alloys can only form body-centered cubic (BCC) or face-centered cubic (FCC) solid solution simple phases, and the number of phases formed is much less than the maximum number of phases allowed by Gibbs' phase rule.

(2) Lattice distortion effects: Zhao et al [14] quantitatively evaluated lattice distortion in a series of single-phase, bcc-structured, Nb-based, and other atomic alloys and found that the magnitude of lattice distortion in bcc alloys does not necessarily increase with the number of components and is greater than the degree of lattice distortion in fcc-Ni-based and other atomic alloys; in removing the strength contribution from all possible mechanisms, the current per c- Nb-based alloys lattice distortion can significantly produce much higher hardening effects than in fcc-Ni-based isoatomic alloys, and much higher frictional stresses in bcc-HEAs compared to fcc-HEAs, which may be attributed to the presence of smaller dislocation nuclei. The present results suggest that the significant strength enhancement of high-entropy alloys may be caused by high frictional stresses, which in turn are caused by lattice distortions.

(3) Slow diffusion effect: The existence of multiple primary elements in high entropy alloys causes diffusion crowding, which increases the diffusion difficulty and affects the long-range diffusion. On the one hand, under high temperature conditions, high entropy alloys have good thermal stability because it is difficult to recrystallize and the grains will be refined, on the other hand, the slow diffusion rate causes the generation of supersaturated solid solution phase and precipitation of nanocrystalline phase in the alloy, and the precipitation strengthening improves the hardness and strength of high entropy alloys. Yeh [15] studied the vacancy formation and composition distribution in high entropy alloys and compared the pure metal, stainless steel and high entropy alloys diffusion coefficients of elements in the three types of alloy systems and found that the order of diffusion rates in the three types of alloy systems was: high entropy alloy < stainless steel < pure metal. The sluggish diffusion effect promotes the generation of nanoscale precipitates due to the easier growth of nuclei more slowly, as exemplified by the as-cast CuCoNiCrFe alloy, where nanoprecipitates of different diameters (d=7~50 nm) were observed by transmission electron microscopy images, close to the FCC phase in the form of spinodal plates, and it was also found that the microstructure of certain high-entropy alloys is very complex and can include nanoprecipitates, ordered/disordered solid-solution phases, and even amorphous phases.

(4) The “cocktail” effect [16]: since high-entropy alloys generate single, two, three, or more phases during composition and processing, the overall alloy properties come from the overall contribution of the constituent phases, which is related to the size, shape, distribution, phase boundaries, and properties of each phase. For example, if more lightweight elements are used, the overall density will decrease; if more oxidation-resistant elements are used, the oxidation resistance at high temperatures can be improved; if an element such as Al is added, it has a strong bond with other elements present, which will promote the formation of the BCC phase, and the strength will increase. Therefore, it is critical for alloy designers to understand the relevant factors before selecting the appropriate composition and process.

4. Conclusion

This paper introduces the development trend and research progress of hard coatings, describes the evolution trend of coating structure, and lays the foundation for the development of high-performance hard coatings.

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