ELSEVIER

Surface and Coatings Technology 71 (1995) 82–87

SURFACE & COATINGS TECHNOLOGY

An improved ion assisted deposition technology for the 21st century

N.A.G. Ahmed

Plasmion Ltd, Salford Tramways Building, PO Box 50, Frederick Road, Salford M6 6BY, UK

Abstract

In recent years technologies based on physical and chemical vapour deposition (PVD and CVD) have had a significant impact on the performance of a range of products including cutting tools, aircraft and automotive parts, decorative and electronic products. However, it is envisaged that further improvements in material properties and hence improved product performance will only be likely if these processes are modified to incorporate ion assistance. Preliminary results have shown that adhesion, hardness, structural, optical and electrical properties of the deposited coatings improve when ion-assisted deposition is used instead of conventional PVD and CVD technologies. The major general improvements are lower deposition temperatures and higher deposition rates, opening up many new applications previously considered outside the realm of this technology. As examples, to illustrate the improved technology, the deposition of Cd, Al, W, diamond-like carbon and TiN are considered in detail in relation to applications in industry. The relationships between the process parameters and the coating characteristics were also investigated. This process can be easily automated, is suitable for production use and is likely to produce a profound effect on manufacturing in the 21st century.

Keywords: Ion assisted deposition; Reactive coating; Wear resistance; Corrosion protection

1. Introduction

Ion assisted deposition (IAD) is widely used to deposit coatings for applications including corrosion protection, wear resistance, dry lubrication, optical and ophthalmic lenses, and electrical and electronic components [1,2]. The adhesion, structure and durability of a coating on a substrate are vital requirements for any surface engineering application. However, over the past few years it has been shown that the adhesion, structure and durability of coatings on various substrates can be substantially improved by irradiating the substrate and the condensing film with ions and energetic neutrals in the energy range of a few electron volts to several kiloelectron volts [3,4]. Therefore, IAD has become a rapidly growing industrial technique mainly in the area of surface engineering. This technique utilizes the inherent properties of materials by supplying some kinetic energy and/or enhancing the chemical activity through the ionization process. The presence of ionized and energetic neutrals greatly influences the critical parameters of the condensing film on a particular substrate and enhances the chemical reaction [5–7]. Therefore, the film properties such as mechanical, optical and crystallographic properties can be controlled and used to design coatings with particular characteristics.

This paper reviews recent advances in the technology and applications of IAD. The paper also gives a brief introduction to the science of IAD and considers effects of ion bombardment on the formation and properties of the coatings deposited using this technology.

2. The role of energetic particles in ion assisted deposition

IAD is a term applied to the utilization of ions and energetic gas particles during the deposition of coatings by techniques such as evaporation or sputtering [2]. The substrate is usually attached to a negative d.c. power supply and the ions can be supplied either through a gaseous discharge or by bombarding the substrate with ions from an ion gun. The simplest technique involves backfilling the vacuum chamber with inert gas, such as argon, then initiating a discharge between the negatively biased substrate and the grounded chamber (Fig. 1). Ions generated by these methods usually transfer their energy, momentum and charge to the substrate prior to coating and to the condensing film during the coating process [3,8,9]. In practical terms the substrate and the coating will be continuously bombarded with a mixture of high energy ions and neutrals of the carrier gas and coating material as well as electrons. The average energy of arriving ions and neutrals at the biased substrate in

SSDI 0257-8972(94)01003-2

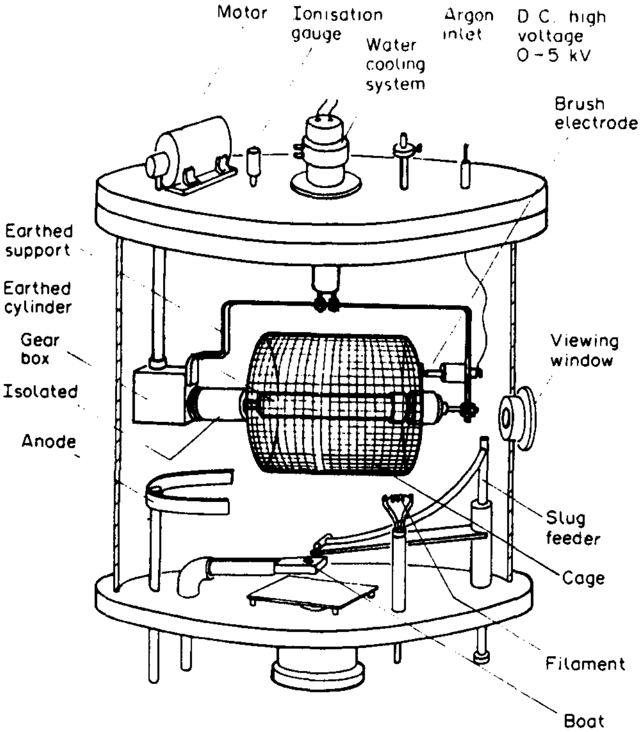

Fig. 1. Schematic diagram of an IAD system for coating small components using thermionically assisted triode discharge to enhance ionization.

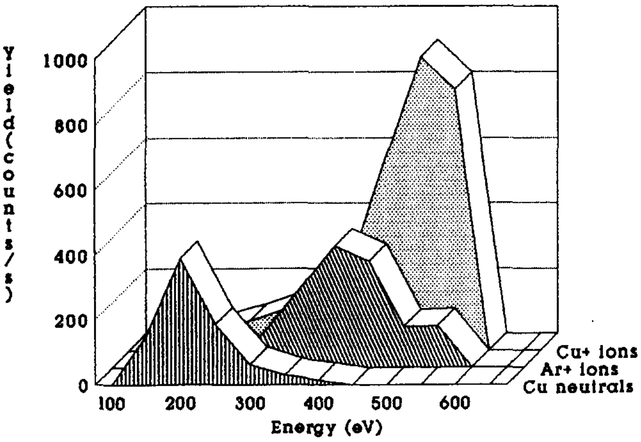

Fig. 2. Energy distribution of ions and neutrals during the evaporation of Cu in an Ar discharge at 0.01 Torr pressure and 1.2 kV discharge bias.

Table 1
Fundamental effects of plasma bombardment on film formation

Process	Effect
Defect formation	Nucleation sites, interfacial layer, increased bonding
Coating–substrate mixing	Interface formation
Surface cleaning	Adhesion Improvement, removal of oxides, chemical reaction
Deep etching	Mechanical bonding
Ion species	Chemical reaction, removal of contaminants
Surface diffusion	Change in morphology, epitaxial film
Continuous bombardment	Change in morphology, nucleation growth, heating effects
Ion implantation	Interface formation

gaseous discharge type IAD ranges from one-third to one-half of the typical discharge voltage of 2–3 kV [2,3,8]. Fig. 2 shows the energy distribution of Cu^+ and Ar^+ ions and Cu neutrals during the IAD of Cu film [8]. Consequently, the early stages of film growth are controlled by a complex mixture of processes involving collision, penetration and entrapment of high energy particles. Knock-on sputtering effects in which surface atoms are knocked into, rather than out of, the substrate may also be important even though the penetration depth is very small [10]. However, ion implantation plays only a comparatively minor role in the actual material growth owing to the small energy involved (typically below 1 keV). Thus the kinetic energy of ions and energetic neutrals has beneficial effects on the film formation particularly interface formation, nucleation and migration, heating, chemical reactions, compositional effects and crystallographic structure (Table 1). The continuous ion bombardment can produce a graded rather than sharp interface which enhances the adhesion of the coating to the substrate [9,11]. Ion bombardment of the condensing atoms enhances the surface mobility of adatoms, accelerates the nucleation and growth of the nuclei and coalesence at the initial stage of film formation, creates or activates sites that stimulate nucleation processes as well as decreasing stress and increasing the bonding energy between the deposited film by energetic ions [2,5,12]. If the condensing atoms react strongly with the surface, the surface mobility will be limited and the nucleation density will increase. This will lead to the formation of a continuous monolayer on the substrate surface [13,14]. If there is a chemical reaction or diffusion, the condensing atoms will react with the surface to form compound or alloy layers which extend both normally and laterally to the surface. Such a chemical reaction may also produce a strong heat of formation of a compound, which can assist diffusion and ion beam mixing. This mode of growth will tend to decrease the interfacial porosity and "grade" the properties of the interfacial regions [15]. However, extensive interfacial diffusion reaction may degrade the interface by the formation of porosity owing to differential diffusion rates or by high intrinsic stresses generated by thick interfacial compound layers [16]. Very thin contamination layers on the surface can convert the diffusion–reaction nucleation mode to the non-reaction mode with an attendant undesirable interfacial mode. Fig. 3 shows the effect of ion bombardment on the formation of a dense structure which improves the various characteristics of the coating.

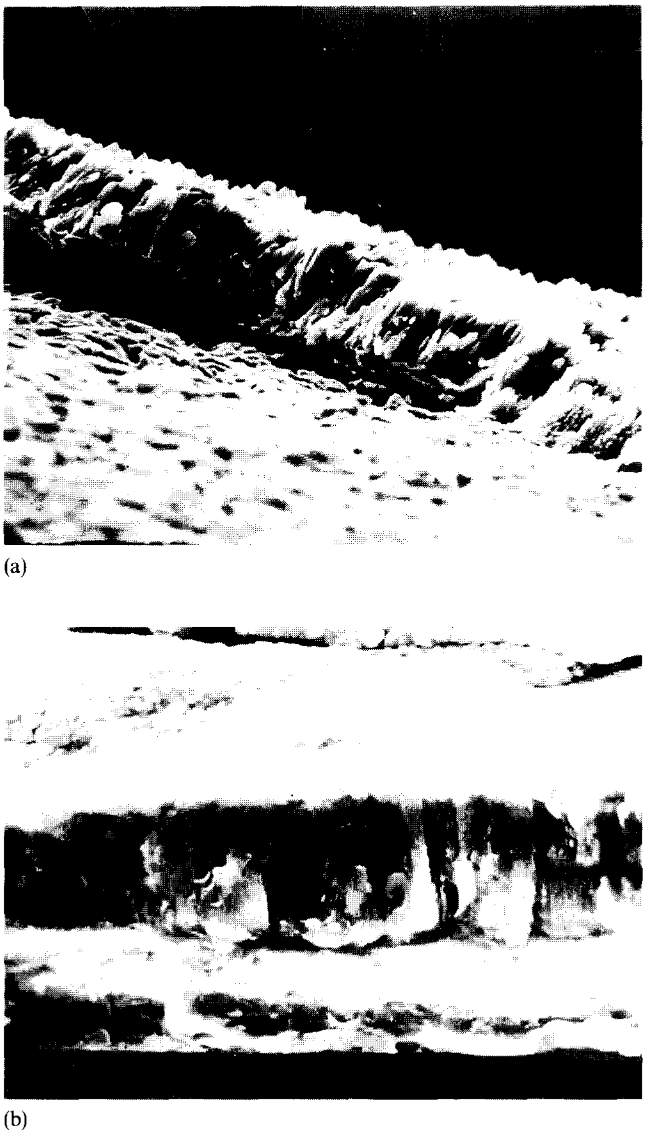

Fig. 3. Effect of ion bombardment on coating structure: 2 kV bias, 0.01 Torr pressure, (a) 0.1 mA cm^{-2} current density, (b) 0.5 mA cm^{-2} current density.

3. System configuration

A typical IAD system consists of an electrically isolated substrate holder which can be biased with a d.c. or r.f. negative potential (Fig. 1). The substrate holder can also serve as a cathode to strike a gaseous discharge with respect to the earthed chamber. An alternative arrangement is to use an ion beam gun to bombard the biased substrate with ions at a defined range of energies. The coating material can either be evaporated from resistance heated boats or electron beam guns, or can be sputtered using balanced or unbalanced magnetron sputtering targets [17–19]. The ionization rate can also be enhanced by using a triode arrangement with negatively biased filament and a positive anode (Fig. 1) [20]. Other methods employed to enhance the ionization efficiency include the utilization of a Helmholtz coil around the vacuum chamber to produce a magnetic field in the vicinity of the substrate [21]. Prior to coating, the substrate is bombarded with ions to clean the surface on an atomic level to enhance the adhesion of the film to the substrate. During this stage the temperature of a metal substrate does not normally exceed 180–230 °C after 10 min continuous bombardment with ions, using a current density of 0.3 mA cm^{-2} and discharge voltage of 3 kV (Fig. 4). For depositing wear resistant coatings, such as titanium nitride, the substrate temperature has to be increased to 400–500 °C in order to obtain a highly adherent coating with the correct stoichiometric structure [22,23]. However, to attain high quality coatings reproducibly, many parameters have to be controlled and optimized for each particular coating/substrate combination. Reactive systems, in particular, require a high degree of independently controlled parameters to achieve the required reaction [24]. In general, there are three major processes that have to be controlled in order to achieve a reproducible coating with excellent characteristics. These are pre-treatment, IAD and post-treatment.

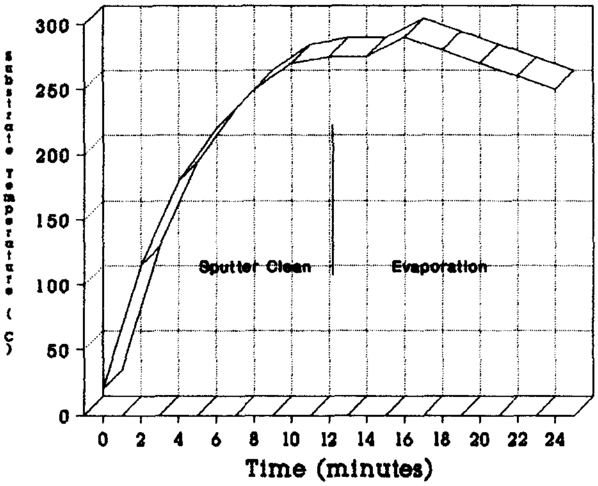

Fig. 4. Effect of sputter cleaning and evaporation on the temperature rise of a steel substrate at 2 kV bias, 0.1 mA cm^{-2} discharge current and 0.01 Torr Ar pressure.

4. Industrial applications of ion assisted deposition

In spite of excellent laboratory results, a new process will only be used for industrial applications if its control can be supervised or automated and if the results obtained at the laboratory stage can be reproduced on an industrial scale. At present there are many industrial applications for IAD ranging from coatings for corrosion protection, wear resistant and optical coatings, and coatings for laser applications. Table 2 summarizes the various applications of this technique using different

Table 2
Industrial applications of ion assisted deposition

Application	Coating material	Substrate material	Thickness (μm)	Deposition rate (μm min^{-1})	Production details	Substrate temperature (°C)
Corrosion	Al	U, steel, Ti, alloy	$\leqslant 40$	2	40–60 kg fasteners h^{-1}	250–300
	Cd	Steel				100–150
	Zn	Steel			30 m min^{-1}	150–300
High temperature corrosion protection	MCrAlY, Ni/CrAlY	Ni or Co base super-alloy	125	5	$\leqslant 1400$ blade/day	
	TiHfN, TiCN	Alloy				
	Cr, Al_2O_3, Si_3N_4	Steel, Mo				
Wear Resistance	HfN, ZrN	Steel	1–5	0.08–1	1/4 inch diameter round shank tools, 2.5 h^{-1}	400–500
	TiN, TiCN, BN, TiC, WC	Steel, cemented carbide, high speed steel, die steel				
Electrical	Pt, Al, Au, Ag	Si	1	0.5–1		250–300
	Al	GaAs				
	In(Ga)	CdS				
	Cu	Al_2O_3				
	Si_3N_4	Si–Mo				
Lubrication	Pb, Au, Mg, MoS_2, Al, $MoSi_2$	Metals	0.1–1	0.1–1		50–100
	PbSn alloy, graphite	Plastic				
Optical and decorative	Cr, In(Sn)O	Plastic	$\leqslant 10$	0.5–1		
	SiO_2, ZrO_2	Glass, plastic				
	TiN, Zrc, TiC	Metals				
Bonding	Ag	Be	$\leqslant 10$	1	50–100	
	Cu	Ta, W, Nb, oxides				
X-ray anodes	Al, Mg, Ag	Cu	$\leqslant 40$		20 anodes h^{-1}	100–250

types of coating. This technique is currently employed for coating steel parts with cadmium, aluminium or zinc for corrosion protection in production [25,26]. IAD is used in this respect to eliminate hydrogen embrittlement problems and any toxic effluent compared with electroplating. Fig. 5 shows aircraft parts coated with cadmium using this technique to increase the corrosion protection against sea water. The other major industrial application is to deposit hard wear materials such as titanium nitride, titanium carbide, tungsten and tungston carbide for wear resistance. These coatings are deposited onto cemented carbide and alloy steel cutting tools and forming tools, such as dies and punches [27,28]. Fig. 6 shows drills coated with titanium nitride is bright gold and has a hardness in the range 2500–3000 HV. Titanium carbide is dull grey in colour and is an excellent wear resistant coating which has a superior hardness in the range 3300–4000 HV. These coatings are used to increase the tool life and improvements by factors of 2–10 have been observed depending on coating properties such as thickness and the deposition process characteristics. All of these coatings are applied to a thickness in the range 3–10 μm depending on the performance requirement and particular application. Other coatings of major interest in the tool industry include diamond-like carbon, aluminium oxide, silicon nitride, tungsten carbide, chromium nitride, cubic boron nitride and zirconia [29]. IAD technologies can reproducibly deposit hard coatings with highly dense structure, which is important in practical applications since a coating composed of weakly bonded columns can never achieve the full hardness of the bulk material [23]. IAD is also used to deposit solid lubricants such as MoS_2, Sn, graphite, Ag, PTFE and Pb onto bearing surfaces for

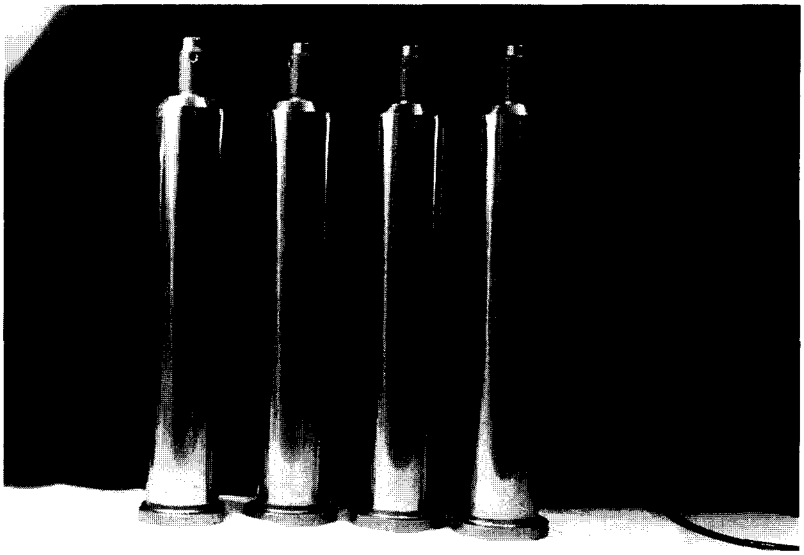

Fig. 5. IAD of cadmium onto aircraft parts for corrosion protection.

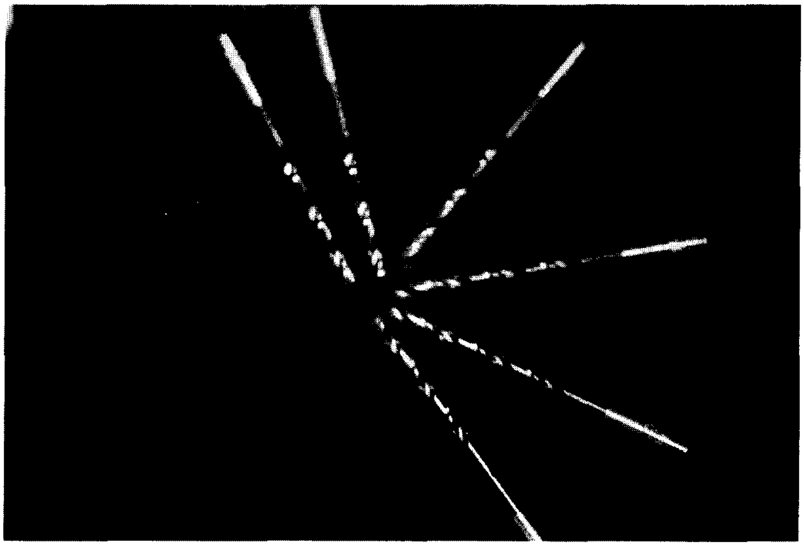

Fig. 6. IAD of titanium nitride onto drills to increase wear resistance.

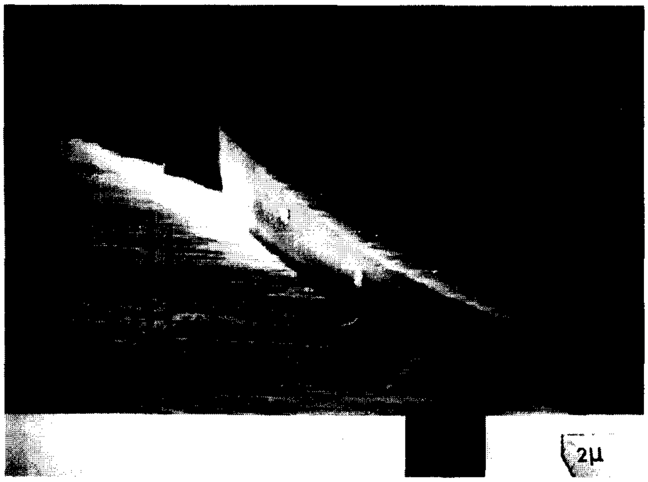

Fig. 7. IAD of diamond-like hard carbon for wear resistance.

use in vacuum and space satellites [30,31]. These low friction films, 0.2 µm thick, are very effective in improving the frictional and wear characteristics and in increasing the endurance life. The recent interest in the deposition of thin films of diamond-like hard carbon (DLC) coatings has resulted in extensive investigations of various deposition techniques. IAD has been used to sputter deposit amorphous carbon (a-C) diamond-like films during concurrent ion bombardment [32]. However, films produced by this method have a hard amorphous carbon structure (Fig. 7). High temperature corrosion protection layers for turbine blades are also effectively deposited by IAD. Thick NiCrAlTi and CoCrAlY coatings have been deposited onto turbine blades to provide excellent corrosion resistance to the nickel alloy substrate even after 1200 h exposure to hot corrosive gases, compared with 100 h for aluminide and other coatings [32]. In the optical components industry, IAD is used to deposit oxide and nitride coatings onto unheated insulating substrates including glass. For this purpose, a low voltage, high current plasma beam (hot cathode type) is used to activate and ionize the evaporating material [33]. Films produced by this technique show amorphous and very fine grained polycrystalline structure with good optical properties.

5. Conclusions

The technology and applications of IAD have been reviewed. It has been shown that IAD results in superior quality films compared with conventional sputtering and evaporation processes. This is related to the process physics and key deposition parameters. A detailed understanding of these will enable the process engineer to produce novel materials, develop new processes and optimize coating characteristics and throughput for industrial scale applications.

References

[1] R.F. Bunshah, in R.F. Bunshah (ed.), *Deposition Technology for Films and Coatings — Development and Applications*, Noyes, Englewood Cliffs, NJ, 1982, p. 83.

[2] N.A.G. Ahmed, *Ion Plating Technology, Development and Applications*, Wiley, New York, 1987.

[3] N.A.G. Ahmed, *J. Phys. E, 13*, (1980) 295.

[4] D.M. Mattox, *Proc 4th Int. Colloq. on Plasmas and Sputtering, Nice*, Société Français du Vide, Paris, 1982, p. 187.

[5] T. Takagi, *Proc 5th Int. Conf. on Ion Sources and Ion Assisted Techniques, Kyoto University, 1–5 June 1981*, Kyoto, 1981, p. 173.

[6] S. Kadlee, J. Musil and W. Munz, *J. Vac. Sci. Technol. A, 8* (1989) 1318.

[7] B. Window and G.L. Harding, *J. Vac. Sci. Technol. A, 9* (1990) 1277.

[8] D.G. Armour, H. Valizadeh, F.A. Soliman and G. Carter, *Vacuum, 34* (1984) 295.

[9] D.M. Mattox, Interface formation, adhesion and ion plating, *Trans. SAE*, (1969) 2175.

[10] D.G. Armour, G. Carter, R.P. Webb, D.C. Ingram and R. Newcombe, *Radiat. Effects Lett., 50* (1980) 45.

[11] J.M. Harper, J.J. Cuomo, R.J. Gambino and H.R. Kaufmann, in O. Auciello and R. Kelly (eds.), *Ion Bombardment Modification of Surfaces: Fundamentals and Applications*, Elsevier, Amsterdam, 1984, p. 127.

[12] N.A.G. Ahmed, *Thin Solid Films, 52* (1978) 415.

[13] D.M. Mattox, in R.F. Bunshah (ed.), *Deposition Technologies for Films and Coatings* Noyes, Englewood Cliffs, NJ, 1982, Chapter 6.

[14] M.A. Nicolet, *Thin Solid Films, 52* (1978) 415.

[15] D.M. Mattox, *Jpn. J. Appl. Phys.*, Suppl 2, (1) (1974) 443.

[16] J.L. Vossen and W. Kwrn (eds.), *Thin Film Processes*, Academic Press, New York, 1980.

[17] B. Window and N. Savvides, *J. Vac. Sci. Technol. A, 4* (2) (1986) 196.

[18] A.G. Spencer, K. Oko, R.W. Lewis and R.P. Howson, *Vacuum, 38* (1988) 857.

[19] J. Musil, S. Kadlec, J. Vyskocil and V. Poulek, *Surf. Coat. Technol., 39–40*, (1989) 301.

[20] N.A.G. Ahmed, *Thin Solid Films, 144* (1986) 103.

[21] I.W. Fischbein and A. Sastri, *US Patent 3, 682, 795* 1972.

[22] B.O. Johansson, J.E. Sundgren and J.E. Green, *J. Vac. Sci. Technol. A, 3*(2) 1985 303.

[23] B.E. Jacobson, R. Nimmagadda and R.F. Bunshah, *Thin Solid Films, 63* (1979) 333.

[24] R.F. Bunshah and K.V. Deshpandy, *J. Vac. Sci. Technol. A, 3* (3) (1985) 553.

[25] N.A.G. Ahmed, *Product Finish.*, (June 1991) 23.

[26] N.A.G. Ahmed, *Anti-Corrosion Methods Mater, 31*(12) (1984) 4.

[27] R.L. Hatschek, *Am. Machinist, Special Rep., 752*, (1983) 129.

[28] Y. Pauleau and Ph. Gouy-Pailler, *J. Mater. Res.*, 7(8) (1992) 20, 70.

[29] H. Kajioka, K. Higuchi and Y. Kawashimo, *Mater Sci. Eng., A163* (1993) 201. K.S. Fancey, S.J. Young, A.S. James and A. Matthews, *Mater. Sci. Eng., A163* (1993) 171. P. Ballhouse, B. Hensel, A. Rosat and H. Schussler, *Mater. Sci. Eng., A163* (1993) 193.

[30] T. Spalvins, *Thin Solid Films, 84* (1981) 267.

[31] Y. Pauleau and P.H. Gouy-Pailler, *Mater. Lett., 13*(23) (1992) 157.

[32] J.P. Coad and J.E. Restall, *Proc. Conf. on Ion Assisted Surface Treatments, Techniques and Processes, 14 September 1982*, The Metals Society, London, 1982, p. 13.1.

[33] S. Scaglino, D. Flori, I. Soymie and A. Piegari, *Thin Solid Films, 214* (1992) 188.