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# Magnetron sputtering: a review of recent developments and applications

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**Abstract**

Magnetron sputtering has become the process of choice for the deposition of a wide range of industrially important coatings. Examples include hard, wear-resistant coatings, low friction coatings, corrosion resistant coatings, decorative coatings and coatings with specific optical, or electrical properties. Although the basic sputtering process has been known and used for many years, it is the development of the unbalanced magnetron and its incorporation into multi-source 'closed-field' systems that have been responsible for the rise in importance of this technique. Closed-field unbalanced magnetron sputtering (CFUBMS) is an exceptionally versatile technique for the deposition of high-quality, well-adhered films. The development, fundamental principles and applications of the CFUBMS process are, therefore, discussed in some detail in this review. Also discussed are other important recent developments in this area, including the pulsed magnetron sputtering process, variable field magnetrons, and the combining of sputtering techniques with other surface coating, or surface modification techniques in duplex production processes. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Closed-field unbalanced magnetron sputtering; Pulsed sputtering; Variable magnetrons

## 1. Introduction

Magnetron sputtering has developed rapidly over the last decade to the point where it has become established as the process of choice for the deposition of a wide range of industrially important coatings. The driving force behind this development has been the increasing demand for high-quality functional films in many diverse market sectors. In many cases, magnetron sputtered films now outperform films deposited by other physical vapour deposition (PVD) processes, and can offer the same functionality as much thicker films produced by other surface coating techniques. Consequently, magnetron sputtering now makes a significant impact in application areas including hard, wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings and coatings with specific optical, or electrical properties [1].

The basic sputtering process has been known and, despite its limitations, used for many years. The introduction of what are now termed 'conventional', or 'balanced' magnetrons in the early 1970s [2,3] was an important step forward in overcoming these limitations. However, it was the development of the unbalanced magnetron in the late 1980s [4–6] and its incorporation into multi-source 'closed-field' systems in the early 1990s [7,8] that transformed the capabilities of this technique, and has subsequently been responsible for its rise in importance. Closed-field unbalanced magnetron sputtering (CFUBMS) is an exceptionally versatile technique, suitable for the deposition of high-quality, well-adhered films of a wide range of materials at commercially useful rates. The development and fundamental principles of this process are, therefore, discussed in some detail in this paper. Also discussed are examples and applications of advanced coatings produced using this technique, including the latest generation of carbon-based and molybdenum disulphide-based coatings.

The pulsed magnetron sputtering (PMS) process is another very important recent development in the sputtering field [9]. The DC reactive sputtering of fully dense,

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defect-free coatings of insulating materials, particularly oxides, is highly problematic. The process is hampered by low deposition rates and the occurrence of arc events at the target, which are detrimental to the structure, properties and composition of the coating. However, pulsing the magnetron discharge in the mid-frequency range (10–200 kHz) has been found to prevent arc events and stabilise the reactive sputtering process. High-quality oxide coatings can now be deposited using the PMS process at rates approaching those achieved for metallic coatings. The PMS process is discussed in Section 7 of this review.

Two other recent developments are also discussed; variable field magnetrons and duplex production processes. In all PVD processes, ion bombardment of the growing film is a critical parameter which strongly influences the structure and properties of the growing film [10,11]. In a magnetron sputtering system, for any given set of deposition conditions, the ion current delivered to the growing film depends on the strength and design of the magnetic array in the magnetron. Clearly, in most cases this is fixed. However, new magnetrons have now been developed in which the magnetic array can be varied in situ without the use of electromagnets [12]. This facility allows the ion current to the substrate to be controlled and optimised at all stages of the deposition process.

Finally, there is now a move towards combining magnetron sputtering with other deposition, or surface modification techniques, in so-called duplex surface engineering processes (this title can actually be applied to any process which combines two surface engineering techniques) [13]. The aims in such cases are to extend the performance of the component beyond that which either process can achieve on its own, and to allow the use of cheaper base materials in high-performance applications. A typical example would be the plasma nitriding of a low alloy steel component, followed by coating it with a wear-resistant material, such as titanium nitride (TiN). The hardened nitrided layer provides additional load support to the TiN coating, improving its adhesion. The resulting component combines high wear resistance with high load-bearing capacity and good fatigue strength [14]. This, and other examples of duplex processes, are discussed in Section 9.

## 2. Magnetron sputtering

In the basic sputtering process, a target (or cathode) plate is bombarded by energetic ions generated in a glow discharge plasma, situated in front of the target. The bombardment process causes the removal, i.e., 'sputtering', of target atoms, which may then condense on a substrate as a thin film [1]. Secondary electrons are also emitted from the target surface as a result of the ion bombardment, and these electrons play an important role in maintaining the plasma. The basic sputtering process has been known for many years and many materials have been successfully deposited using this technique [15,16]. However, the process is limited by low deposition rates, low ionisation efficiencies in the plasma, and high substrate heating effects. These limitations have been overcome by the development of magnetron sputtering and, more recently, unbalanced magnetron sputtering.

Magnetrons make use of the fact that a magnetic field configured parallel to the target surface can constrain secondary electron motion to the vicinity of the target. The magnets are arranged in such a way that one pole is positioned at the central axis of the target and the second pole is formed by a ring of magnets around the outer edge of the target. Trapping the electrons in this way substantially increases the probability of an ionising electron–atom collision occurring. The increased ionisation efficiency of a magnetron results in a dense plasma in the target region. This, in turn, leads to increased ion bombardment of the target, giving higher sputtering rates and, therefore, higher deposition rates at the substrate. In addition, the increased ionisation efficiency achieved in the magnetron mode allows the discharge to be maintained at lower operating pressures (typically, $10^{-3}$ mbar, compared to $10^{-2}$ mbar) and lower operating voltages (typically, $-500$V, compared to $-2$ to $-3$ kV) than is possible in the basic sputtering mode.

The differences in design between a conventional magnetron and an unbalanced magnetron are only slight. However, the difference in performance between the two types of magnetron is very significant. In a conventional magnetron the plasma is strongly confined to the target region. A region of dense plasma typically extends some 60 mm from the target surface. Films grown on substrates positioned within this region will be subjected to concurrent ion bombardment, which, as mentioned earlier, can strongly influence the structure and properties of the growing film. Substrates placed outside this region, however, will lie in an area of low plasma density. Consequently, the ion current drawn at the substrate (typically, $< 1$ mA/cm$^2$) is generally insufficient to modify the structure of the film. The energy of the bombarding ions can be increased by increasing the negative bias applied to the substrate. However, this can lead to defects in the film and increased film stress, and therefore, be detrimental to the overall film properties. Thus, it is difficult to deposit fully dense films on large, or complex components using conventional magnetrons [17].

To deposit dense films without introducing excessive intrinsic stresses, a high flux ($> 2$ mA/cm$^2$) of relatively low energy ($< 100$ eV) ions is generally preferred [18]. These conditions are readily provided by unbalanced magnetrons.

## 3. Unbalanced magnetron sputtering

In an unbalanced magnetron the outer ring of magnets is strengthened relative to the central pole. In this case, not all the field lines are closed between the central and outer poles in the magnetron, but some are directed towards the substrate, and some secondary electrons are able to follow these field lines. Consequently, the plasma is no longer strongly confined to the target region, but is also allowed to flow out towards the substrate. Thus, high ion currents can be extracted from the plasma without the need to externally bias the substrate. Earlier studies had shown that in some magnetron designs not all the field lines closed in on themselves [19] (indeed, very few, if any, magnetrons are truly fully balanced). However, it was Windows and Savvides who first appreciated the significance of this effect when they systematically varied the magnetic configuration of an otherwise conventional magnetron [4–6]. They, and other researchers, have subsequently shown that substrate ion current densities of 5 mA/cm$^2$ and greater, i.e., approximately an order of magnitude higher than for a conventional magnetron, can be routinely generated when using an unbalanced magnetron [6,20,21]. A comparison between the plasma confinement obtained in different magnetron modes is shown schematically in Fig. 1.

Thus, in addition to providing a high flux of coating atoms (compared to a basic sputtering source), an unbalanced magnetron also acts as a very effective ion source. Furthermore, the ion current drawn at the substrate is directly proportional to the target current. Deposition rate is also directly proportional to target current. As a result, and unlike other ion-plating processes [22,23], the ion-to-atom arrival ratio at the substrate remains constant with increasing deposition rate [24].

The design of unbalanced magnetron discussed above was termed ‘type-2’ by Window and Savvides. However, they also considered the opposite case (‘type-1’), where the central pole was strengthened relative to the outer pole. In this case the field lines which do not close in on themselves are directed towards the chamber walls and the plasma density in the substrate region is low (see Fig. 1). This design is not commonly used, because of the resulting low ion currents at the substrate. However, a recent project at Salford utilised this characteristic for the production of novel, high surface area, chemically reactive metallic films [25]. Through a systematic study of the deposition process, conditions were determined under which coatings with a controlled and reproducible porosity were obtained. Indeed, coatings with porosities of the order of 1000 times greater than a fully dense material were produced [26]. Further, as shown in Fig. 2, the temperature at which these coatings spontaneously reacted in air was shown to be dependent on the effective surface area of the films, as determined by AC impedance testing. Films of this type have a number of diverse potential applications, such as catalysts, pyrophoric devices, or non-reflective coatings.

## 4. Closed-field unbalanced magnetron sputtering

Despite the benefits offered by unbalanced magnetrons, it is still difficult to uniformly coat complex components at acceptable rates from a single source. Therefore, in order to commercially exploit this technology, multiple magnetron systems have been introduced.

In a multiple magnetron system, the magnetic arrays in adjacent magnetrons can be configured with either identical, or opposite magnetic polarities. In the former case the configuration is described as ‘mirrored’ and in the latter case ‘closed field’, and both configurations are shown in Fig. 3. In the mirrored case, the field lines are directed towards the chamber walls. Secondary electrons following these lines are lost, resulting in a low plasma density in the substrate region. Conversely, in the closed

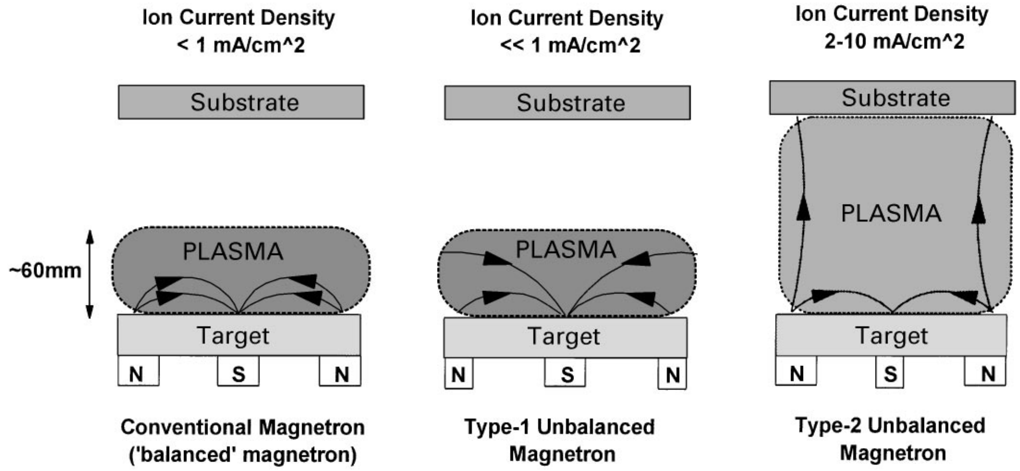

Fig. 1. Schematic representation of the plasma confinement observed in conventional and unbalanced magnetrons.

field configuration, the field lines are linked between the magnetrons. Losses to the chamber walls are low and the substrate lies in a high density plasma region. The effectiveness of the closed field configuration is shown in Fig. 4, which is taken from a study at Salford University [27]. As can be seen, operating in the closed field mode results in an ion-to-atom ratio incident at the substrate some 2–3 times greater than that obtained under the same conditions in the mirrored, or single unbalanced magnetron configurations. Also, the influence of the closed magnetic field on the ion-to-atom ratio becomes more marked as the distance from the target increases.

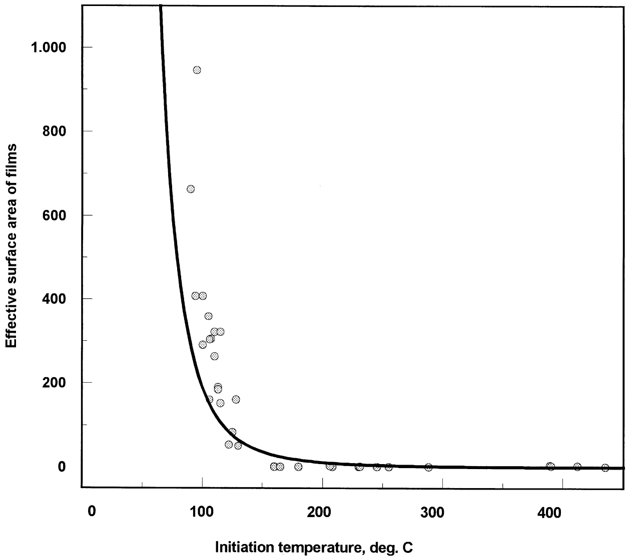

Fig. 2. The relationship between effective surface area (relative to fully dense material) and ignition temperature for chemically reactive metallic films.

In the UK, Teer Coatings Ltd. were quick to recognise the potential of multiple magnetron systems, and, in the early 1990s, developed a patented design of commercial and research scale CFUBMS systems [28]. In these, and other similar systems developed elsewhere [8,29], an even number of vertically opposed magnetrons surround the rotating substrate holder. Adjacent magnetrons have opposite magnetic polarities and the field lines are closed. As stated above, such systems are capable of transporting high ion currents to the substrate. However, recent developments in magnetron design and the use of high strength rare earth magnets in the magnetic arrays have led to significant further increases in the magnitude of the ion currents drawn at the substrate. Early magnetrons generally made use of ferrite magnets which gave a maximum field strength of the order of 300–500 G at the target surface [27,30]. With improved magnetron design and the introduction of rare earth magnets, field strengths in excess of 1 kG are now obtainable at the target surface. The increased field strength increases the ionisation efficiency in the plasma, which in turn, results in much higher ion currents at the substrate. This effect is illustrated in Fig. 5, which consists of data supplied by Teer Coatings [31], and compares the ion current measured at the substrate for single balanced and unbalanced magnetrons; an early (pre-1995) CFUBMS system using ferrite magnets; and a more recent, modified CFUBMS system using rare earth magnets.

## 5. Advanced coatings by CFUBMS

In general, the most commercially useful coatings tend to be ceramic materials, including oxides, nitrides and carbides. These materials can be deposited by sputtering

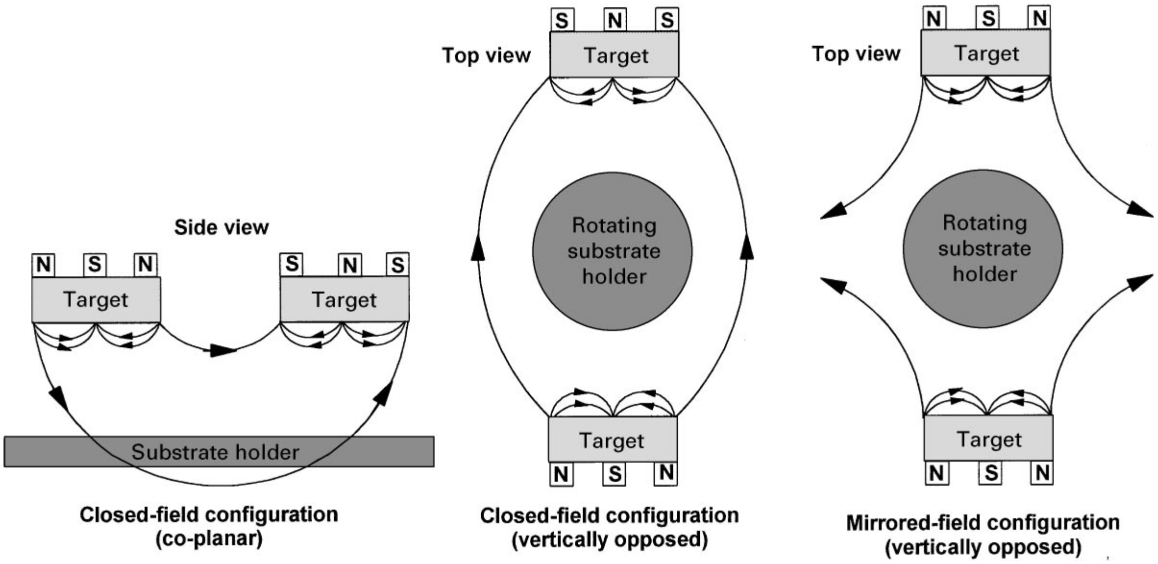

Fig. 3. Dual unbalanced magnetron configurations.

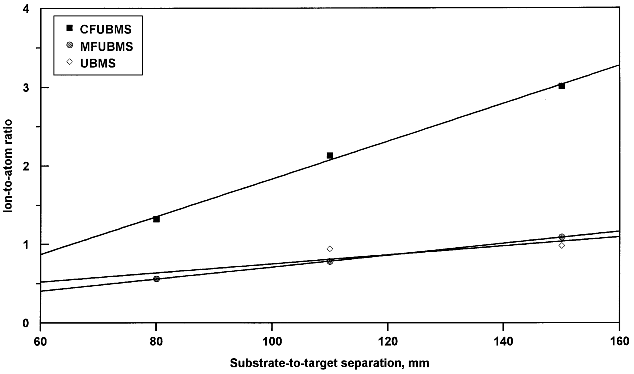

Fig. 4. The variation with substrate–to-target separation in the ion-to-atom ratio incident at the substrate for closed field (CFUBMS), mirrored field (MFUBMS) and single magnetron (UBMS) configurations.

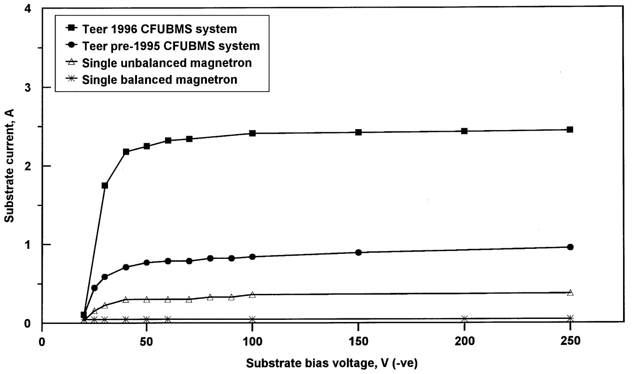

Fig. 5. A comparison of the current–voltage characteristics for various Teer Coatings Ltd. magnetron sputtering systems (after Ref. [30]).

a metallic target in the presence of the appropriate reactive gas. Single element nitrides, most commonly titanium nitride, are now routinely produced by magnetron sputtering. However, the multiple magnetron CFUBMS systems are ideally suited to the deposition of multi-component, or alloy nitrides, as each of the magnetron targets can, in principle, be of a different material. In this manner, materials such as (TiAl)N, (TiZr)N and (CrZr)N have all been deposited. In each case, these coatings can exceed the performance of TiN in specific applications [32]. By sputtering the targets at different rates, any desired alloy composition can be attained. Further, by varying either the sputtering rates, or the flow of reactive gas during deposition, composition, and, therefore, properties can be graded through the thickness of the coating. In this manner, properties can be optimised, both at the coating/substrate interface for adhesion, and at the coating surface for the desired functionality.

The production of diamond-like carbon (DLC) coatings by CFUBMS combines many of the features described above and offers a good example of how the versatility of this process has recently led to significant improvements in the performance of the coating [33]. This process is discussed in more detail in Section 9. Other examples, again highlighting the versatility of the CFUBMS process, are the production of novel multi-layer pyrotechnic coatings [34] and corrosion resistant supersaturated Al/Mg alloy coatings [35]. In these two examples an alternative closed field arrangement was used, with two magnetrons in co-planar positions, rather than vertically opposed (see Fig. 3).

Two other recently developed, commercially available coating materials which also make use of the attributes of the CFUBMS system are the molybdenum disulphide ($MoS_2$)-based MoST coatings [36] and the carbon-based Graphit-iC[1] coatings [37].

MoST coatings are $MoS_2$/metal composite coatings which are much harder, more wear resistant and less sensitive to atmospheric moisture than traditional $MoS_2$ coatings, yet they still retain the low friction characteristics of $MoS_2$. These coatings are deposited by CFUBMS in four-magnetron systems incorporating three $MoS_2$ targets and one titanium target. An initial titanium interlayer ( ~ 100 nm thick) is deposited to optimise adhesion. The MoST coating is then deposited by simultaneously sputtering from the three $MoS_2$ targets and the Ti target, whilst the substrate holder is rotated. Analysis has determined that the coating structure is an amorphous, homogeneous solid solution of Ti in $MoS_2$, the titanium content of which can be readily varied by controlling the relative $MoS_2$ and Ti target powers.

The MoST coating combines a number of remarkable properties. Indentation tests show a hardness of greater than 15 GPa, whilst scratch adhesion tests indicate a critical load greater than 120 N, and friction coefficients as low as 0.005 have been recorded in dry nitrogen. One of the major advantages of MoST coatings over traditional $MoS_2$ coatings is the ability of the coating to perform in humid conditions. $MoS_2$ coatings are generally only suitable for use in dry or vacuum conditions. However, many tests have confirmed MoST coatings can perform successfully in atmospheres of 40–50% humidity, under which conditions the coefficient of friction can be as low as 0.02 [36].

MoST coatings have many industrial applications. They are particularly suitable for the dry machining of steels, cast irons, and aluminium, titanium and nickel alloys. By way of example, Fig. 6 shows the improvement in tool life offered by MoST coatings over traditional $MoS_2$ coatings in a dry punching operation. Also, Fig. 7 shows the improvement in feed rate obtained using a MoST coated tool, compared to other tools, for end mill operations on a wrought aluminium alloy [38].

Graphit-iC coatings are a new type of hard carbon coating that can outperform established DLC coatings in

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[1] MoST and Graphit-iC are trademarks of Teer Coatings Ltd.

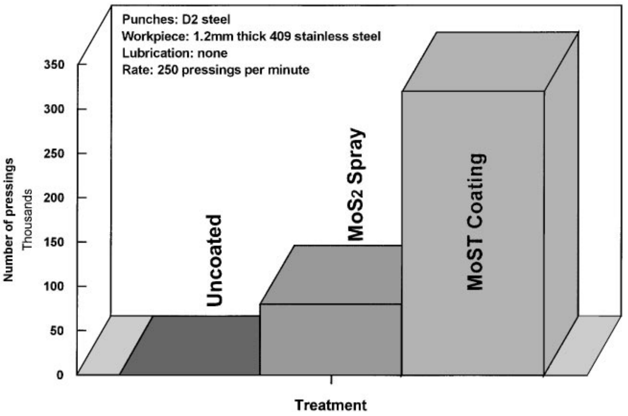

Fig. 6. An example of the improvement in life offered by MoST coatings over conventional $MoS_2$ and uncoated tools in a dry punching operation (after Ref. [37]).

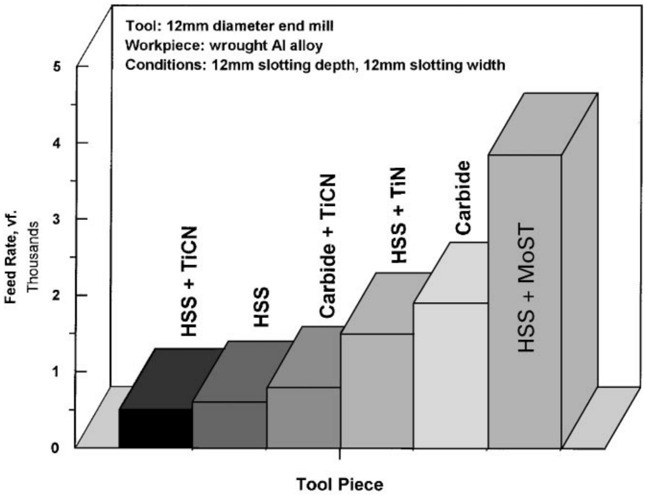

Fig. 7. A comparison of feed rates achieved for uncoated and coated end mill tools (after Ref. [37]).

certain applications [37,39]. The coatings are again deposited in a four magnetron system. In this case, though, there are three carbon targets and one chromium target. A thin chromium bond layer is deposited, followed by a pure carbon coating. Alternatively, by controlling target powers and substrate rotation speed, a metal/carbon multi-layer coating can be deposited. Analysis by Raman spectroscopy has shown that Graphit-iC coatings exhibit predominantly $sp^2$-type bonding, unlike DLC coatings, where the bonding is mainly $sp^3$-type. Despite this, coating hardness values of between 15 and 40 GPa have been recorded, depending on deposition conditions. In addition, Graphit-iC coatings exhibit lower coefficients of friction, lower wear rates and higher load bearing capacity than DLC coatings. Typical applications for these coatings include automobile engine parts, cutting and forming tools and moving parts, such as taps and valves, operating in an aqueous environment.

## 6. The development of a structure zone model for the CFUBMS system

Much has been made in the preceding sections of the ability of the CFUBMS system to deliver high ion currents to the substrate. The impact of this factor on the properties of coatings deposited using this technique has been assessed in extensive studies at Salford University [40]. One aim of this study was to develop a new structure zone model relating to this technique.

Structure zone models (SZMs) have long been used as a convenient means of displaying the relationships between process parameters and the structures and, therefore, the properties of PVD coatings. Several such models have been developed to describe the structure of coatings deposited by various sputtering processes [41–44], the best known being the one developed by Thornton [41]. In this, and all similar models, the homologous temperature, $T/T_m$, (where $T$ is the substrate temperature, and $T_m$ is the melting temperature of the coating material) of the coating is used to describe the thermally induced mobility of the coating atoms. A second variable attempts to describe the influence of the simultaneous bombardment of the growing film by energetic particles. Parameters chosen for this second axis include coating pressure [41,44], substrate bias voltage [42], and a combined energy parameter described as the average energy per depositing atom [43]. In these models, the coatings are categorised as having one of three main structural types. At low homologous temperatures (‘zone 1’) atomic shadowing is the dominant growth mechanism, and the coating structure consists of tapered columnar grains separated by pores, or voids. The term ‘porous columnar’ is, therefore, used to describe this type of structure. At higher homologous temperatures (‘zone 2’) atomic mobility is increased, allowing surface diffusion processes to dominate. In this zone the structure still has a distinct columnar appearance, but there are no voids between the columns, and the structure is described as ‘dense columnar’. At still higher homologous temperatures (‘zone 3’) the bulk diffusion processes of recrystallisation and grain growth can occur, and the coatings have ‘fully dense’ equiaxed grain structures.

In the Salford study [40], aluminium, zirconium and tungsten coatings were deposited by CFUBMS under systematically varied conditions, and characterised in terms of their structures and properties. Also, for each set of conditions, the ratios of the fluxes of ions and condensing atoms at the substrate were estimated from ion current density and deposition rate measurements. The system chosen for characterisation was a Teer Coatings Ltd. UDP 450 CFUBMS rig.

Aluminium coatings were deposited at homologous temperatures over the range 0.43 to 0.68. All had fully dense, highly ductile structures, which 'necked-down' completely on fracture. SEM and TEM investigations confirmed that all had zone 3-type structures, using the classification system described above. The zirconium and tungsten coatings were deposited at homologous temperatures over the ranges 0.22–0.28 and 0.13–0.17, respectively, and all had dense columnar, zone 2-type structures. By way of an example, Fig. 8 shows a through thickness TEM micrograph of a tungsten coating deposited at $T/T_m = 0.13$. Large (100–200 nm) polygonal grain-like regions are clearly visible, separated by regions of high dislocation density. No pores are visible between the columns, confirming the zone 2 classification.

The formation of zone 2 structures at $T/T_m$ as low as 0.13, and zone 3 structures at $T/T_m$ as low as 0.43 are major departures from the Thornton structure zone model. This is illustrated in Fig. 9, which compares, in terms of homologous temperature, the positions of the zonal boundaries given in other published SZMs for sputtered coatings [41,42], with the boundaries observed in the Salford study. It is clear that operating in the closed field mode has suppressed the formation of porous structures and promoted the formation of fully dense structures at relatively low substrate temperatures. Consequently, since none of the existing SZMs models are adequate to describe the CFUBMS process, Kelly and Arnell developed a new SZM relating to this system [40].

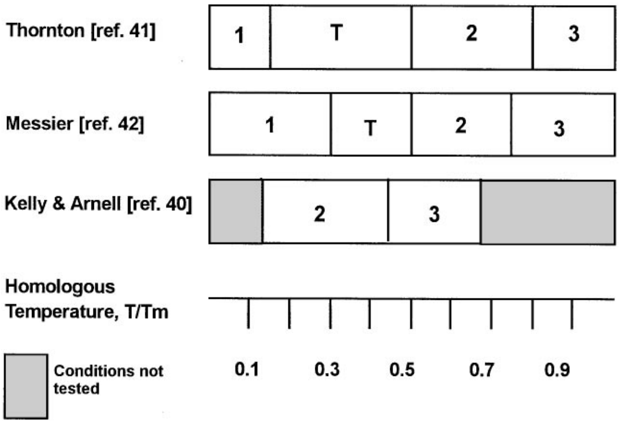

Fig. 9. A comparison, in terms of homologous temperature, of the positions of the zonal boundaries given in published structure zone models relating to other sputtering systems with the boundaries observed for the CFUBMS system.

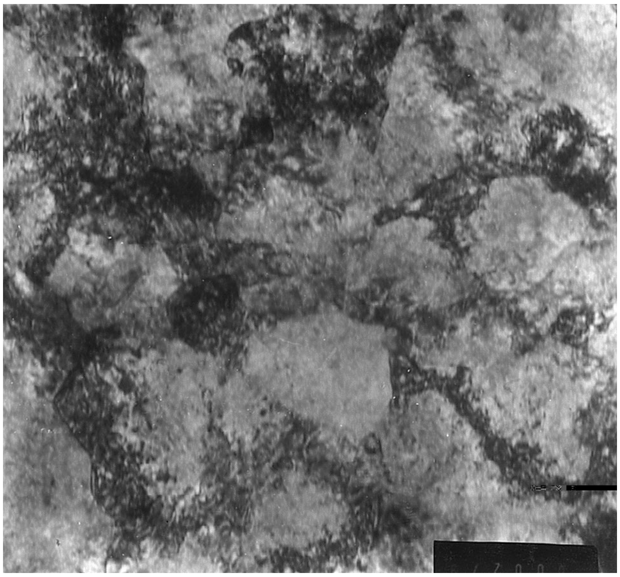

Fig. 8. Through thickness TEM micrograph of a tungsten coating deposited at $T/T_m = 0.13$. The lighter regions in the micrograph are polygonal grain-like regions, which are surrounded by darker regions of high-dislocation density.

As mentioned earlier, several attempts have been made to describe, in terms of a single parameter, the role played by energetic particle bombardment in determining the structure of sputtered films. One approach is to use an energy parameter which combines both ion energy and ion flux [43,45]. However, it is widely recognised that this approach is of limited applicability and that ion energy and ion flux must be considered separately when modelling the effects of concurrent ion bombardment on coating microstructure [46–49]. Thus, in order to incorporate both of these factors, and the homologous temperature of the coating, a novel three-dimensional SZM has been developed. In the model, which is shown as Fig. 10, the coating structure is described in terms of homologous temperature, ion-to-atom ratio and bias voltage (to represent ion energy). The conventional schematic representation of structure is dispensed with, as it is assumed to be well known. Being a three-dimensional model, the zone 2/zone 3 boundary shown on the model approximates to the surface of a quadrant of a hemisphere. A second boundary is also shown on the model, inside the zone 2 region. This boundary marks the lowest levels of each parameter used in the study, and effectively represents the lower limits of normal operating. This boundary should not be taken as the zone 1/zone 2 boundary, as only coatings with zones 2 and 3 structures were actually produced in this study. It was found that the CFUBMS system inherently produces operating conditions which effectively suppress the formation of porous columnar zone 1-type structures.

By allowing coatings to be described in terms of three critical parameters, the Kelly-Arnell model is a significant advance on existing models. However, it is clear that a number of assumptions were made in the development of this model. There are sources of error in the estimation of ion-to-atom ratio, and, in using bias voltage to represent ion energy, it is assumed that the plasma potential is constant. However, the development of this model is on-going, and it is felt that it will, ultimately, accurately

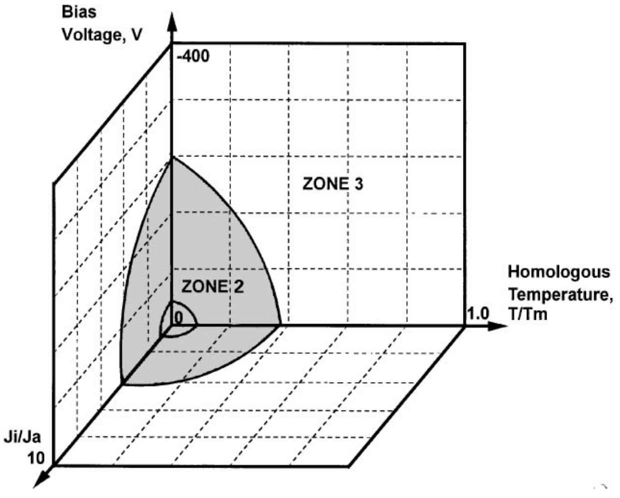

Fig. 10. Structure zone model relating to the CFUBMS system, in which structures are described in terms of homologous temperature, ion-to-atom ratio and bias voltage.

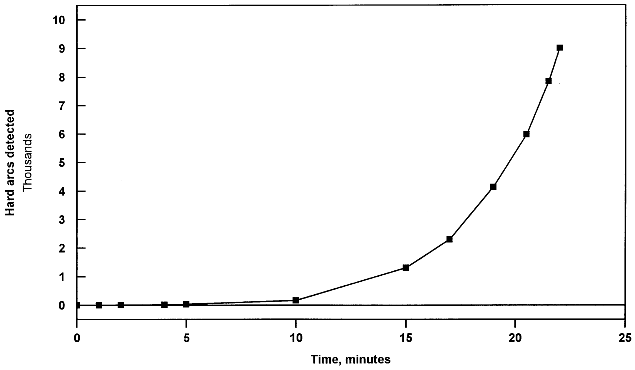

Fig. 11. Variation with time of the cummulative number of hard arcs detected during the deposition of an aluminium oxide film by reactive DC magnetron sputtering.

reflect the parameters which determine coating structure in the CFUBMS system.

## 7. Pulsed magnetron sputtering

The pulsed magnetron sputtering (PMS) process has transformed the production of highly insulating films, particularly oxides such as alumina. Oxide coatings can be produced by the reactive magnetron sputtering of a metallic target in a controlled oxygen atmosphere. They can also be produced by the direct RF (radio frequency; usually 13.56 MHz) sputtering of an oxide target. However, both of these processes are problematic. RF sputtering can produce high-quality films, but deposition rates are very low (typically in the μm/h range). Also, RF sputtering systems are complex and difficult to scale up for commercial applications.

The problems associated with the reactive magnetron sputtering of highly insulating materials are widely reported [9,50–54]. As the deposition process proceeds, areas on the target away from the main racetrack become covered with an insulating layer, as do the target earth shields. This coverage of the target with the reaction product is referred to as 'target poisoning'. The poisoned layers charges up, until breakdown occurs in the form of an arc. Arc events at the target can result in the ejection of droplets of material from the target surface. The ejected material can cause defects in the growing film, which are particularly detrimental to the performance of optical, or corrosion-resistant films. Also, the damaged area on the target may become a source of further arc discharges, leading to an increasing frequency of arcing, an effect which is clearly illustrated in Fig. 11 [55]. The reactive sputtering process is controlled by a feedback loop. Arc events prevent stable operation of the process by causing rapid fluctuations in the deposition parameters. This, in turn, can affect the stoichiometry of the growing film. In summary therefore, arc events during reactive sputtering are a serious problem, because they can affect the structure, composition and properties of the growing film, and can also lead to damage of the magnetron power supply.

The recently developed pulsed magnetron sputtering process (PMS) overcomes many of the problems encountered when operating in the reactive sputtering mode. It has been found that pulsing the magnetron discharge in the medium frequency range (10–200 kHz) when depositing insulating films can significantly reduce the formation of arcs and, consequently reduce the number of defects in the resulting film [9,50–54]. Furthermore, deposition rates during pulsed reactive sputtering approach those obtained for the deposition of pure metal films [53,54,56], i.e., of the order of tens of microns per hour. The PMS process, therefore, now enables the high rate deposition of defect-free ceramic films. As such, this process has attracted considerable commercial interest, and has led to the development of a new generation of magnetron power supplies and pulse units.

Although AC power supplies are becoming available, the PMS process generally utilises pulsed DC power. In this case, the target is sputtered at the normal operating voltage (typically, − 400 to − 500 V) for a fixed 'pulse-on' time. The pulse-on time is limited, such that charging of the poisoned regions does not reach the point where breakdown and arcing occurs. The charge is then dissipated through the plasma during the 'pulse-off' period by switching the target voltage to a more positive value. There are two modes of operation: unipolar pulsed sputtering, where the target voltage is pulsed between the normal operating voltage and ground; and bipolar pulsed sputtering, where the target voltage is actually reversed and becomes positive during the pulse-off period.

Due to the much higher mobility of electrons in the plasma than ions, it is usually only necessary to reverse the target voltage to between 10 and 20% of the negative operating voltage to fully dissipate the charged regions and prevent arcing (if the target voltage is not fully reversed, this mode should most accurately be described as ‘asymmetric bipolar pulsed DC’).

Fig. 12 shows a schematic representation of the target voltage waveform for a pulsed DC power supply operating in the asymmetric bipolar pulse mode. In this example the pulse frequency is 20 kHz, the pulse-off time is 5 μs (i.e., 10% of the full pulse cycle), and the reverse voltage is set to 10% of the normal operating voltage. The effectiveness of operating in this mode is amply illustrated by the micrographs shown as Figs. 13a and b (taken from Ref. [54]). Fig. 13a is a SEM micrograph of the fracture section of an aluminium oxide coating deposited by DC reactive sputtering. In this case, the deposition process was completely unstable, with arcing occurring at the target throughout. The coating has a granular, porous structure and a sub-stoichiometric composition. By contrast, Fig. 13b is a SEM micrograph of the fracture section of an aluminium oxide coating deposited by pulsed DC reactive sputtering, using the operating conditions described above. Arc events were suppressed during deposition, and the process was highly stable. Consequently, the coating has a stoichiometric $Al_2O_3$ composition, and is extremely dense with no discernible structural features or defects.

The coating shown in Fig. 13b was deposited using an Advanced Energy MDX DC magnetron driver in conjunction with an Advanced Energy SPARC-LE 20 pulse unit. In the SPARC-LE 20 unit, the pulse parameters are fixed. However, the more sophisticated SPARC-LE V unit allows control over pulse frequency, reverse time (i.e., pulse-off time) and reverse voltage. Recent work at Salford, investigating the deposition of alumina films, has shown that each of these parameters play an important role in the overall deposition process [55]. For example, pulsing the magnetron discharge at frequencies below 20 kHz was found to be ineffective at suppressing arcing. Whereas, at frequencies of 20 kHz and above, arc events can be completely suppressed, but reverse time becomes the critical parameter. At these frequencies, the most effective arc suppression was observed when the reverse time was increased to the point at which the pulse-off time approached, or was equal to the pulse-on time (i.e., 50% of the full pulse cycle). Reverse voltage did not appear to influence the number of arc events detected. However, it did have a significant effect on the deposition rate of the coating. Indeed, increasing the reverse voltage from 10 to 20% of the normal operating voltage, whilst maintaining all other parameters constant, resulted in an increase in the deposition rate of almost 50%. This effect has been attributed to enhanced target cleaning during the voltage reversal at the end of the pulse-off periods [57]. Optimum conditions for the deposition of alumina films, therefore, appear to be pulse frequencies of 20 kHz

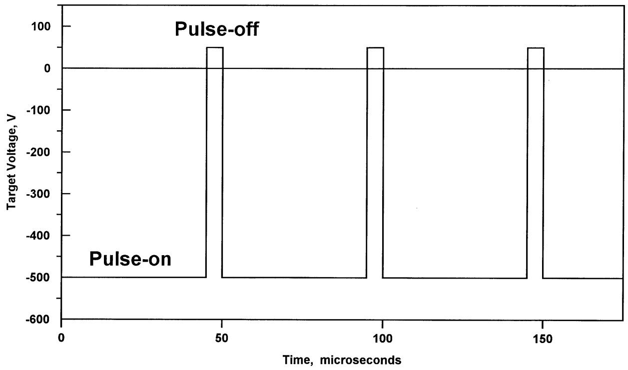

Fig. 12. Schematic representation of the target voltage waveform for a pulsed DC power supply operating in asymmetric bipolar pulse mode.

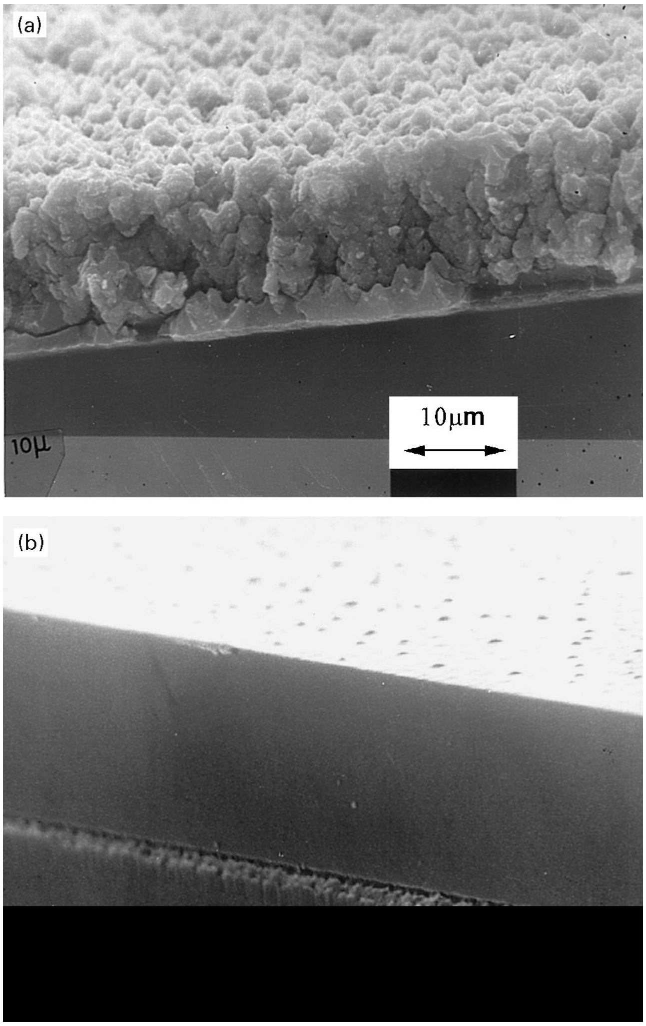

Fig. 13. SEM micrographs of the fracture sections of aluminium oxide deposited by (a) DC reactive sputtering, and (b) pulsed DC reactive sputtering.

and above, with equal pulse-on and pulse-off times, and the reverse voltage set to 20% of the normal operating voltage.

In addition to the dramatic improvements obtained in structure seen in Fig. 13, significant improvements are also obtained in the physical properties of alumina coatings deposited using the conditions described above. For example, Fig. 14 shows the transmission spectra for aluminium oxide coatings deposited by DC reactive sputtering and pulsed DC reactive sputtering, using the SPARC-LE 20 pulse unit. At a wavelength of 550 nm, the transmission of the PMS coating is > 97%. In contrast, the DC sputtered coating has a transmission of only 45% at this wavelength [58].

The PMS process has also been extended to dual magnetron systems [59]. In this case, both magnetrons are attached to the same pulse unit, and the process is described as dual bipolar pulsed sputtering. Each magnetron acts alternately as an anode and a cathode. By operating in this manner, the anode and cathode surfaces are prevented from poisoning, and very long-term process stability is achieved ( > 300 h). Industrial applications of this process include the deposition of high-quality optical coatings on materials such as architectural, or automotive glass and polymer web [60,61].

One final recent development in this field is the use of pulsed DC power at the substrate. Pulsing the substrate bias voltage has been found to significantly increase the ion current drawn at the substrate. In magnetron systems, the current drawn at the substrate normally saturates at bias voltages of the order of − 100 V [4]. Further increases in bias voltage do not lead to a further increase in current (see Fig. 5 for examples of magnetron current–voltage characteristics). It is generally assumed that the saturation current is an ion current, as any electrons approaching the substrate will be repelled at this voltage. Recent work by Teer Coatings [62], though, has shown that if the bias voltage is pulsed, not only is the magnitude of the saturation current greater than for the DC bias case, but the current drawn at the substrate continues to increase as the bias voltage is increased. In addition, as can be seen in Fig. 15, both of these effects become more marked as the pulse frequency is increased. The exact mechanism causing these effects is not yet clear. However, it is known that plasmas generated by oscillating fields are more energetic (i.e., have higher plasma densities and electron temperatures) than DC plasmas [63]. Pulsing the substrate bias voltage, therefore, offers a novel means of controlling the ion current density drawn at the substrate. This could be utilised, both during deposition to optimise the coating structure and adhesion, and also during sputter cleaning and substrate heating, where enhanced ion currents could allow shorter process times.

## 8. Variable field strength magnetrons

For any given set of deposition parameters, the performance of a magnetron, i.e., the fluxes of ions and coating atoms that it can deliver to the substrate, is determined by the design of the magnetic array and the strength of the magnets in that array. As discussed in Section 6, the ion-to-atom ratio incident at the substrate is one of the fundamental parameters which determine coating properties. However, both ion current and deposition rate are directly proportional to target current. Thus, when using magnetrons of fixed magnetic configuration, the ion-to-atom ratio can be varied only over a very limited range [40]. To overcome this limitation, new magnetrons have been designed in which the degree of unbalancing can be varied in situ, without the use of costly and cumbersome electromagnets [12]. In order to achieve this, both the inner and outer sets of magnets in the magnetic array can be moved relative to each other. This system allows the magnetron to operate in all modes from virtually balanced, to strongly unbalanced. Further, the degree of unbalancing, and, therefore, the ion-to-atom ratio at the substrate, can be varied at any stage of the deposition

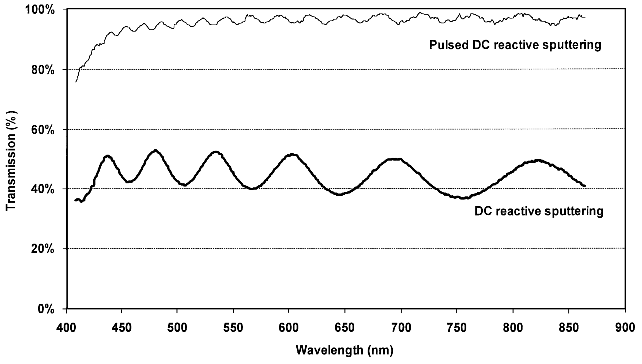

Fig. 14. Transmission spectra for aluminium oxide coatings deposited by DC reactive sputtering and pulsed DC reactive sputtering (after ref. [57]).

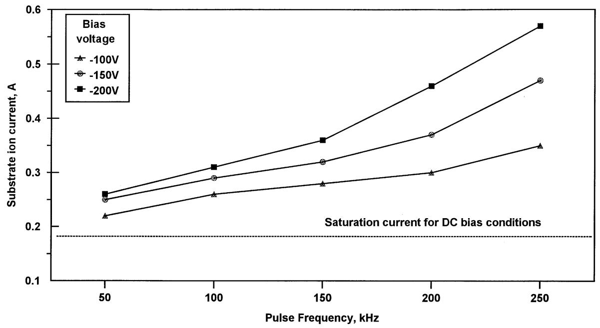

Fig. 15. The variation with pulse frequency and bias voltage of the substrate ion current for pulsed DC bias conditions (after ref. [61]).

process, or even continuously throughout the deposition process.

The effect of varying the magnetron configuration on the magnetic field is shown in Fig. 16 [12]. This figure shows the magnetic field strength at the target for a Gencoa VT130450 VTech variable magnetron operating in balanced, intermediate (i.e., weakly unbalanced) and strongly unbalanced configurations. The measurements were made with a 6 mm thick copper backing plate installed on the magnetron in place of a target. In the balanced mode the outer pole is fully retracted from the target and the inner pole fully advanced, in the intermediate mode both poles are fully advanced, and in the strongly unbalanced mode the outer pole is fully advanced and the inner pole fully retracted. In this design, the range of movement from fully advanced to fully retracted is of the order of 15 mm. The variation in the relative strengths of the inner and outer poles as the magnets are moved can be clearly seen in Fig. 16. It should be noted that, although, in principle, variable magnetrons could be designed to operate from 'type-1' unbalanced, right through to 'type-2' unbalanced (see Fig. 1), there is little commercial demand for 'type-1' systems. Thus, the range of movement of the magnets has been limited in these magnetron designs.

Variable magnetrons add an extra dimension to the sputtering process. They allow the operator to fine tune the fluxes of atoms and ions incident at the substrate during the deposition process. For example, high levels of ion bombardment during the initial stages of deposition may be beneficial to coating adhesion. However, continued excessive bombardment may be detrimental, because it can result in the formation of high stresses and defects in the coating. Variable magnetrons allow the operator to reduce the ion-to-atom ratio at any stage during deposition to counteract these problems. Furthermore, during the deposition of graded, or multi-layer coatings, variable magnetrons allow conditions to be selected to optimise the properties of each component in the coating. Also, the characteristics of a target change as it erodes. This can lead to variations in deposition rate over the life of a target. In processes where this is critical, variable magnetrons offer the potential of maintaining constant target characteristics and, therefore, constant erosion rates.

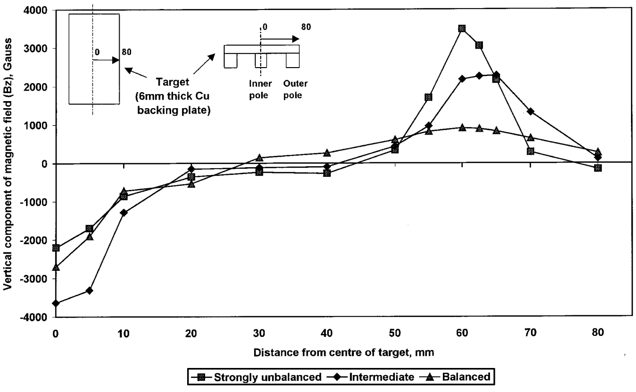

Fig. 16. The variation in magnetic field strength across the target, from the central pole to the outer pole, for a variable magnetron operating in balanced, weakly unbalanced (intermediate), and strongly unbalanced modes. Sign convention: + ve values are north poles, − ve values are south poles.

## 9. Duplex surface engineering

The recent developments in magnetron sputtering, described in this paper, now allow very high-performance coatings to be produced. Indeed, in many applications, magnetron sputtered coatings now outperform coatings produced by other techniques. However, their market penetration is currently limited to certain 'niche' sectors. Traditional surface engineering techniques still dominate the market place, and are likely to do so for several years to come [13]. Part of the reason for this is the perceived high cost of sputter (and other PVD) coated components [64]. However, this is deceptive, as the cost of a component is more than compensated for when the subsequent increase in performance is considered. For example, data from Balzers Ltd. suggests that coating a forming punch by PVD can add 35% to the cost of the tool, compared to only 8% for a gas-nitrocarburising treatment. However, the PVD coated tool can offer an increase in life over an uncoated tool of up to 32 times, compared to the 1.5–4.5 times increase in life offered by the other technique [65]. The economics are further enhanced if reduced downtime to change tools and the reduced number of rejected components are also considered. In another example from Balzers [66], it was found that using PVD-coated high-speed steel taps to machine steel tubes, in place of uncoated tools, reduced the total manufacturing costs per 100 parts from SFr 108.35 to only SFr 42.85.

Another factor which has limited the exploitation of advanced PVD processes is their unsuitability for use with many substrate materials such as low alloy steel and titanium alloys. In the case of hard coatings, this is due to the lack of load-bearing support provided by the substrate; whereas, in the case of corrosion resistant coatings, pin-hole defects have compromised the performance of the coating. To address these problems, and to extend the commercial viability of advanced PVD processes, duplex surface engineering processes have been developed.

Bell describes duplex surface engineering as 'the sequential application of two (or more) established surface technologies to produce a surface composite with combined properties which are unobtainable through any individual surface technology' [14]. Two general groups are identified; those in which the individual processes complement each other and the combined effects result from both processes (group 1), and those where one process supplements, or reinforces the other, acting as a pre-, or post-treatment, and the resultant properties are mainly related to one process (group 2). Examples from both groups of process are given in Refs. [13,14].

PVD treatment of a pre-nitrided steel is a good example of a group 1 process. Plasma nitriding produces a relatively thick ( ~ 500 μm), hardened ( ~ 10 GPa) sub-surface. A 3–5 μm thick titanium nitride (TiN) layer can then be deposited onto the nitrided surface using various PVD techniques, including magnetron sputtering. Components treated in this way exhibit the low wear characteristics of the ceramic coating, combined with the high load-bearing capacity and high fatigue strength characteristics of the nitrided layer. The effectiveness of this technique is shown in Fig. 17, which compares the wear volume for various untreated, individually treated and duplex treated En40B steel specimens in a ball-on-wheel test. Bell illustrates how the substrate, plasma nitriding treatment and the PVD coating all contribute to the overall composite component with the required properties in a convenient manner [14], which is reproduced here as Fig. 18.

A similar example of duplex surface engineering is the DLC coating-oxygen diffusion process for titanium alloys [14]. Titanium alloys combine high strength-to-weight ratios and exceptional corrosion resistance, but are also characterised by poor tribological properties and poor load bearing capacity. Again, the tribological properties of the titanium alloy could be significantly improved through the use of a PVD coating. However, premature failure of the coating will occur in high load situations. A duplex solution to this problem has been developed, combining an oxygen diffusion pre-treatment with a CFUBMS deposited graded DLC coating (as referred to in Section 5). The oxygen diffusion process provides a hardened sub-surface for improved load bearing, and the DLC coating provides excellent low friction and wear characteristics at the surface. However, DLC coatings are usually associated with high levels of residual stress and poor adhesion when deposited directly onto a component. The versatility of the CFUBMS process has provided a solution to this problem. An intermediate layer is deposited in which the composition is graded from titanium, through titanium nitride, to titanium carbo-nitride and finally to titanium carbide. The DLC coating is then deposited onto this layer. Control of the CFUBMS process allows the whole procedure to be carried out without interruption and there are no sharp interfaces. The intermediate layer is only some 1–2 μm thick, yet by grading the composition in this way high interfacial stresses are avoided and the coating adhesion is significantly improved.

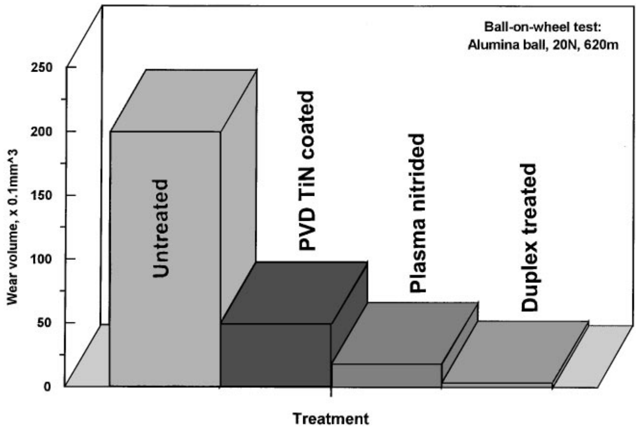

Fig. 17. Ball-on-wheel wear test results for untreated, PVD TiN coated, plasma nitrided and duplex treated En40B steel (after Ref. [14]).

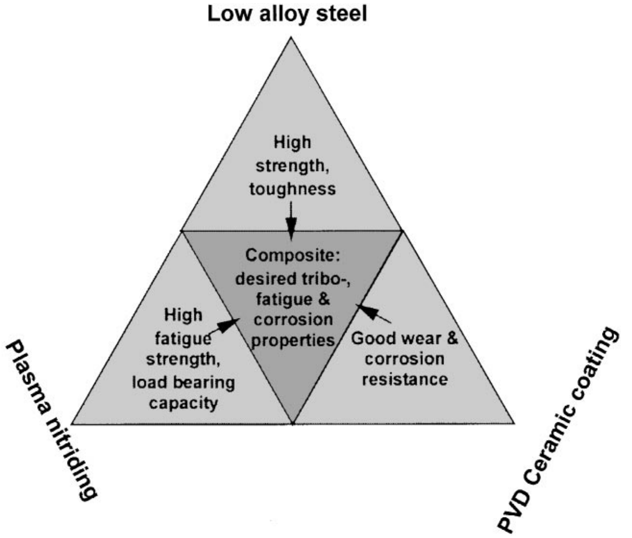

Fig. 18. The design philosophy behind obtaining improved properties through duplex surface engineering processes (after Ref. [14]).

## 10. Conclusions

Several recent developments made in the magnetron sputtering field have been discussed in this paper. These include closed field unbalanced magnetron sputtering, pulsed magnetron sputtering, variable field strength magnetrons and duplex surface engineering techniques. Together, these developments have transformed the capabilities of magnetron sputtering, and helped to establish it as the process of choice for the production of many industrially important coating/substrate systems. The results of a number of recent fundamental studies in this field have also been included and several industrial applications are discussed. Overall, therefore, this paper provides a review of the current status of the magnetron sputtering process and considers future areas of exploitation for this technique.

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