

# State of Art: Thermal Spraying and Performance of Hard Coatings: A Review

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## Abstract

All engineering materials used for severe cutting, stamping or bearing conditions including humid and corrosive environments, as well as temperature fluctuation require a combination of chemical, mechanical, and tribological properties. To increase the life of materials, specific coatings employed with the help of thermal Spraying are frequently used. Desired properties can be achieved in hard films based on carbides, borides and nitrides of transition metals by alloying with metallic (Al, Cr, Zr) or nonmetallic (O, P, Si, Ca) elements. In the present manuscript the role of wear, corrosion and effect of hard coatings with focus to enhance desirable properties of various engineering materials used for different applications in various industries have been reviewed. An introduction to the thermal spray coating processes has been reported emphasizing their advantages over other types of coating processes.

## Keywords

Thermal Spraying, Wear, Corrosion, Hard coatings; AlCrN, TiAlN, Nitrides.

## I. Introduction

Surface engineering is an economic method for the production of materials, tools and machine parts with required surface properties such as wear and corrosion resistance [1]. Surface engineering is the name given to a range of technologies that modify the surface of a component to improve its performance characteristics. The vast majority of engineering components fail as a direct consequence of a surface-initiated failure, be it fatigue, corrosion or wear [2]. Coatings can be applied to surfaces to improve the surface characteristics over those of the bulk properties and are widely used in tribological applications. One of the foremost coating methods is thermal spraying [3].

It is well established that thin, hard coatings deposited on tools and machine parts by various thermal spray deposition processes can significantly improve the performance of these products. The benefits associated with these coatings include high hardness, wear resistance, corrosion resistance and many more [4, 5].

There are increasing numbers of applications where the mechanical and chemical properties of the binary nitrides are not sufficient. Recently, research has been carried out into the development of new ternary nitrides comprised of transition elements and other metals. From the development of titanium aluminium nitride, it has been reported that the addition of aluminium results in improved oxidation resistance at elevated temperatures [6]. Since the addition of Al increases the oxidation resistance of Ti-N coatings, a similar effect on the oxidation resistance of Cr-N coatings should be expected. Recent studies have confirmed that increasing the aluminium content in both Ti-N and Cr-N coatings increases the oxidation resistance of the coating film. This is due to the formation of an aluminium oxide layer on the surface, which prevents the diffusion of oxygen into the bulk [7-9]. However, the Al<sub>2</sub>O<sub>3</sub> layer formed was reported to be a poor thermal conductor, and heat was preferentially lost in the chippings instead of being

transferred to the body of the tool [10]. Substitution of Ti by Al and of Cr by Al is also expected to alter other physical, chemical and mechanical properties of the coatings. This paper reports the results obtained from a comparative study into the characterisation of Cr-Al-N and the more established, "industrial standard" Ti-N, Cr-N and Ti-Al-N coatings. The performance of Cr-Al-N is compared to that of Ti-N and Ti-C-N using data received from actual industrial applications. All the coatings investigated were produced under similar deposition conditions using electron beam plasma-assisted physical vapour deposition.

## II. Thermal Spray Coating Process

Thermal spraying is the generic name for a family of coating processes in which a coating material is heated rapidly in a hot gaseous medium, and simultaneously projected at a high velocity onto a prepared substrate surface where it builds up to produce the desired coating. A coating material is fed to a heating zone to become molten, and is propelled from there to a base material (substrate), as shown in fig. 1 [11].

There are many coating techniques available; the strength of thermal spray coating technology is that almost any substrate can be coated with almost any material. Spraying can be done on site (except for vacuum spraying or for protective/controlled atmospheric spraying), which eliminates time consuming and expensive shipments and limits downtime in production. There are no dimensional limits to components sizes (except when spraying in a vacuum chamber). This process has the ability to deposit a wide variety of materials from low to high melting temperature materials, and from pure metals to many types of mixtures. Fast coating deposition is another added advantage. Nearly all materials can be thermally sprayed, and micro structure & properties of thermally sprayed materials can be varied to reach highest sputter yield.

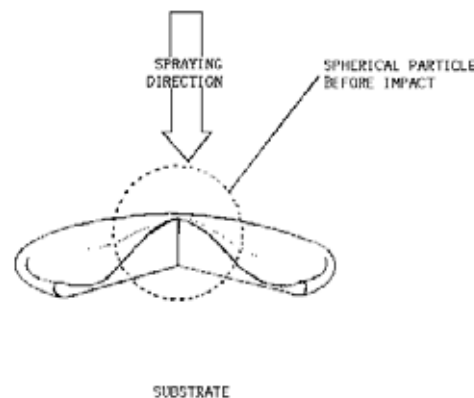


Fig. 1: Schematic of a thermal spray process [12].

Unlike some other processes this process is environment friendly and no volatile organics are employed as is the case with many techniques [13]. Other advantages of thermal sprayed coatings include portability, ability to seal or topcoat, abrasion and erosion resistance, and lack of curing requirements [14].

There are many thermal spray coating techniques available, and choosing the best process depends on the functional requirements, (size, shape, and metallurgy of the substrate), it also depend on adaptability of the coating material to the technique intended, level of adhesion required, and availability and cost of the equipment. Fig. 2 shows commonly used thermal spray coating processes, where the broad classification is based upon the type of energy source, which may be combustion, plasma or electric energy for heating. The HVOF and DS spray processes drive their energy by combustion process as reported in the fig.. The plasma spray process has different variations ranging from shroud, vacuum and inert plasma spray processes.



Fig. 2: Classification of thermal spray coating processes [13].

### III. Thermal Spray Process Types

#### A. Plasma Spray

A typical plasma torch is shown schematically in Fig. 3. Gas, usually argon

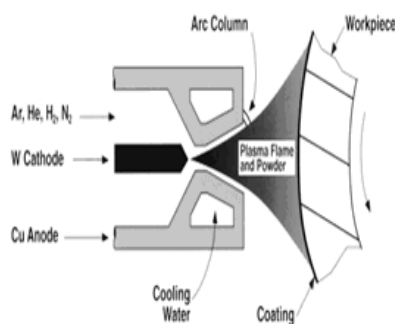


Fig. 3: Schematic of plasma spray process [15].

and/or nitrogen, with hydrogen or helium and mixed in some cases, flows through cylindrical copper anode which forms a constricting nozzle. A direct current arc is maintained between an axially placed tungsten cathode and the outer or expanding portion of the anode. Gas plasma (ionized gas) is generated with a core temperature of about 50,000°F (30,000°C). The coating powder, with a particle size ranging up to about 100 microns, is fed into the plasma stream in a variety of ways and locations. The powder is heated and accelerated by the plasma stream, usually to temperatures above its melting point, and to velocities ranging from 400 to almost 2,000 ft/sec. The actual powder distribution and velocity are strongly a function of the torch design. The gases chosen for plasma do not usually react significantly with the powder particles; however, reaction with the external environment, normally air,

may lead to significant changes in the coating. The most significant reaction with metallic and carbide coatings is oxidation. To reduce degradation during deposition, coatings may be produced using either an inert gas shield surrounding the effluent or by spraying in a vacuum chamber under a low pressure of inert gas. Argon is usually used in both cases as the inert gas [15].

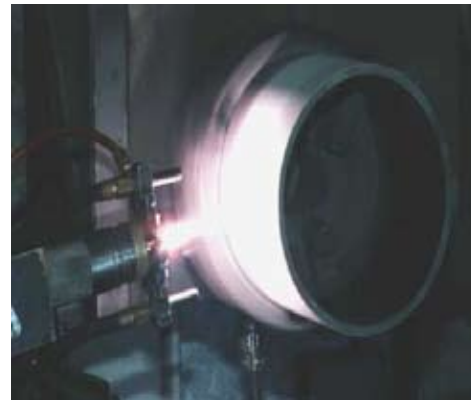


Fig. 4: Plasma spray gun coating a cylindrical part [16]

Plasma spraying produces a high quality coating by a combination of a high temperature high energy heat source, and a relatively inert spraying medium and high particle velocity. However, inevitably some air becomes entrained in the spray stream and some oxidation of the spray material may occur. The surrounding atmosphere also cools and slows the spray stream [16]. A plasma spray gun depositing coating to a cylindrical part has been shown in Fig. 4.

#### IV. High-Velocity Oxy-Fuel Spray

A recent addition to the thermal spraying family, high velocity oxy fuel spraying has become established as an alternative to the proprietary, detonation (D-GUN) flame spraying and the lower velocity, air plasma spraying processes for depositing wear resistant tungsten carbide-cobalt coatings [16].

The process utilizes a combination of oxygen with various fuel gases including hydrogen, propane, propylene, hydrogen and even kerosene. In the combustion chamber, burning by-products are expanded and expelled outward through an orifice where at very high velocities, often times they produce "shock diamonds" exiting the spray gun as shown in Fig. 5 below. Powders to be sprayed via HVOF are injected axially into the expanding hot gases where they are propelled forward, heated and accelerated onto a surface to form a coating. Gas velocities exceeding Mach 1 have been reported with temperatures approaching 2,300°C (4,172°F). The coupling of inertially driven/highly plasticized particles can achieve coatings approaching that of theoretical density [17].

The HVOF process produces exceptionally high quality cermet coatings (e.g., WC-Co), however it is now also used to produce coatings of metals, alloys and ceramics [16]. A HVOF spray Gun in operation has been shown in Fig. 6.

Due to the high velocity and high impact of the sprayed powder, the coating produced is less porous and has higher bond strength than that produced by other methods [11].

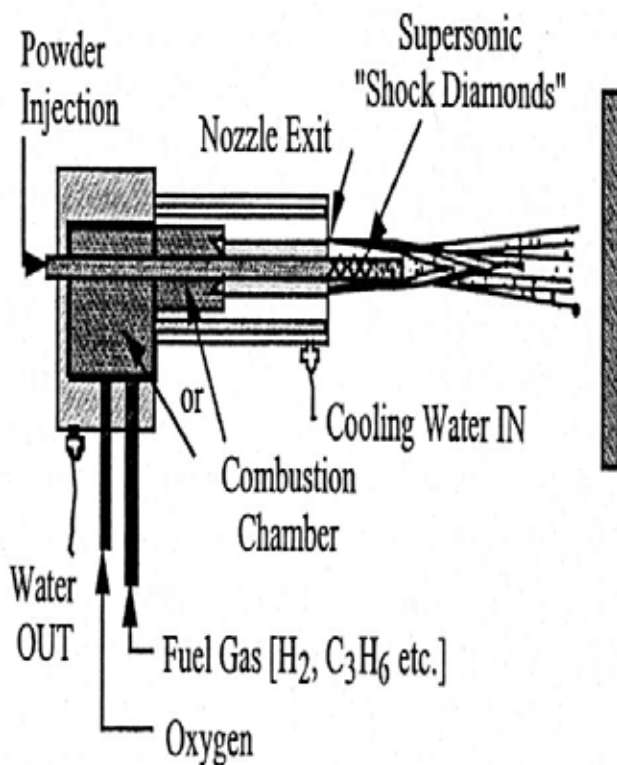


Fig. 5: Schematic of high velocity oxy fuel spray process [17].

The high velocity oxygen fuel (HVOF) powder spray process represents the state-of-the-art for thermal spray metallic coatings and results in very dense, tightly adherent coatings with little or no oxidation during the application & low residual stresses [18].

#### V. Detonation Gun Flame Spraying

Detonation flame spraying is a thermal spray process variation in which the controlled explosion of a mixture of fuel gas, oxygen and powdered coating material is utilized to melt and propel the material to the work piece [17].

A detonation gun consists of a water cooled barrel several feet long and about one inch in diameter with some associated valving for gases and powder, as shown schematically in Fig. 7.

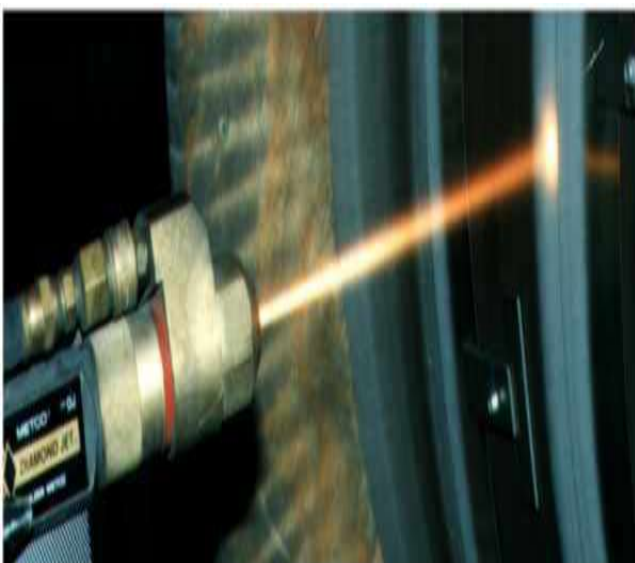


Fig. 6: A high velocity oxy fuel(HVOF) gun in operation [12].

A carefully measured mixture of gases, usually oxygen and

acetylene, is fed to the barrel along with a charge of powder (usually with a particle size less than 100 microns). A spark is used to ignite the gas and the resulting detonation wave heats and accelerates the powder as it moves down the barrel. The gas is traveling at a supersonic velocity and the powder is entrained for a sufficient distance for it to be accelerated to a supersonic velocity as well, typically about 760 m/sec (2400 ft/sec).

A pulse of nitrogen gas is used to purge the barrel after each detonation. This process is repeated many times a second. Each individual detonation results in the deposition of a circle (disk) of coating a few microns thick and about one inch in diameter. The coating is made of many overlapping disks. Carefully automated, disk placement results in a very uniform coating thickness and a relatively smooth, planar surface. Detonation gun coatings thus consist of multiple layers of densely packed, thin lenticular particles tightly bonded to the surface.

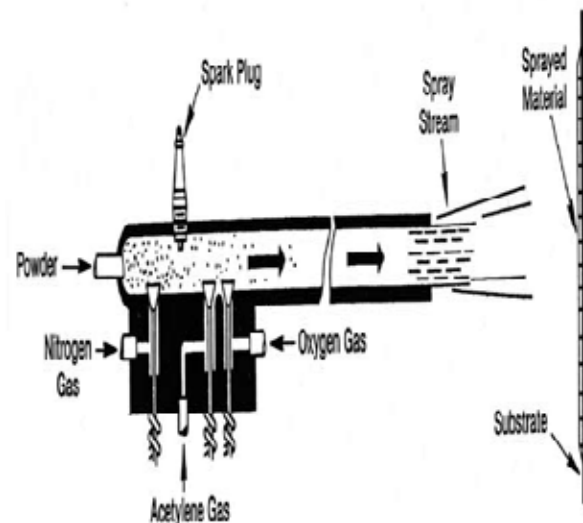


Fig. 7: Schematic of detonation gun spray process [17].

Primarily because of their high density and high bond strength, D Gun coatings have become the standard of excellence for thermal spray coatings. The as-deposited surface roughnesses of D-Gun coatings vary with the type of coating from about 60 to over 300 micro inch, Ra. Although for many applications the coating is used as-deposited, most are ground or ground and lapped to 1 to 10 micro inch, Ra. Typical coating thicknesses range from about 0.002 to 0.020 inch, but both thicker and thinner coatings are used on occasion depending on the specific application. The detonation gun process is called "line-of-sight" because the end of the barrel must be able to "see" the area being coated [15].

#### Hard Coatings - TiAlN and AlCrN (ALCRONA)

Hard protective coatings are widely used to expand the usability of cutting- and metal forming tools. Important requirements are sufficient hardness, high wear-, corrosion-, and oxidation resistance as well as good thermal stability. In modern cutting applications such as high-speed and/or dry cutting, the temperature at the cutting edge can exceed 10000C. Consequently, the applied protective coating must be capable of withstanding these extreme conditions. AlCrN provides high hardness, superior oxidation resistance, and good tribological behavior. These properties depend on chemical composition and microstructure and when optimized, excellent performance in cutting tests can be obtained. While the oxidation resistance is discussed intensively in the literature, the temperature dependent structural and compositional evolution is essentially unexplored. Two stability-related questions are

discussed in the literature. The first addresses the limit of Al solubility in the face-centered cubic (fcc) CrN phase, while the second deals with the onset of decomposition of the supersaturated phase into its stable constituents. The results obtained by author clearly demonstrate the potential of AlCrN coatings for ageing processes with precipitations. These microstructural changes offer an explanation for the reported good mechanical properties at high temperatures [19].

AlCrN protective films were deposited onto Organic Photo Conductor surface by RF magnetron sputtering method, and these films ( $x < 36\%$ ), show high transmissivity. The deposited film can increase the OPC surface hardness by a factor of 1.5–3.2. The OPC surface protected by (Al100-XCrX) N ( $x < 71.3\%$ ) film is harder than that by AlN film, and the surface hardness reaches a maximum value with 47% Cr content. The acceptance voltage, the contrast potential, the dark decay rate and the photo discharge rate of OPC coated with AlCrN film are further improved when the Cr content in (Al100-XCrX) N film is  $< 36\%$ . The deposition of this new (Al100-XCrX) N ( $x < 36\%$ ) protective film can significantly increase the micro hardness of an OPC surface without causing a deterioration in the electro photographic properties of the OPC. The new (Al100-XCrX) N ( $x < 36\%$ ) protective film will be useful in extending the operating life of OPC, and is better than the AlN protective film [20].

TiN-based coatings have been widely used by industry for cutting tools protection. Among various alloying TiN-based coatings applied on tool inserts, TiAlN and TiAlCrN are most commonly discussed by many researchers. In particular, Luo et al. too investigated the tribological behaviors of TiAlN/CrN and TiAlCrN coatings by different deposition methods. The authors reported that the wear rate for all these coatings was at least ten times lower than the uncoated tool insert [21].

The addition of Cr to TiN coatings improved the plasticity of the coating. The authors proved that the simultaneous addition of Al and Cr in the complex TiN-based nitride weaken the long range bonds, further improve the plasticity of the compound and prolong the cutting tool life under heavy wear conditions. The authors reported that the wear rate of TiAlN/CrN was stable while that of TiAlCrN was sensitive to change in cutting speed. Their conclusion stated that both the nitride coatings increased the wear resistance of tool steel by upto 10 times [22].

Coatings are, usually, based on TiN, TiC and Ti(C, N) but most success has been achieved by supplementing the metallic phase with Al or Cr. TiAlN and AlCrN, for example, have shown great advantages over other coatings since Aluminum can react with oxygen forming Al<sub>2</sub>O<sub>3</sub>, whose ceramic properties are much more adequate for interaction with hot and abrasive chips. The use of coatings on PCBN substrate can clearly bring benefits to tool life, extending it up to 38%, from 17.8 to 24.5 km, using TiAlN - nanocoating, within the tested cutting conditions. With the other coatings, TiAlN and AlCrN, tool life can be extended up to 21% and 11.8%, meaning to 21.6 and 19.9 km, respectively, within the tested cutting conditions [23].

In TiAlN, Al results in improved oxidation resistance at elevated temperatures. Since the addition of aluminium increases the oxidation resistance of Ti–N coatings, a similar effect on the oxidation resistance of Cr–N coatings should be expected. Recent studies have confirmed that increasing the Al content in both Ti–N and Cr–N coatings increases the oxidation resistance of the coating film. This is due to the formation of an Al oxide layer on the surface, which prevents the diffusion of oxygen into the bulk. However, the Al<sub>2</sub>O<sub>3</sub> layer formed was reported to be a poor thermal conductor, and heat was preferentially lost in the

chippings instead of being transferred to the body of the tool. Substitution of Ti by Al and of Cr by Al is also expected to alter other physical, chemical and mechanical properties of the coatings. The performance of Cr–Al–N is Cr–Al–N has proved effective in outperforming “more established” PVD coatings in several applications, prolonging tool life by two to three times compared to the already enhanced tool lifetimes offered by Ti–N and Ti–C–N compared to that of Ti–N and Ti–C–N using data received from actual industrial applications [24].

Metallic nitrides are widely used as a barrier thin film in electronics, as hard coatings and as special refractory materials. In all cases, corrosion resistance is very important and nitride coatings can significantly improve the corrosion performance of steel. TiAlN films showed that the oxidation resistance of TiAlN in air (and corresponding drill cutting performance) is increased with Al content [25].

TiAlN offers superior performance for a range of metal machining and manufacturing applications. The reason for this better performance is the formation of aluminium oxide on the surface, which increases its operational temperature range. Advanced PVD coatings based on TiAlN presents enhanced high-temperature oxidation and wear resistance. Typical strategy to enlarge the temperature range of TiAlN is the addition of metals such as chromium, molybdenum, yttrium or vanadium in order to generate high resistant oxides. Coatings consisting of CrN/TiAlN nanolayers have excellent performance for cutting tools in machining difficult alloys like Inconel or refractory steels [26].

## VI. Conclusions

Ti–Al–N and Cr–Al–N have higher plastic hardness which results in better wear performance. Cr–Al–N has also been shown to have exceptionally high wear resistance and is known to have higher oxidation resistance. These attributes contribute to many times life increase in operational performance. Likewise, in real industrial applications, Cr–Al–N outperforms Ti–N and Ti–C–N by 2–3 times. In one example, tooling costs are halved and a saving of 3% in production time over the Ti–N coated tools is achieved; a significant saving in today’s highly competitive markets. Cr–Al–N is expected to play a very important part in the future of Surface Engineering, manufacturing industry and in preventing wear of critical components in a wide range of applications.

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