Materials and vapour-phase techniques for the synthesis of ceramic coatings

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A survey on recent advances in the synthesis of hard ceramic coatings is given, including materials processes and techniques. Emphasis is made on the parameters which control the coating properties (crystalline structure, morphology, etc), namely arrival energy of the atoms to the growing surface and substrate temperature. Some relevant coating materials are discussed in relation to their applications either as hard protective coatings or with decorative purposes, namely: the family of metal nitrides, carbides, and oxides, in different layer structures (monolithic, multilayers and nanocomposites) and ternary compounds of the BCN system.

Keywords: Ceramic coatings, physical and chemical vapour deposition, hardness.

Materiales y técnicas de fase vapor para la síntesis de recubrimientos cerámicos

Se hace un descripción de los avances recientes en la síntesis de recubrimientos duros de tipo cerámico, depositados mediante técnicas de deposición en fase vapor. Se dedica especial atención a los parámetros del proceso de deposición que controlan las propiedades finales de las capas (estructura cristalina, morfología, etc), tales como la energía de llegada de los átomos a las superficie en crecimiento, y la temperatura. Finalmente, se hace una revisión de los materiales más relevantes en lo que se refiere a sus aplicaciones como recubrimientos duros y protectores, o como recubrimientos decorativos, entre ellos, la familia de los nitruros, carburos y óxidos metálicos, depositados en diversos tipos de estructuras (monolíticas, multicapas y nanocomposites), y los compuestos ternarios del sistema BCN.

Palabras clave: Recubrimientos cerámicos, deposición física y química de fase vapor, dureza.

1. INTRODUCTION

Ceramic coatings obtained by vacuum techniques have found widespread use in multitude of applications in modern technology. Most of these applications are aimed towards the protection of surfaces under working conditions from aggressive environments, which may cause degradation and fatal wear (corrosion wear, abrasion and erosion wear, scratch wear, etc). Examples of these applications appear in a large variety of technological sectors, such as hard and tribological coatings for machine parts and cutting tools, thermal barriers for turbine blades, decorative coatings for automotive and domestic items including tiles, selective films for architecture glass panels and for optical systems, protective coatings food packaging envelops and bottles, functional films for biomedical prosthesis, etc.

Despite the diversity of functions of the coatings, all these applications have in common strict requirements for the constituent materials: Chemical stability at moderate or high temperatures in aggressive environments (i.e. they must be corrosion resistant), medium/high hardness (> 20 GPa) and toughness, high wear and scratch resistance, low friction coefficient (in the case of tribo-coatings), absence of internal stresses, good adherence with the substrate, etc. It is evident that the achievement of these requirements leads to the need

of materials with good thermal and mechanical properties, i.e. close or even better than those of bulk structural ceramics.

In this paper, we discuss the materials and vacuum deposition techniques used for the preparation of ceramic films and coatings, i.e. metal nitrides or carbides as well as some carbon-based compounds, which have been extensively investigated in the last decades. These materials are currently being applied either for the protection or decoration of mechanical parts and domestic pieces, including ceramic tiles.

2. MATERIALS AND PROPERTIES OF CERAMIC COATNGS

From the point of view of their ceramic properties, the coating materials can be classified according to the nature of the atomic bond. Following Holleck's scheme (1), three different groups can be considered: pure covalent, pure ionic or pure metallic-type bonds. Covalent materials (diamond, boron nitride, silicon carbide, etc) are characterised by strong and directional bonds, with a high degree of overlapping and short bond distances between atoms. Every atom is

Bol. Soc. Esp. Ceram. V., 46, 4, 171-176 (2007)

171

surrounded by 3-4 nearest neighbours, giving the crystalline lattice a high degree of interconnectivity. As a consequence of the strong bond, these compounds usually exhibit good chemical inertness, high hardness and excellent thermal and optical properties. However, they are difficult to synthesise and, besides, the coatings are generally subjected to intense internal stresses, which poses severe limitations to the adhesion on common substrates.

The group of oxide ceramic materials (silica, alumina, zirconia, ceria, etc) is made of crystalline oxides, where the oxygen anions have a large ionic radius as compared to the metal cations. The bond strength of the ionic bond is inferior to the covalent one and, consequently, its chemical stability and hardness is lower. Nevertheless, these compounds are generally in its higher oxidation state, thus offering outstanding oxidation resistance to the underlying metal substrates even at high temperatures.

Finally, the third group is occupied by the metallic-like materials, comprising a wide group of nitride, carbide and boride compounds or certain transition metals, such as Ti, Al, Cr, Zr, W, Nb, etc. The atomic bond in this case resembles that of pure metals, due to the overlapping between the atomic orbitals of the cations, with much large ionic radii as compared to the anions (N, C, B) in the crystalline structure. The properties of these compounds derive from this peculiar bond structure: they show metallic character (i.e. high electrical conductivity, metallic lustre, with different vivid colours, and some plasticity) and, at the same time, they offer relative high hardness, chemical stability and adhesion to metal and ceramic substrates. Besides, these metallic-like compounds are easy to prepare by vacuum deposition techniques and for these reasons they are extensively used in the coating technology.
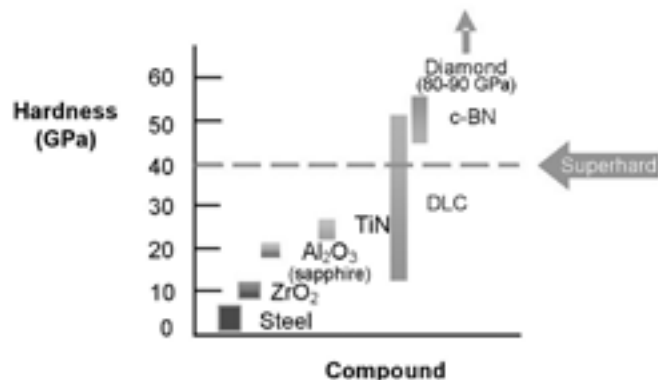

Fig. 1- Hardness values of some typical coating materials

Hardness, i.e. the resistance to plastic deformation, is generally used as a key parameter to evaluate the quality of the ceramic material, since it is directly linked to its wear properties as well as to the chemical stability and inertness. Fig. 1 shows the range of hardness values of some typical coatings used for mechanical protection. The hardness of diamond and cubic boron nitride (c-BN) are well above of the so-called superhardness limit (40 GPa). In other allotropic forms, the atomic bonds of carbon may show either a tetrahedral coordination, as in diamond, or a triangular coordination, as in graphite (through hybrid sp^3 or sp^2 orbitals, respectively), giving rise to a large variety of coating materials, known generically as 'amorphous carbon' (a:C) or 'diamond-like carbon (DLC). In addition, DLC compounds may incorporate large amounts of hydrogen originated from the chemical synthesis. The hardness of these DLC compounds covers a wide range of values depending on the percentage of the graphite or diamond bonding in their atomic structure, as well as on the hydrogen content typically incorporated during the deposition process (see below). Finally, the ionic and metallic-like compounds usually exhibit hardness well below diamond and c-BN, i.e. around 25-30 GPa, as a consequence of their weaker molecular bonds.

It is important to realise that in all of these materials the hardness and other mechanical properties are strongly dependant not only on the microstructure and morphology, but also on the coating structure. As we shall discuss later, different coating layers (graded layers, multilayers and nanocomposites) have been designed to improve the mechanical properties.

3. VACUUM DEPOSITION TECHNIQUES AND PROCESSES

Vacuum deposition techniques rely on the condensation of a vapour material on the substrate surface, hence the name 'vapour phase techniques' as they are known. The need of a vacuum (or an inert atmosphere) is strictly required since most of the vapour molecules are extremely reactive in air. In the case of the 'Physical Vapour Deposition' or PVD techniques, the source material is a solid which, by heating at high temperatures or by bombarding with ions, may supply a stream of vapour atoms to be deposited on the substrate surface. In the case of 'Chemical Vapour Deposition' or CVD techniques, the source is a liquid, a gas or a mixture of them, directly fed into the reactor, where reaction occurs, yielding a solid product in the form of a coating. The microscopic atomic mechanisms giving rise to the growth of the film (namely, species transport in the gas phase, gas reaction either in the gas phase or at the surface, the arrival and adsorption on the surface, surface diffusion, nucleation, etc) are very complex and depend on the experimental parameters: nature and chemical state of the species, rate of arrival to the surface, arrival energy of the atomic or molecular species, surface temperature, chamber pressure, etc. All these parameters determine in its turn the properties and characteristics of the final coatings (morphology, crystallinity, stoichiometry, etc.)

The atom (or molecule) arrival energy and surface temperature are perhaps the most important parameters in the first stages of nucleation of coatings since they determine to a large extent the mobility of these particles on the substrate surface and hence the probability to reach a site with the highest bonding energy, where they may become permanently attached. Once the film growth starts, the new species may diffuse through the grain boundaries or even through the inside of the grains. The activation energy for all these processes scale with the melting temperature of the material coating (T_m), so that the higher is T_m, the lowest is the species diffusion in any of these processes. On the contrary, the deposition temperature, T, favours the species mobility and hence the diffusion distance on the surface.

According to the model of Movcham and Demchysim (2), in the case of metal coatings, the ratio T/T_m controls the mobility of the atomic species on the surface and therefore the coating morphology. For increasing T/T_m values, the morphology may adopt successive forms: a low-density dendrite structure

with voids, columnar grains with some voids, a denser structure made of microcrystalline and columnar grains and, finally, equiaxed crystalline grains, whose diameter may reach the film thickness. Lately, Thornton considered also the effect of the deposition pressure on the arrival energy of the atoms in the particular case of the sputtering discharges (3). Due to the scattering of the vapour atoms with the inert atoms of the discharge (generally Ar), the atom arrival energy and the surface mobility are in this case lower than in vacuum, giving rise to a shift in the succession of zones for increasing T/T_m values. Fig. 2 shows a scheme of the morphology changes that may appear in coatings grown at different normalised temperature values, according this 'TMD zone model'.
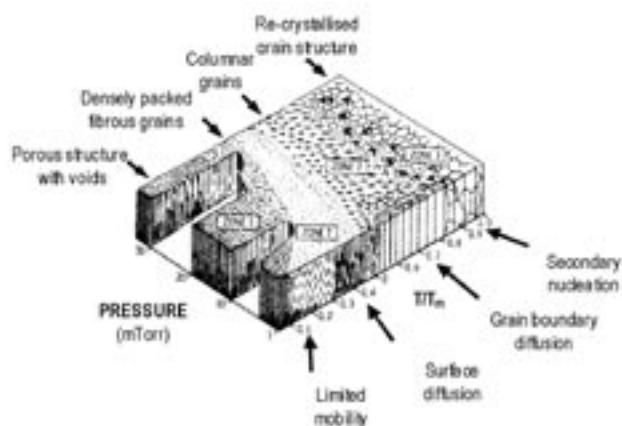

Fig. 2- Morphology changes for films growth at different T/T_m according to the TMD zone Model (adapted from ref. (3).

The above facts emphasises the necessity of increasing the surface mobility of the incoming species during the film growth to obtain denser materials with improved performance. Most of the deposition techniques are addressed to increase the surface mobility of the arrival atoms (or adatoms), either by increasing the deposition temperature or by some sort of ion bombardment on the growing surface.

a) PVD Techniques:

The different PVD techniques can be classified according to the energy source for the phase change from solid to vapour: pure thermal, ion bombardment and photon (laser) irradiation. Electrical Joule heating is perhaps the simplest and commonest method of thermal evaporation, although limited to metals of low evaporation temperature. Electron beam heating is used as an alternative for materials of high melting point (fig. 3a). Both methods present difficulties to evaporate alloys and, in addition, the vapour atoms have relatively low arrival energy (0,1-0,4 eV) at the substrate surface thus giving rise to low dense coatings.

Alternatively, the bombardment of a material target with high ions in the energy range of $10^2 - 10^3$ eV is an efficient way to produce a vapour without the need of heating. The evaporation is achieved through a mechanism of momentum transfer between the bombarding ions and the atoms of the target surface. This phenomenon produces the ejection of the atoms from the target, which eventually may condensate on the substrate as a coating. The high arrival energy of atoms at the surface in this case (~ 4-8 eV) makes the films denser and more adherent to the substrate.
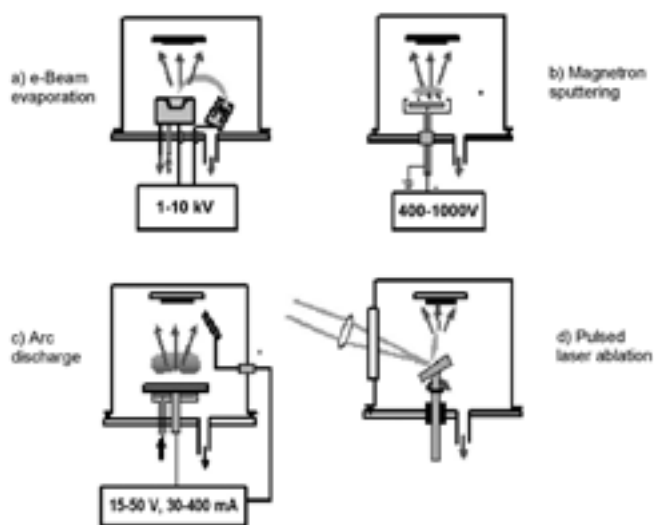

Fig. 2- Scheme of some typical PVD techniques: a) electron beam evaporation, b) magnetron sputtering, c) arc discharge, d) pulsed laser ablation,

There is a large variety of methods based on this procedure, among them the most popular are sputtering and cathodic arc discharges (Fig. 3b and 3c). In both techniques, a plasma discharge is produced between two electrodes, in an inert gas atmosphere (Ar). The target material is the cathode of the discharge so that it is sputtered by the Ar ions. Arc discharges are very effective to produce compact films due to the intense bombardment with the ions of the discharge. In some cases, the substrates are biased at negative voltages to attract the atoms from the plasma discharge thus increasing their arrival energy on the substrate surface. The temperature of the process is normally kept low, and the evaporation rate is easily controlled, making these techniques very attractive in mass production.

In another approach, the plasma is produced inside an independent source (ion source) and ions of the plasma are extracted an accelerated up to a definite energy as beam. These ion beam sources are often used in parallel with other evaporation sources in order to impart a high energy on the evaporated atoms arriving on the surface (Ion Beam Assisted Evaporation, or IBAD). The advantage of IBAD systems is the possibility to control the bombarding parameters, i.e., ion energy and dose, angle of bombardment, etc, which in turn determine the different effects that take place on the film growth. However, IBAD methods are difficult to implement at large scale fabrication.

Finally, laser beams are also used as a source of energy for the production of vapour atoms. In the laser ablation technique, a pulsed laser beam of high power is focused on the surface of a target material. Every laser pulse produces local melting and evaporation of the surface atoms. Laser ablation, along with arc discharges, which shares some similarities with, produces large clusters of excited atoms so that the arrival energy on the substrate surface is extremely high. The films are then dense and well adhered to substrate (Fig. 3d).

b) CVD Techniques:

In the CVD techniques, a mixture of gas vapours, coming either from liquid or gas sources, are introduced into a chamber, previously evacuated or purged with an inert gas. There they react to produce either a fine powder (homogeneous reaction

in the gas phase) or a solid coating covering the reactor walls and substrate surface (heterogeneous reaction on the surface). In order to avoid the production of powders, which may disturb the thickness homogeneity of the coating, the heterogeneous reaction is promoted by decreasing the gas pressure in the chamber. The by-products of the reaction are finally extracted from the reactor by the vacuum pumps.

There is a large number of variants of the CVD processes and they are classified according to the activation method of the reaction, which otherwise would proceed at low rates (4). Among them, thermal heating and plasma discharges are generally used although intense radiation with UV light or laser lamps is also applied. Depending on the gas pressure and frequency of the plasma discharge, many different techniques have blossomed in last decades: Low-Pressure CVD or LPCVD, Radiofrequency CVD or RFCVD, Microwave-CVD or MWCVD, Electron Cyclotron Resonance CVD or ECR-CVD, among others. Since there is not way to excite a unique reaction path by these methods, the final deposit incorporates very often a certain fraction of radicals and other by-products, thus degrading the coating purity. Despite of this, CVD techniques are able to synthesise chemical compounds difficult to obtain by other methods, and the thickness of the deposited layers are very homogeneous even on 3D samples of complex geometry.
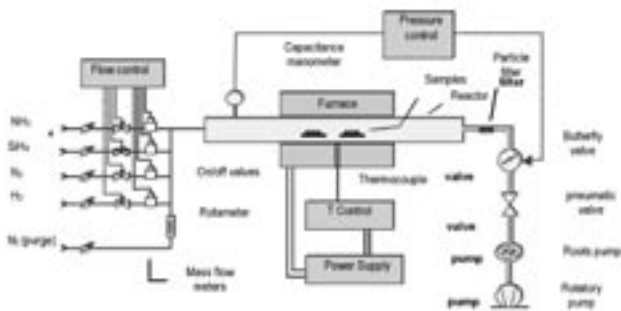

Fig. 4- Scheme of a typical CVD system used for the deposition of silicon nitride coatings using silane and ammonia as gas precursors.

Figure 4 shows a scheme of a typical LPCVD system, designed for the deposition of silicon nitride coatings using silane and ammonia as gas precursors. These gases are handled and mixed through appropriate valves and gas flow controllers, and then they are fed into the reactor, which is heated by a furnace up to 800 ºC. During the deposition process, the gas pressure in the reactor chamber is kept constant automatically at a fixed value by means of a butterfly valve actuated by a capacitance manometer. The gases are evacuated through a pumping system composed of a Roots pump (of high pumping rate) backed with a rotatory pump.

The application of plasma discharges allows the deposition reaction to occur at much lower temperatures than in conventional LPCVD reactors. The most efficient energy transfer to the gas molecules in plasmas discharges takes place when the plasma is excited in alternate electric fields of very high frequencies, in the range of the mega- or giga-hertz. In the later case, the presence of a magnetic field of appropriate intensity (a few Gauss) causes the electrons of the discharge to rotate around the field with a frequency in resonance with that of the oscillation of the electric field

(Electron Cyclotron Resonance, or ECR). Under the resonance condition, the plasma density (concentration of charged particles) is maximum, thus optimising the energy transfer to the reacting molecules.

4. MONOLITHIC AND NANOSTRUCTURED COATING MATERIALS

Since the advent of the hard coating technology in the 1970's decade, TiN has played a key role in many applications, because it is easy to synthesise by PVD and CVD methods and besides it combines a relative high hardness (~20 GPa) with good chemical stability up to ~ 700 ºC, good adhesion to metallic substrates and a brilliant golden colour. In a later stage, TiAlN, TiCrN, TiCN and other nitride and carbonitride alloys were also applied to improve the oxidation resistance of TiN compounds. In parallel, the properties of carbon based materials, as diamond or DLC, were also exploited in other applications, due to their low friction coefficient. However, these materials are subjected to high internal stresses and, besides, they react with oxygen at relative low temperatures (~ 400 ºC). Both groups of metallic-like and covalent materials were the first generation of monolithic ceramic coatings.

In later developments, the coating properties and more particularly hardness, were optimised by appropriate mixing of these compounds in different coating structures: nanometric multilayers and nanocomposites, making it possible to increase both hardness and toughness to much higher values that those expected from the rule of mixtures. In the following, we discuss the coating materials more commonly used in two industrial applications, hard and decorative coatings, where the ceramic properties of the materials (i.e. hardness, scratch resistance, and corrosion resistance) plays a key role.

a) Carbon-based monolithic coatings

Due to the high temperature requirements for diamond deposition by CVD techniques (~900 ºC) and the difficulties to nucleate the films on ferrous substrates (as consequence of the high solubility of C at the deposition temperatures), many efforts have been addressed to synthesis of other hard covalent compounds, as cubic BN and B_4C, which can be deposited at much lower temperatures (< 450 ºC). Despite being softer than diamond, they are more stable in oxidising atmospheres offering better compatibility with metal substrates. However, they also suffer from other disadvantages, among them the occurrence of high internal stresses in the case of c-BN and the low thermal conductivity and brittleness of the B_4C films. The possibility of synthesising crystalline C_3N_4 films, predicted to be even harder than diamond, has not been realised yet. Nevertheless amorphous CN_x coatings show low friction and wear rate and are being exploited as solid lubricant coatings for hard discs and recorder heads (5).

Both, DLC and CN_x films can be obtained by CVD methods from CH_4/Ar and $CH_4/Ar/N_2$ gas mixtures, respectively. The ECR-CVD technique allows intense bombardment with the positive ions of the discharge, accelerated to the samples by the application of a negative voltage bias. For a bias of –100 V(corresponding to an ion energy of about 100 eV), amorphous carbon films present a fullerene-like structure of curved graphitic planes (sp^2 bonds), leading to good mechanical and tribological properties (hardness 20 GPa, friction coefficient < 0.1). The wear rate, 10^{-7} mm^3/Nm observed in this material is close to that found for ta-C films with much higher sp^3 content (6).

Finally, ternary BCN compounds have been hypothesised to combine the advantages of C and BN, namely, extremely high hardness, chemical stability at high temperatures, and low residual stresses. Interestingly, carbon and boron nitride crystallise with the same crystalline structures (cubic and hexagonal), where the -C-C- pairs are isoelectronic with the -B-N- pairs. In both cases, the cubic structure present superior characteristics as compared with the hexagonal or amorphous forms. Therefore, it is reasonable to assume that the substitution of -B-N- pairs by isoelectronic -C-C- pair in the cubic BN lattice will render a cubic ternary BC_xN compound with intermediate properties between that of diamond and c-BN.

In a previous work (7), we have shown the possibility to synthesise BCN materials by IBAD techniques, either by evaporation of B_4C lumps by a single e-gun evaporator or by independent evaporation of B and C by a dual e-gun evaporator, in both cases with concurrent N_2^+ ion bombardment (range 100-1000 eV). The dual evaporator allows to obtain different films within a wide C/B ratios, necessary to attain true ternary compounds within the BC_xN stoichiometry. We have observed that the increase of the C flux during evaporation gives rise to an increase of the C content in the films and produces, with Ar bombardment and annealing, a transformation of the bonding structure from a hexagonal-like configuration to a diamond-like BCN material. This fact is indicated by the increase of sp^3 hybrids that improves the mechanical properties of the BC_xN films, i.e. a low friction coefficient and wear rate. The hardness and elastic modulus are 17 GPa and 170 GPa, respectively. For C contents over 70%, the wear rate of BCN coatings is similar to that of the ta-C. The advantage of BCN films over ta-C is the lack of internal stress since they do not peel off even for a film thickness above 1 μm, what is a promising result for future industrial applications.

b) Metal nitride and carbide based materials (layered and multilayered structures)

The most common materials used as hard and decorative coatings are based on certain metals and alloys (Al, Ni, Cr, etc) as well as the oxides nitrides and carbides of the four column of the periodic system (i.e. the transition metals Ti, Zr, Hf). The nitrides and carbides exhibit a metallic- covalent atomic bond, combining a high meeting point, high hardness and good thermal and chemical stability, as discussed above. Among them, titanium and zirconium nitrides are the most successful materials as decorative coatings for metal, ceramic and polymer components. Their golden colour makes it possible the use as alternative material instead of gold, since they are more abrasion resistant.

For decorative purposes, the addition of a second element (metal oxide or carbide) widens the range of obtainable colours and, at the same time, improves the mechanical properties. Thus, binary and ternary systems, such as TiAlN, TiZrN, TiAlZrN and TiAlVN, show important advantages with respect to hardness, wear and corrosion resistance, and the colour can be controlled either through the nitrogen content in the compound or the relative metallic content (8,9). For instance, the colour of TiAlN is determined by the relative atomic percentage of Al and Ti in the compound. The composition can be easily controlled during the deposition process by PVD techniques (sputtering or arc evaporation), using either two sources or one target with the appropriate mixture of the metals. Furthermore, the reaction of some of the binary compounds (TiN, TiC, ZrN) with oxygen or carbon allows to expand the range of tints, from golden to red (8-10).

The role of carbon typically consists in the stabilisation of the colour due to the structural changes induced in the material.

Recently, metal nitride based coatings are beings used for decorative purposes in floor tiles, wall tiles and other ceramic enamelling products. Apart from their versatility for producing decorative effects, these ceramic glazed products should be impervious and highly resistant in water and in those acids and bases which they may contact in normal use. Although TiN and TiN-based coatings still are the most popular coating materials for decorative applications, zirconium nitride and chromium nitride layers are significantly most resistant to acids and bases.

From the point of view of mechanical applications, these compounds have been also used successfully to enhance the life of cutting tools and other mechanical parts where friction and wear are major issues. These metallic-like coatings are relatively hard (20-30 GPa), but show a certain plasticity or ductility which makes them adherent to metallic substrates. They present certain interaction tendency with oxides materials, thus contributing to increase the adhesion.

In later developments, the combination of these compounds was realised in complex layers structures, as multilayers (superlattices) and nanocomposites. This approach followed the same arguments as in the Hall-Petch (H-P) effect for conventional ceramics, which predicts a linear increase of the yield strength (and thereby hardness) with the inverse of the root square of the grain size. The H-P effect in coarse-grained materials is attributed to the grain boundaries, acting as efficient obstacles to dislocations, nucleated mostly from Frank–Read sources. The starting point of material strengthening in thin film nanostructures was theoretically studied by Koehler (11) for multilayers of two alternating materials with the same crystal structure, where the abrupt interfaces between the layers were predicted to inhibit the motion of dislocations.
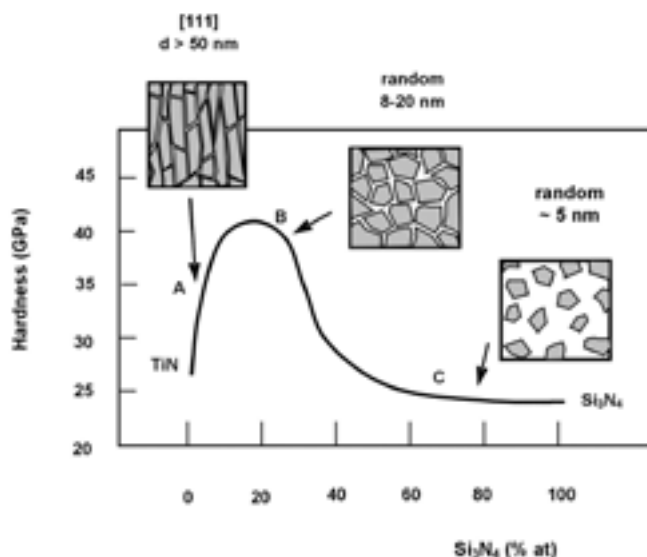

Fig. 5- Hardness variation of TiN/Si_3N_4 nanocomposite coatings as a function of the Si_3N_4 content. The inserts show the a scheme of the nanostructure at different compositions (adapted from Patscheider (12)).

Following this trend, different laboratories have confirmed that multilayered hetero- epitaxial coatings, consisting of two alternating layers of hard phases (e.g. TiN/NbN) show a hardness increase by more than a factor of two when the

thickness of the individual layers was of the order of several nanometres. Differences in the shear moduli of the phases and a small lattice mismatch were identified as prerequisites for such hardness rise.

The suppression of the dislocation activity can also be achieved by mixing of hard phases as in nanocomposite materials, made of hard amorphous matrix (e.g. Si_3N_4) with a dispersion of equiaxed nanocrystallites, also of a hard material (TiN), with a grain size < 10nm. Fig. 5 shows the results of Patscheider for that system, obtained by co-sputtering of Ti and Si in a nitrogen atmosphere (12). The ratio of the amorphous to the crystalline phase in the matrix can be varied by proper adjust of the power applied to each cathode in the sputtering system. As can be appreciated, a maximum in hardness is achieved for small Si_3N_4/TiN ratios (3-4% at. Si), where the TiN nanocrystallites are covered by a monolayer of Si_3N_4. Larger ratios give rise to a disperse phase of TiN crystals, allowing crack propagation, thus reducing the hardness to the Si_3N_4 values. On the contrary, at smaller ratios the TiN crystal growth is not inhibited, and the hardness results approaches to that of TiN.

5. CONCLUSIONS

Covalent and metallic type compound materials, such as DLC, BN, TiN, TiC, etc show excellent properties for hard and decorative applications. The requirements as protective coatings, are not far of those demanded for structural ceramics: strong bonds, high atomic density and chemical stability at high temperatures. As distinct properties, the coatings should exhibit elevated hardness, good adhesion and wear resistance under operating conditions. For decorative applications they should offer vivid metallic colours. Most of these properties are met through adequate selection of materials and deposition parameters. In this regard, advanced vapour phase techniques, plasma-assisted, have been designed to promote intense ion bombardment on the surface during the growing process aiming to increase the arrival energy of the atomic species, thus allowing to obtain denser and more adherent coatings. As in the case of bulk structural ceramics, a large improvement in hardness and wear resistance has been achieved through the development of complex multilayers and composite structures with feature sizes in the nanometre range.

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176

Bol. Soc. Esp. Ceram. V., 46, 4, 171-176 (2007)