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PVD and CVD Coatings for the Metal Forming Industry

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Abstract:

Metal forming applications are, by their very nature, taxing on the tools and machines used to achieve a finished component. Material degradation and wear is of critical importance in any such operation as a failing in the tool or machine has the potential to cause health hazards and/or significant monetary losses. The wear of material is due to the contact of two opposing surfaces and their subsequent motion relative to each other. It can take many forms some examples of which are: a two or three body abrasive type, a rolling fatigue type or an adhesion type.

Much research has been done in the area of surface treatment for cutting and forming tools; with the aim of preventing premature failure of components in mechanical processes. Of particular interest are the PVD and CDV approaches to surface treatment, both of which have held prominent positions in this field for the last two decades. In the metal forming area research has ranged from production of low-friction coatings for sheet metal forming[1] to coatings designed for high hardness in metal cutting applications[2].

A large percentage of researchers aim to improve or optimise a coating; concentrating on performance in a particular area of interest (e.g. frictional performance) or for a particular application (e.g. milling tools). To achieve this extensive knowledge of the variables influencing coating quality is essential. The characteristics of the coating produced depend primarily on the materials selected, the deposition process, the substrate being coated and on post/pre treatment of the coatings. These areas can be further refined to produce a more comprehensive list of coating parameters. Optimisation of the coating must be guided by an analysis of these parameters; this analysis should influence material selection and also the selection of deposition parameters.

To supplement practical experiments, computational techniques have been used extensively to increase the understanding of these coatings; both the material deposition and the material breakdown during operation. These investigations have ranged from improvement of the deposition processes[3] to modelling voids and inclusions in the coating. The complexity of coating technology is reflected in the diversity of studies to be found in the literature.

The aim of this work is to review recent developments in PVD and CVD coatings with specific focus on those utilised to enhance the performance and working life of punch and die sets.

Keywords: Coatings, Wear, Tribology, Metal Forming, PVD, CVD.

1. Introduction

Wear, in its many forms, can be observed in an extremely wide range of applications. Material loss is inevitable if there is motion at the contact interface between two bodies; the engineer must determine what mechanism will occur and the rate of material being lost. This can be said even for the hardest and toughest of surfaces. Tribology is the study of bodies in contact, relative motion, friction, lubrication and wear. Historically the topics of friction lubrication and wear were considered in isolation up to the 1960's; it was realised that the three core ideals are closely interlinked and will have a direct impact on one another.

The economic impact of wear is vast and can significantly influence the operational costs of an organisation. Wear can result in damaged to machine components, requiring replacements and downtime in operation. It can also occur in pipe-work and fluid carrying duct work as a result of erosive wear. In 1966 the Jost report posited that a saving of 1% of England's gross national product could result from a greater understanding and application of tribological theories[4, 5]. At the time this figure was thought to be an extreme over exaggeration however the author based his estimate on the energy lost due to friction and did not account for wear and its ancillary problems. As a result machine downtime, component replacement and machine replacement were over looked. Machine downtime is of particular interest as three costs can be incurred: labour costs, component replacement and finally the loss of productivity.

To inhibit the onset and reduce the impact of wear an engineer must be aware of the different wearing mechanisms that can affect materials. The core processes are as follows: abrasive, adhesive and contact fatigue type. Once the process is determined there are two main solutions that can be employed: using a lubricant to reduce contact between the surfaces or using a surface treatment to improve the performance of the component. If the latter is selected than a decision on the type of surface treatment must be made on which type of surface treatment should be used. There are three main approaches to consider: changing the surface of the material without altering the chemistry, changing the surface by altering the chemistry and finally adding material to the component surface. Any solution must provide a sufficiently resilient barrier to degradation and wear of the material, as decided upon by the engineer. Component wear can pose a health risk in the workplace if it results in the sudden breakdown of a machine or mechanism. For the aforementioned reasons design engineers should consider the tribological conditions that will be occurring as a result of their design

Material wear can also have serious implication on safety in the workplace and also in everyday life. For an extreme example take the following case: an airplane jackscrew nut, of aluminium bronze, suffered severe wear which lead to a very severe accident[6]. As a result of this damage the pilot lost control of the aircraft[7]. This case should be used to make engineers aware of all possible repercussions of high wear rates in materials. There are countless other examples of accidents caused by wear and subsequent failure in components, for example combined erosion-corrosion wear mechanisms are of particular concern in the oil refinery industry[8].

Modern technology has developed significantly in the area of surface treatment and surface engineering. Voevodin et al. have used laser surface texturing to create reservoirs or dimples in a TiCN coating[9]. Lasers remove a small amount of material from the surface and this small void is filled with a solid lubricant through PVD. In this way a hybrid performance is possible, combining the hard wear resistance of the TiCN with the lubricating properties of MoS_2. Two very prominent coating technologies are the PVD and CVD coating methods. Coatings produced are of a very high quality; they are homogenous, contain few defects, excellent surface finish (dependant on substrate) and the diversity of coating materials is extensive. Ion implantation and nitriding are two other surface treatments that are used to alter the chemistry of the surface rather than adding material.

The application chosen for this study is a punching process where a hardened tool steel punch is used to remove material from a blank in one stage of a manufacturing process. The conditions experienced by the punch and die during this process are relatively harsh with sudden impact coupled with highly concentrated loads acting on the punch and die edges. This requires a structurally strong tool to support the loads applied and the sudden nature of their application, however a very hard surface is also required to withstand the wear occurring on the surface of the tool. The main mechanisms of wear occurring are two body abrasion, three body abrasion and adhesion.

2. Existing Technology

Current technology can be grouped on the nature of the process used, the temperature of the operation and on the characteristics of the coatings produced. The latter is a logical beginning when selecting the most suitable technology for a particular application. In the case of PVD and CVD the characteristics of the coating are quite similar in the following respects: thickness, density and surface finish. This is relative to the flame spraying techniques whose coatings are generally thick, prone to porosity and have rough finishes. Due to the nature of the coatings they produce the vapour deposition techniques are of interest for this application.

2.1 Chemical Vapour Deposition (CVD)

Chemical vapour deposition is a process that has been in existence from the early part of the last century and is termed a mature technology[10]. One of the first examples of this technique is the Mond Process which was used to refine nickel. The process involved the vaporisation of an impure nickel source, simultaneously combining it with a carrier gas, transportation, contact with a substrate and subsequent chemical reaction which bonded nickel to its surface[11]. It had advantages over electroplating methods of the time in that the coverage for complex geometries or sharp edges was better. However its high level of toxic products was problematic.

Currently the term CVD has been developed to include a wide range of technologies that have progressed from the original concept of vaporising a metal and using chemical reactions at the substrate to bond a coating to it. A general schematic of the CVD process is shown in Figure 2.1. Generally there are four stages during deposition: formulation of the reactant vapour, transport of this vapour, chemical reaction between the vapour and the heated substrate and finally removal of by-products. These must be carried out in a contained vessel or reactor due to the volatile nature of the chemicals involved. The pressure within the vessel is either at or below atmospheric. The temperatures within the reactor can reach up to 1500^{o}C depending on the specific process underway[12].

The coatings deposited contain few pores and defects and are very dense, almost reaching 100%. CVD coatings are characteristically thicker than those deposited using PVD, from 10μm to 1mm. Coating properties are dependant on the materials, the deposition temperature, the pressure within the vessel, the type and flow rate of the carrier gas. A very wide range of materials can be deposited using this technique ranging from nickel and chrome to the refractory type metals. The latter are used extensively with this process to improve the mechanical, thermodynamic or electrical properties of a substrate. TiN and TiC have been used extensively in the manufacture of cutting tools and can increase wear resistance of a D3 tool steel by up to 24%[13, 14]. In the case of TiN CVD coatings the hardness is effected by the deposition temperature to a large degree with hardness increasing with higher temperatures[15]. The range of substrates that can be deposited upon is extensive and the coverage of the coating is very good i.e. it is possible to coat irregular shaped components due to the high throwing power.

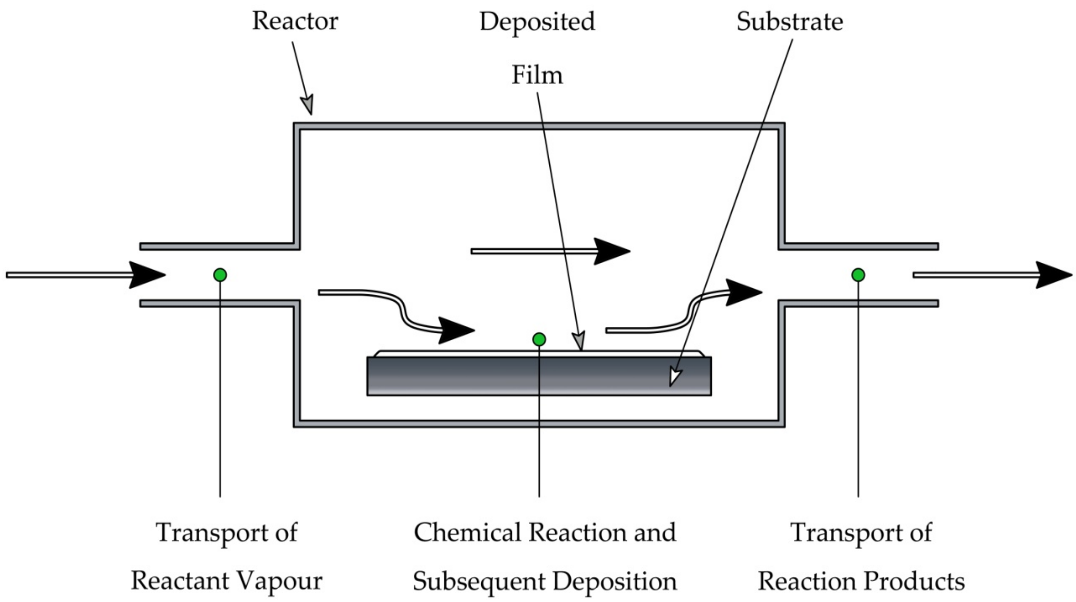

Figure 2.1 CVD Process

One area of advancement in this technology has focused on reducing the operating temperature of the process, therefore allowing different substrates to be used. One successful example is the plasma assisted CVD (PACVD). There is a significant reduction in the substrate temperatures required, however there is also a significant reduction in the operating pressure and hence the rate of deposition is decreased[12].

2.2 *Physical Vapour Deposition (PVD)*

This is a mature technology that has been employed in the aerospace, cutting tool and energy production industries, among others. The use of this technology has increased significantly in recent years due to the high quality of coatings produced. In addition this process does not produce harmful by-products that can damage the environment. Unlike the electrodeposited coating procedures it does not have outputs that must be treated/ contained after completion. Even the chemical vapour deposition process produces toxic vapours that can be extremely harmful; coupled with this problem is the costs incurred for safe disposal of these chemicals and gasses, which can be significant and complicate the production line. As a result PVD is a very attractive process for applying coatings for a wide range of applications and uses, for example: wear resistance, corrosion resistance, electronic and optical uses. Other desirable characteristics are the lower process temperature and the wide range of materials can be deposited. However one drawback is that the deposition is line of sight and hence very complicated geometries cannot be coated evenly.

There are a number of different methods to achieve PVD all of which operate by vaporising a material, transition of atoms towards a substrate and subsequent deposition of material. One of the oldest and most widely used processes is the method of vacuum evaporation. For this process a current is passed through a target that we want to evaporate and through Joule (resistance) heating the material is vaporised. There are limitations on the materials that can be deposited, depositing alloys can be problematic, and also on the applications of the coatings. A more versatile form of PVD is the sputtering form of deposition, as depicted in Figure 2.2. To produce the vapour a target of the coating material is bombarded with ions. The kinetic energy of these ions is such that when impact occurs coating atoms are ejected from the target and sent towards the substrate.

The general operating conditions for PVD are: low operating temperature generally from 200 to 300^{o}C, as the vapour is produced without heating of the target, very low pressure in the reactor, in the range of 0.5-1Pa, deposition speed is in the range of 0.1μm/min. This slow rate of deposition has been greatly improved by the advent of the magnetron source. In addition to these variables, the method of ion production will have a bearing on the coatings produced. There are three main methods of ionising the gas within the reactor: DC diode, RF and magnetron. It has been found that of the three the magnetron is the most efficient and produces the best results.

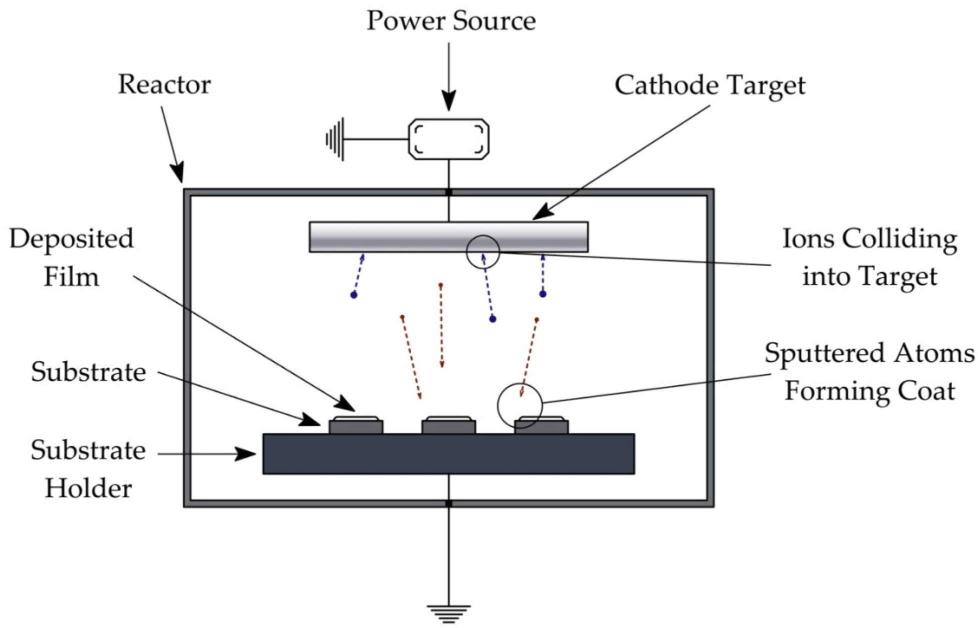

Figure 2.2 PVD Schematic

One of the main advantages of this system is the very wide range of materials that can be deposited. Ranging from standard nickel and chrome coatings to deposition alloys, ceramics, oxides and other compounds (e.g. TiN). It is also capable of producing coatings of some polymers. The versatility of the process is again due to the method of vapour production i.e. liberating atoms from the surface through ion bombardment. Due to the low deposition temperature it is possible to coat a wide variety of substrates. Coatings that are produced are thin, very dense, can have very good surface finishes although this is dependant on the quality of the substrate surface finish.

3. Punch and Die Application Characteristics

Clear application definition is essential to any design process including coating design and selection. Therefore an informed design process can be carried out where the demands of an application can be resolved through intelligent design decisions.

In the case of coated components: the conditions that a coating will be exposed to should be laid down and these will dictate the properties that are required in the coating. For mechanical applications the core conditions are loading, movement, chemical environment, contact and temperature. Coating properties to be considered are hardness, toughness, density/ porosity, coefficient of thermal expansion, surface roughness, corrosion and wear resistance (the latter is an amalgamation of some of the above). Coating material, deposition process and process variables are then chosen to provide a coating with the desired properties.

In the case of a punch and die application there will be a focus on the mechanical characteristics of the coating. The application will subject the punch and die to the following events:

- A sudden impact with a blank surface that is rough, relative to the tool
- A severe deformation of the opposing contact surface resulting in new contact surfaces being created
- Complete shearing of blank with rough edges now moving past the tool faces
- Possibility of small particles interposed between the punch and the die as the stroke is completed

During metal forming the punch and the die will experience normal and shearing loads applied to their surfaces and acting through the material. These loads and forces are process specific and dependant on the geometry of the material to be shaped and also on the properties of the blank. There are also other considerations such as the required surface finish from the blank, the size of burr produced and the geometry of the cutting surfaces to consider. The sudden nature of the loading and the high loads that are applied will have a large bearing on the coating that is selected. It must be able to withstand multiple impacts and the subsequent build up of internal stresses.

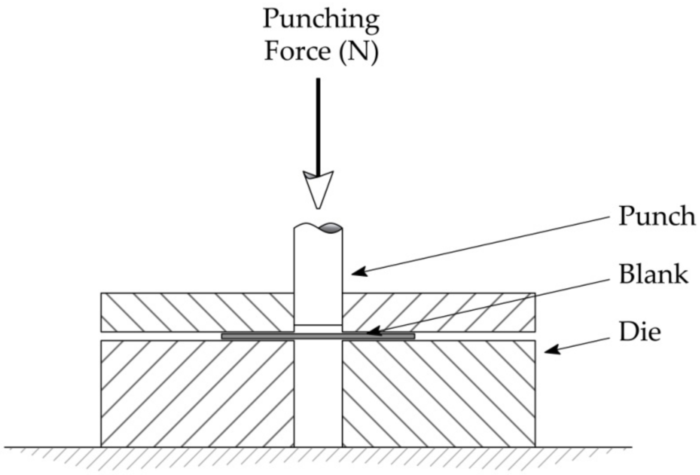

Figure 3.1 Blanking Punch

The next consideration is the movement of the surfaces relative to each other. The punch will move towards and impact upon the blank, forming a contact surface. It will keep on travelling downward, thus shearing the blank material between the punch and the die. There will be new material exposed as shearing continues which will come into contact with the punch and die respectively. These new surfaces will be roughened due to the nature in which they are formed, i.e. though shear failure of the material. New, rough, contact surfaces formed will be forced against both the punch and die. Once the punch has moved through the blank and material has been removed there will be little movement between the punch, die and the blank; or rather there will be movement but low loads between the punch, the blank, the die and the removed materials.

Wear is defined as the loss of material due to contact between two bodies subsequent motion between those two bodies. The contact, caused by loading of the two bodies, is to be considered next. Contact conditions are irreparable linked to the loading and motion sections discussed above, therefore it may be defined by these two parameters. Other factors influencing the contact conditions are: the condition of opposing surfaces, the presence of a lubricant and the formation of oxide films. In the chosen application the contact will be between a smooth, uniform and very hard surface and a soft, rough and severely deforming surface. Due to the nature of the deformation, the smooth surface will be exposed to new surfaces that have been formed due to the shearing action and hence more rough (due to sudden failure) than the initial contact surface. The contact area will be altering constantly during the formation process with most exposure/ contact located at the sharp edges of the tool.

Temperature conditions will have a large influence on the selection of a coating material and also coating process. This parameter affects the component in two possible ways: increasing the adhesion (localised welding of asperities) wear mechanism and thermal expansion problems. With reference to this application there will be localised heating at the sharp edges of the punch and die.

Wear in the material will be due to the repeated contact between the tool surfaces and the softer punch material. The mechanisms that are occurring in a tribological pair can vary depending on the materials in contact, the speed, temperature, and loads applied and also on the surface conditions (roughness, area of contact etc.). Therefore knowledge of these parameters is essential to determine the probable wear mechanisms. Actual testing, where possible, and evaluation of wear scars should be utilised to confirm the theoretical evaluation of wear and contact. For a punching application the main mechanisms are abrasion and adhesion. Abrasion is defined as: wear due to the movement of hard asperities across a softer body, penetrating into and removing material from the surface of the softer material [16-18]. It has been observed [19] that abrasive wear can result from hard inter-metallic particles contained in a soft material impinging on a hard surface and removing material. In this case the punch was constructed of a carbide insert in conjunction with a tool steel holder which was used to form thin aluminium components. In other cases a hard coating may be worn down due to wear of one particular constituent of the coating. Myint *et al.* have documented the degradation of a hard tungsten carbide coating due to removal of a soft binder material in the coating[20]; as a result the hard carbide particles are removed and the wear continues. Adhesive type wear can also cause serious damage to the tool. In this case local welding occurs between two opposing asperities leading to a junction that must be broken as sliding continues between the surfaces. This separation can result in damage to one or both of the surfaces. In another case[21] tool wear due to adhesion of particles resulted in a variance of stress across the tool surface leading to crack formation.

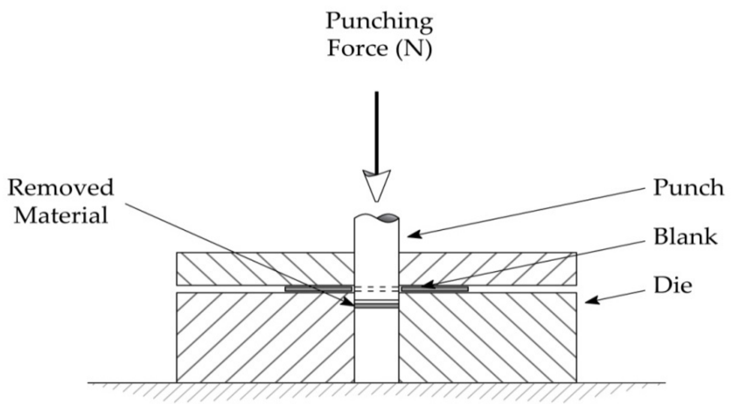

Figure 3.2 Shearing blank material

Adjacent process characteristics that are co-dependant with the wear mechanism are the rate of material removal and the type/shape and chemical composition of debris produced. Both of these factors will affect the wear mechanism and can influence the lifetime of the component. The wear debris formed in the contact area can either reduce the effects of wear or it can aggravate them[22], depending on the mechanism at work and the materials in contact. In some cases a material's oxide can behave like a solid lubricant improving the frictional characteristics of the contact pair, while in others the debris can behave as a hard, abrasive body that will gouge into both surfaces[23].

4. Coatings for punch and Dies

Traditionally high speed and tool steels were used to make cutting tools and dies. However as coating technology has developed and become more accessible, they have played an increasingly important role in this area. Some examples of hard, wear resistant coatings are: TiN, WC, TiC, CrAlN, MoN, CrN, WC-Co, TiAlV, AlTiN, TiB_2, SiCN,[24-28]. The number of investigations in the area of coating technology is extensive especially with regards to the titanium and tungsten-based coatings. Receiving less interest are the molybdenum based coatings even though the material can produce a very hard nitride coating and its disulphide, MoS_2 is a well known solid lubricant.

As discussed coating properties must be dictated by the requirements of the application. In this case a hard and tough coating must be used that can withstand the impact and subsequent wear mechanisms of adhesion and abrasion. The material should have the following properties: a very hard, a very good surface finish with good adhesion to the substrate (i.e. able to withstand the impact of the forming process), very dense with little inclusions and pores and a coefficient of thermal expansion to match that of the substrate (which will generally be a tool steel, either D2 or D3). These types of substrates have high percentages of carbon and chromium, as well as vanadium and molybdenum. Each property of key importance will be discussed in the following section and following this individual coatings of interest will be examined.

4.1 Material Properties.

Consideration of the substrate when selecting coating properties is essential for a number of reasons. In regards to mechanical properties, if the coating is very hard and brittle and the substrate less so there will be greater deformation of the substrate then the coating leading to fracture, de-lamination and failure of the coating. Thermal properties of the pair can be equally important if it is a high temperature process; if the rate of thermal expansion of the pair is not equal than there is the possibility of de-lamination of the coating from the substrate or increased stresses in the coating. Finally the chemical aspect of the pair needs to be considered; corrosion-assisted wear can be very aggressive in terms of the rate of material removal and if there is a high humidity in the working environment, or if it is a high temperature process this regime is possible. To combat corrosion the substrate and the coating must be chemically neutral towards each other and similarly the coating and the work piece should be chemically inert where possible.

Coating hardness for punch applications can range from 17 to 35 GPa for a PVD or PACVD deposited TiN coating[28-30]. Hardness is an important property in resisting impact wear, as a material must be able to resist the impingement of opposing asperities and hard phases that will move against the coating. Elastic and plastic behaviour of the material are also of concern[21]. In one case comparing a WC-Co coating to a Y-TZP (yittria-tetragonal zirconia polycrystal)[20] plastic flow of the coating was observed which reduced/ eliminated the formulation of micro cracks. Therefore a high hardness is not necessarily the only concern.

As this is a cold forming process the Cp of the materials is not of major concern as there will not be bulk heating of the process. However there is the potential for localised welding, during the adhesion process, and therefore the melting temperatures of the coating and work piece are important. Again for the very common TiN the melting temperature has been recorded as up to 3203K [31]. However the work piece will generally have a lower melting temperature and therefore it will have the limiting/controlling effect on the initiation of local adhesion.

Coating materials that are in use for this application are quite varied: TiN, WC-Co, Y-TZP[20], TiHfCrN[32], TiC, TiCN and TiAlN[29]. Similarly the coating structures are also quite varied. There have been studies on super-lattice coatings[32], nano-gradient[29], metal matrix composites[20] and a number of others.

4.2 Example Studies

In this section two high technology coatings will be presented, both for use in the cold forming process of blanking. These coatings employ different materials as well as different coating structures. One of the coatings is of the superlattice form whereas the second coating is in the form of a metal-matrix composite. In addition both authors use different materials in their coatings. A very close examination of the wear process and the breakdown of the materials would also lead an engineer to understand why one coating was performing better than the other.

4.2.1. Superlattice [32, 33]

Superlattice coatings are a refined form of the multilayer type coating where the layer thickness is in the range of 1-20nm[34]. As the lamellae are so thin a columnar crystal structure will develop through adjacent layers and therefore through the coating thickness. It has been hypothesised that the high hardness reported for these coatings is due to the retardation or prevention of dislocation operations in the material and hardness in the range of 50GPa have been recorded[35, 36]. This high hardness is of interest to the blanking/ punching operations that are of interest to this report.

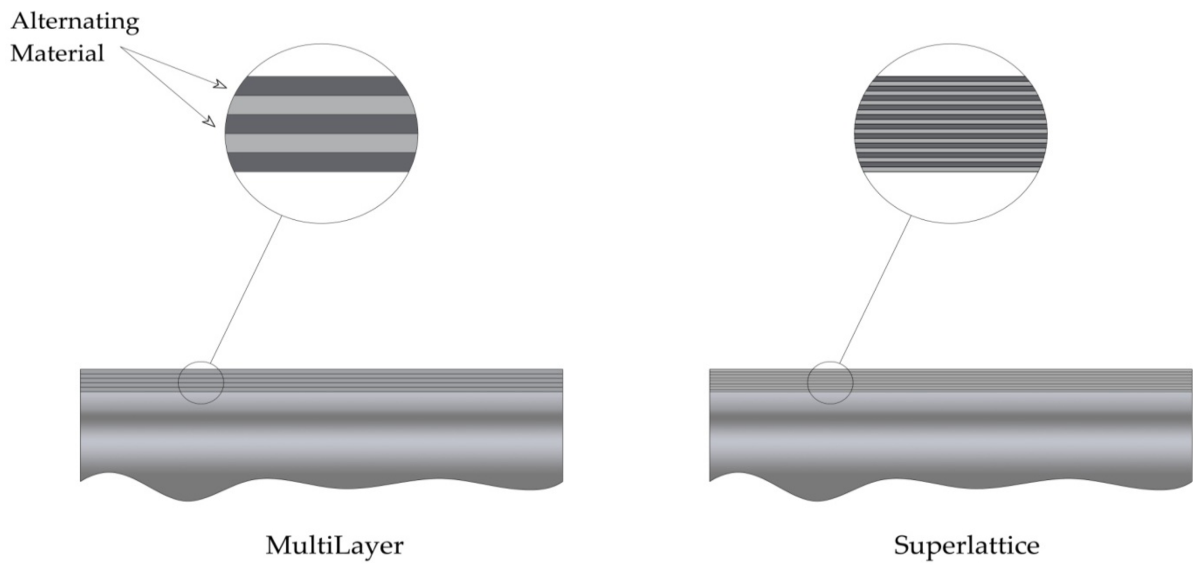

Figure 4.1 Multi-layer and Super-lattice coating structure

The study conducted by *K. Bozin et al* is of particular interest as they compare a multilayer coating against a superlattice coating of TiHfCrN composition. An arc-PVD system was utilised to produce both coatings. The targets in this case were a 70/30% Ti-Hf target and a 99.9% Cr target. In production of the multi-layered coating only one target at a time was activated while the work-piece or substrate was rotated at a constant angular velocity to ensure an even coating. The active target was then alternated to obtain the varying layers. For the superlattice coating both targets were active while the speed of rotation of the substrate determined the thickness of the superlattice lamellae.

Testing of the coatings involved a nano-indentation test and also a pin-on-disc tribo-test. For the nano-hardness test a Berkovich indenter was pushed into the material under examination to determine mechanical properties. Both the hardness and the Young's Modulus can be determined from this test, through analysis of the loading and deflection information during the test. The pin on disc test is used to evaluate the tribological performance of the coating, where a known load is applied to a hard pin which is then moved in a circular pattern on the surface under examination. The frictional characteristics and also the wear behaviour of the tribo-pair can be determined from this test. The conclusion from this study is that there is no correlation between the frictional properties of the coating and its wear performance. In addition there is a marked improvement in the wear resistance with a reduction in the thickness of the superlattice lamellae.

4.2.2.Metal Matrix Composite (MMC)

There has been extensive work on metal matrix composites for a number of reasons. One of the greatest benefits of this coating structure is the potential to combine the properties of two or more dissimilar materials. In this way a material may be formed to resist combined abrasion and corrosion at elevated temperatures. There are possible disadvantages to this approach in that if one material degrades before another than the wear rate can be increased. This has been observed in WC-Co MMC where selective breakdown in the cobalt binder phase has resulted in removal of the hard tungsten carbide particles from the coat.

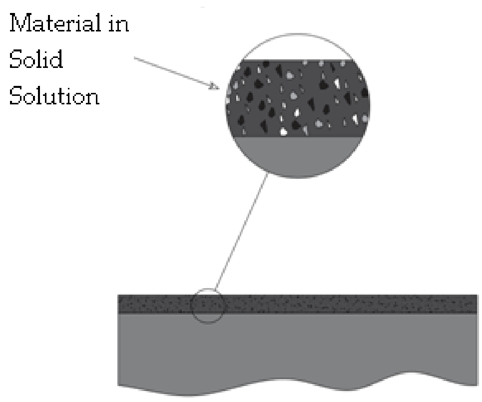

Figure 4.2

In the selected case[20] wear of material has been attributed to hard phases in the blank material removing the cobalt. In addition to this hard oxidised particles formed during the wear process also damaged the binder phase, further increasing the wear rate. This study is of great interest in that it employs a full in-situ study of the punch process and the performance of two dissimilar materials in this application. As a result of this form of selective wear the use of MMC's for the punching process must be used with caution. If the binder phase is insufficiently strong to withstand the environment than any advantage of the hard WC will be lost. However if a relatively hard solid lubricant was used instead of Co the performance of this coating may increase.

5. Discussion

Wear as a form of energy and productivity loss is a major concern for many industries. A design engineer is in a critical position in relation to combating wear and the costs it can incur. Coatings are an economical solution to this problem for a number of reasons: they can increase the lifetime of a component, they can be used to improve the properties of a cheap substrate and finally they can be used in some cases to repair a damaged coating. As a result they are also a very versatile solution to this problem. As discussed, the designer, in consultation with the client, needs to define the environment and application to which the coating will be exposed. With this information the coating properties required can be specified and the coating designed to best meet these requirements. Experimentation with the coating selected is of critical importance to ensure that performs effectively.

In summation coatings are a very useful approach for protecting punch and dies in a blanking application, with superlattice microstructure showing great promise. However due to the severity of the process the material selection must be verified through empirical techniques.

6. Bibliography

1. Carlsson, P. and M. Olsson, *PVD coatings for sheet metal forming processes--a tribological evaluation.* Surface and Coatings Technology, 2006. **200**(14-15): p. 4654-4663.
2. Holzschuh, H., *Chemical-vapor deposition of wear resistant hard coatings in the Ti-B-C-N system: properties and metal-cutting tests.* International Journal of Refractory Metals and Hard Materials, 2002. **20**(2): p. 143-149.
3. Bolt, H., et al., *Experiments and modelling of combined PVD and CVD processes using a hollow cathode arc discharge plasma.* Surface and Coatings Technology, 1998. **108-109**(1-3): p. 520-525.
4. Tichy, J.A. and D.M. Meyer, *Review of solid mechanics in tribology.* International Journal of Solids and Structures, 2000. **37**(1-2): p. 391-400.
5. Jost, P., *Lubrication (Tribology) Education and Research.* UK Department of Education and Science, HMSO, 1966.
6. Blanchet, T.A., et al., *Grease-lubricated wear of aluminum bronze for jackscrew application.* Wear. **255**(7-12): p. 1238-1250.
7. Carmody, C., *Abstract of aviation accident report Alaska airlines flight 261, md-83, n963as Pacific ocean about 2.7 miles north of Anacapa Island California January 31, 2000 ntsb/aar-02/01*

2002. p. 292.

8. Wu, X., et al., *Erosion-corrosion of various oil-refining materials in naphthenic acid.* Wear, 2004. **256**(1-2): p. 133-144.
9. Voevodin, A.A. and J.S. Zabinski, *Laser surface texturing for adaptive solid lubrication.* Wear, 2006. **261**(11-12): p. 1285-1292.
10. Pochet, L.F., P. Howard, and S. Safaie, *CVD coatings: from cutting tools to aerospace applications and its future potential.* Surface and Coatings Technology, 1997. **94-95**: p. 70-75.
11. Wronski, Z.S. and G.J.C. Carpenter, *Carbon nanoshells obtained from leaching carbonyl nickel metal powders.* Carbon, 2006. **44**(9): p. 1779-1789.
12. Grainger, S., *Engineering coatings : design and application*. 1989, [S.l.]: Industrial Press, Inc.
13. Zeghni, A.E. and M.S.J. Hashmi, *Comparative wear characteristics of tin and tic coated and uncoated tool steel.* Journal of Materials Processing Technology, 2004. **155-156**: p. 1923-1926.
14. *ASM Handbook*. Vol. 18. 1992.
15. Wagner, J., et al., *The effect of deposition temperature on microstructure and properties of thermal CVD TiN coatings.* International Journal of Refractory Metals and Hard Materials, 2008. **26**(2): p. 120-126.
16. Gates, J.D., *Two-body and three-body abrasion: A critical discussion.* Wear, 1998. **214**(1): p. 139-146.
17. Williams, J.A., *Wear and wear particles--some fundamentals.* Tribology International, 2005. **38**(10): p. 863-870.
18. Liu, Y., T.E. Fischer, and A. Dent, *Comparison of HVOF and plasma-sprayed alumina/titania coatings--microstructure, mechanical properties and abrasion behavior.* Surface and Coatings Technology, 2003. **167**(1): p. 68-76.
19. Kang, K., *Impact of die wear and punch surface textures on aluminium can wall.* Wear, 2009. **266**(9-10): p. 1044-1049.
20. Myint, M.H., et al., *Evaluation of wear mechanisms of Y-TZP and tungsten carbide punches.* Journal of Materials Processing Technology, 2003. **140**(1-3): p. 460-464.

21. Klocke, F. and H.W. Raedt, *Formulation and testing of optimised coating properties with regard to tribological performance in cold forging and fine blanking applications.* International Journal of Refractory Metals and Hard Materials. **19**(4-6): p. 495-505.
22. Varenberg, M., G. Halperin, and I. Etsion, *Different aspects of the role of wear debris in fretting wear.* Wear, 2002. **252**(11-12): p. 902-910.
23. Bourithis, L. and G. Papadimitriou, *Three body abrasion wear of low carbon steel modified surfaces.* Wear, 2005. **258**(11-12): p. 1775-1786.
24. Wagner, N.J., W.W. Gerberich, and J.V.R. Heberlein, *Thermal plasma chemical vapor deposition of wear-resistant, hard Si-C-N coatings.* Surface and Coatings Technology, 2006. **201**(7): p. 4168-4173.
25. Podgornik, B., S. Hogmark, and O. Sandberg, *Influence of surface roughness and coating type on the galling properties of coated forming tool steel.* Surface and Coatings Technology, 2004. **184**(2-3): p. 338-348.
26. Öztürk, A., et al., *Comparative tribological behaviors of TiN, CrN and MoNCu nanocomposite coatings.* Tribology International, 2008. **41**(1): p. 49-59.
27. Österle, W., et al., *Potential of wear resistant coatings on Ti-6Al-4V for artificial hip joint bearing surfaces.* Wear, 2008. **264**(7-8): p. 505-517.
28. Stoiber, M., et al., *Low-friction TiN coatings deposited by PACVD.* Surface and Coatings Technology, 2003. **163-164**: p. 451-456.
29. Antonov, M., et al., *Assessment of gradient and nanogradient PVD coatings behaviour under erosive, abrasive and impact wear conditions.* Wear, 2009. **267**(5-8): p. 898-906.
30. Holmberg, K., et al., *Residual stresses in TiN, DLC and MoS2 coated surfaces with regard to their tribological fracture behaviour.* Wear. **In Press, Corrected Proof**.
31. *Titanium Nitride (TiN) Coating*. 2010 [cited 2010 10.05.10]; Material Property Table]. Available from: http://www.matweb.com/search/DataSheet.aspx?MatGUID=ffbf753c500949db95e502e043f9a404&ckck=1.
32. Lugscheider, E., et al., *Development of a superlattice (Ti,Hf,Cr)N coating for cold metal forming applications.* Surface and Coatings Technology, 2004. **177-178**: p. 616-622.
33. Yang, Q., et al., *Microstructure and mechanical properties of multi-constituent superlattice coatings.* Vacuum, 2006. **81**(1): p. 101-105.
34. Balaceanu, M., et al., *Properties of arc plasma deposited TiCN/ZrCN superlattice coatings.* Surface and Coatings Technology, 2005. **200**(1-4): p. 1084-1087.
35. Zeng, X.T., *TiN/NbN superlattice hard coatings deposited by unbalanced magnetron sputtering.* Surface and Coatings Technology, 1999. **113**(1-2): p. 75-79.
36. Sproul, W.D., *Reactive sputter deposition of polycrystalline nitride and oxide superlattice coatings.* Surface and Coatings Technology, 1996. **86-87**(Part 1): p. 170-176.