

Review Article

Nanocomposite Coatings : Novel Approach in Thin Film Industry

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Abstract

From the above review it can be concluded that nanocomposite coatings represent the state of art in coatings today. The high hardness of the nanocomposite coatings, especially in nc-ALTiN/a-Si₃N₄ is mainly due to the phase segregation process that forms c-ALTiN rich phase and a-Si₃N₄ rich domains. The three dimensional skeletal structure of silicon nitride and the nanocrystalline grains of metal nitrides reduce and hinder the movement of dislocation. Several studies have been carried out to study the oxidation behaviour. However there is still a need to study the wear mechanism and behaviour of these coatings under dry machining in hard cut materials such Austenitic stainless steel, titanium alloys etc.

Keywords: *Nanocomposite coatings, hardness, oxidation resistance, wear resistance*

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The industries in near future may have to compulsorily adopt dry machining, in order to felicitate the protection of environment and reduce the occupational hazards. Dry machining has several advantages such as reduced cleaning, no pollution to the atmosphere with an added benefit of reduced machining costs. Coolants used in machining sum up nearly 15 to 30% of the total machining cost [1,2].

Dry machining is more demanding and requires tougher grade of tool material, such as K grade type of cemented carbides with suitable coating [1]. In the past decade there has been significant development in the area of thin film coatings for cutting tools. To start with only Titanium Carbonitride (TiCN) and Titanium Nitride (TiN) were the only two

types of coatings available till the late 1980. Later to which Titanium Aluminium Nitride (TiAlN) was added along with Chromium based coatings such as Chromium Nitride (CrN). The oxidation resistance of these coatings were limited to a maximum of 800 °C. By 2011 there were more than 100 commercially available coatings which were used for various applications ranging from the cutting tools, forming tools to the components used in various applications [2–4].

Of these the nanocomposite coatings have captured the eye of market for their high oxidation resistance and wear resistance. In this work a review of the design principles, different techniques used to produce thin films, high temperature oxidation behaviour and applications of

nanocomposite coatings are being discussed.

DESIGN PRINCIPLES AND TECHNIQUES TO COAT NANOCOMPOSITE THIN FILMS

It is well observed from the Hall-Petch model that the strength of a material decreases as the crystallite size of the material decreases. Many metals, alloys and oxides obey this relationship. However this theory was not sufficient to explain the hardness of the nanostructures. Three other theories were proposed to explain the strength enhancement in nanostructures. Koehler's theory proposed that strength enhancement in heterostructures could be achieved between two layers of metal A and B with high and low elastic modulus respectively. The dislocations will only be formed in B and when applied stress exceeds critical value then the dislocations will be forced to cross the interface B/A due to their repelling image in A [5,6].

One more possible explanation was given by Fermi surface-Brillouin zone interaction. In this interaction a composition modulation will create artificial Brillouin zones at $(k \pm q)/2$ where k is the reciprocal lattice vector and q is the wave vector that will create artificial Brillouin zone. This interaction leads to change in electronic structure which leads to increase in hardness. The third mechanism proposed by Jankowaski and Tsakalalos contributed to the Koehler's theory [6].

These theories led to the formation of a basic idea of a nanocomposite coating which could be achieved by following conditions:

- i) Formation of a binary strong binary compound by using quaternary or ternary systems. The phase segregation process is automatically modulated process during fabrication itself. These systems are much easier to fabricate than the heterolayer systems.
- ii) To use low temperature deposition technique to prevent the inter diffusion as in heterolayered structures which leads to reduction in hardness.
- iii) By using an amorphous tissue with high elastic modulus and three dimension skeleton, the lattice mismatch between polycrystalline materials can be avoided. Furthermore, any dislocations in nanocrystals that arise cannot propagate into the amorphous phase and vice versa. Based on these facts it was observed that materials of refractory nitrides that include TiN, ZrN, VN etc. along with amorphous Si_3N_4 are most promising candidates. Silicon nitride is used because of its high elastic modulus of nearly 385 GPa. Moreover, even at very high temperatures these phases do not mix. At low nitrogen activity stable silicates are formed [2, 6–7]. This led to the formation of nc-MeN/ Si_3N_4 coatings [6–7].

The oxidation behaviour of these coatings is investigated by several researchers. Chen *et.al.* studied the oxidation behaviour of AlTiSiN systems at four temperatures 900, 1100, 1200 and 1450 °C respectively [8]. It was seen from the diffraction studies that at high temperatures the coating decomposed into cubic rich TiN and wurtzite-AlN phases. However in the as deposited state wurtzite phase dominated the cubic phase leading to decrease in hardness. Temperatures above 1100 °C led

to the formation of cubic rich phases which increased its hardness.

Further TGA studies reveal that oxidation resistance offered by these coatings is mainly due to retardation in forming α - TiO_2 at the expense of r - TiO_2 which forms porous oxide layer. In addition to this, at

high temperatures these coatings are found to exhibit a dense top layer of Al_2O_3 with dense Titanium silicon oxide rich sub-layers. These layers prevent the inward diffusion of oxygen atoms and outward diffusion of metal atoms. Similar studies are made by Chen *et al.* [9].

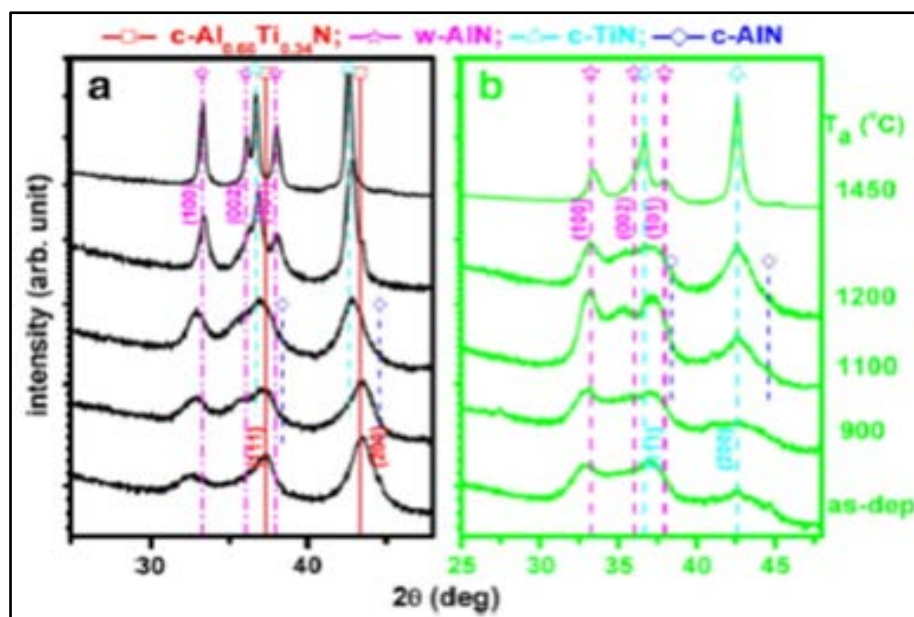


Fig. 1: XRD Patterns Observed at Different Annealing Temperatures for AlTiN and AlTiSiN Coatings [8].

Samani *et al.* made a study on thermal conductivity of TiAlSiN nanocomposite coatings for different $(\text{Al}+\text{Si})/\text{Ti}$ ratios by photo thermal reflectance (PPR) technique to explain the oxidation resistance and wear resistance properties of these coatings [10]. It was established that incorporation of $(\text{Al}+\text{Si})$ significantly dropped the thermal conductivity to nearly 3 W/mK as shown in Figure 2. Phonon transport means heat transport in crystalline solids and phonon scattering means the mean free path of phonon. Introduction of dopant atoms reduces the mean free path of phonon in lattice; also

dopant atoms reduce the columnar structure of coatings.

However there is a limit to the addition of amorphous phase, as reported by Zhi-wen *et al.* Si beyond 15% reduces the hardness due to the increase in amorphous phase, the phase grain separation and blocking effect of grain boundaries become limited [11]. Several methods are described to deposit thin film coatings [1–12]. Of these the physical vapour deposition (PVD) has taken edge over the years. Chemical vapour deposition (CVD) was quite a popular method but it possessed certain limitations. CVD is mainly a high

temperature deposition process, may be about 1000 °C, and was limited to carbide tools. Introduction of Ammonia gas reduced the process temperature however such contained noticeable amount of chlorine which can cause flaking and corrosion on exposure to air. Among the PVD techniques the arc vapour deposition

is most dominantly used in industries due to its high ionization potential, uniform coating properties and dense structure. However, there are certain drawbacks in this process, which include formation of droplets of molten metal and uncontrolled movement of Cathodic spot over the surface.

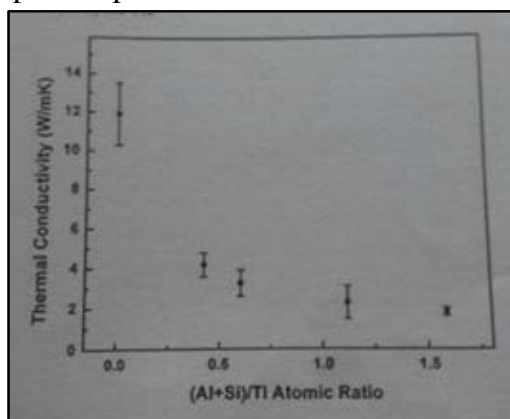


Fig. 2: Drop in Thermal Conductivity with Increasing (Al+Si)/Ti Ratio [10].

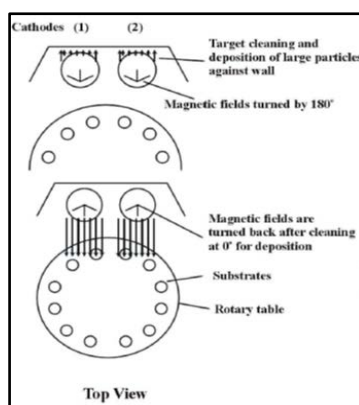


Fig. 3: Virtual Cleaning Process in LARC [12].

This problem is overcome by lateral rotating cathodes (LARC) process. In this technology two laterally rotating cathodes are in continuous rotation and a turnable magnetic system allows the cleaning of target by turning magnetic field and plasma towards the wall of chamber. Further without disturbing the plasma, the magnetic system rotates back and the deposition starts. This process is called Virtual Shutter ® by PLATIT, a leading PVD equipment manufacturers from Swiss. This process ensures smooth

coating, with uniform erosion of cathodes and deposition of coatings.

CONCLUSIONS

The call for high productivity, quality in machined surfaces, and reduced machining costs have put a demand on the improved cutting tools. The recent advancements in development of nanocomposite coatings which consist of crystalline and amorphous phase have made dry machining at high speeds with quality in machined parts a reality. The driving force

behind the superhard structure of such coatings is phase segregation mechanism. In this work, a review of the design principles of nanocomposite coatings and their oxidation behaviours in high temperatures are being discussed.

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