

# for Wear and Cracking Prevention in Die-Casting Dies by the Filtered Cathodic Arc Process

Deepak G. Bhat, Vladimir Gorokhovsky and Rabi Bhattacharya UES Inc.Dayton, OH

Presented by: North American Die Casting Association

Rajiv Shivpuri and Kaustubh Kulkarni The Ohio State University, Columbus, OH

This paper is subject to revision. Statements and opinions edvanced in this paper or during presentation are the number's and are higher responsibility, not the Association's. The paper has been added by NADCA for uniform styling and format. For permission to publish this paper in full or in part, contact NADCA, 8701 W. Higgins Rd., Ste. 880, Rosemont, IL 80018-4721 USA, and the author.

#### **Abstract**

Die wear and failure is a major cost factor for the die casting industry, because of premature failure of dies, high cost of disposal of scrap and loss of productivity. The critical failure modes of die casting dies include erosion, thermal fatigue, soldering and wash out. Various coatings have been used effectively to protect against soldering, but there is still a need for a cost-effective coating and coating process to address the issues of thermal fatique and erosion. In this paper, we describe the preliminary results of development of a new multi-layer coating, deposited by an advanced filtered cathodic arc deposition process. This technique provides a cost-effective way to deposit multi-layer coatings of excellent surface morphology and properties, which can be tailored to address the issues of thermal fatigue and erosion of die casting dies. In the present work, the thermomechanical test cycles were designed to simulate various die casting situations. Results of dip testing in a molten A380 alloy show that the coatings in the present study provided an order of magnitude improvement in hot corrosion/ erosion resistance of the H-13 die steel core pins. The preliminary thermal fatigue tests show a significant improvement in the heat checking resistance of the core pins specially designed to provide varying degrees of stress concentration factors.

#### Introduction

Die wear and failure is a significant issue for the die casting industry because of the high cost of dies. Wear of the die is caused primarily due to the necessity for multiple reuse of the die for a typical production run of more than 100,00 castings at the rate of 2,500 shots per day [1]. At this rate of production, it becomes imperative that

the molten metal be introduced into the die cavity at high flow velocities (typically 40m/sec) and rapidly solidify for quick ejection. This quick thermal cycling results in die temperature gradients of the order of 1000° C/cm. Thus. the dies are subjected to very harsh conditions that combine high temperatures, molten metal impingement, high injection pressure, mechanical cycling and thermal cycling. These extreme and rapidly cycling conditions take their toll on the die and the other components of the die assembly such as the cores and ejector pins. Consequently, the die casting industry experiences a significant cost in terms of die failures, disposal of scrapped dies, loss of productivity and product quality problems. Therefore, methods that can improve the life of die casting dies are of paramount importance in terms of cost savings, energy savings and improvements in industrial productivity.

The most important modes of failure in die-casting dies are erosive and abrasive wear, thermal fatigue, soldering and chemical attack or corrosion [2]. Erosive wear is caused by the high velocity impingement of molten metal against the complex geometrical features like cores, ribs and corners, resulting in a loss of dimensional accuracy of the casting. This necessitates the frequent rebuild of the worn out regions. Thermal cracking, also known as heat checking or thermal fatigue is caused due to the alternate heating and cooling of the die. The large thermal gradients put the die surface in compression during heating and in tension during cooling. This leads to lowcycle thermal fatigue induced surface cracking, deterioration of the surface finish and ultimately die failure. Soldering is caused by the chemical interaction of the casting alloy with the die surface during filling and solidification, leading to sticking of metal at different spots on the die surface. This not only produces defective castings but also an excessive ejection force required to remove

the casting. This causes failure of the ejector pins and damage to the die surface. It also leads to hot corrosion of the die, which further exacerbates the problem of heat checking.

The wear of die casting dies can be reduced by (i) surface treating one or both surfaces in contact, (ii) use of lubricants, (iii) proper dimensional fit, and (iv) polishing of surfaces. In recent years, hard coatings are being extensively used to decrease the wear of dies. Coatings for die casting dies were used in Japan as early as the 1970s, and showed considerable promise for the improvement of die life and productivity [1]. Since then, many different coatings have been applied to die surfaces, including CrN, Cr.C., TiN, TiCN, ZrN, VC and TiAIN [1,3,4]. For example, Physical Vapor Deposited (PVD) CrC and CrN coatings have been shown to perform well because of their high oxidizing temperature (700°C or 1300°F), high hardness (2500 HV) and the ability to withstand die surface expansion/contraction cycle [3]. Coatings deposited by Chemical Vapor Deposition technique (CVD) have also shown major life improvements. These include Cr,C3, TiN, ZrN and VC [4]. Surface treatments such as nitriding, boriding and nitrocarburizing have also demonstrated improved wear and fatigue resistance.

#### Prominent modes of coating failure:

The difference in the coefficient of thermal expansion of the coating and the substrate material is a common cause of coating failures (figure 1) [5]. Rapid cooling of the die surface during lubrication causes the steel substrate to contract, thereby putting the coating in tension. This tension leads to crack initiation in the coating. This crack then expands due to the corrosive and erosive attack of molten aluminum. The molten aluminum then diffuses through the coating and forms inter-metallic compounds with the steel substrate. Volume expansion takes place just below the coating, which stresses the coating and the coating breaks (figure 2). The life of coating would depend on the thickness and strength of the coating. This mechanism is more prominent for the columnar coatings deposited from the vapor phase.



Figure 1: Schematic showing a probable mechanism of coating failure (Difference in coefficient of Thermal Expansion) [5].

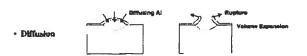


Figure 2: Schematic showing the probable diffusion mechanism of coating failure (Diffusion of metal) [5]

During the coating process, it is possible that a relatively large elemental particle or other source material gets embedded in the coating. This particle would create an imperfection in the coating, which could be a site for pit formation (figure 3). This is a very common problem in the cathodic arc deposition process, is known as "macro-particle" problem [6]. Aharonov recently showed that the presence of macroparticles was a dominant cause of coating failure in cathodic-arc deposited coatings in the die-casting application [7]



Figure 3: Failure due to embedded particle of AI/Cr, during coating Process [5].

Coating thickness is also an important variable. Most coatings deposited from the vapor phase exhibit columnar grain morphology perpendicular to the coated surface (figure 4) [8]; this dictates that the coating has inherent volds and the separation (void size) increases as the coating thickness increases. Moreover, this morphology is quite susceptible to crack formation along the columns under thermal cycling, unless efforts are made to prevent or minimize columnar growth during deposition.

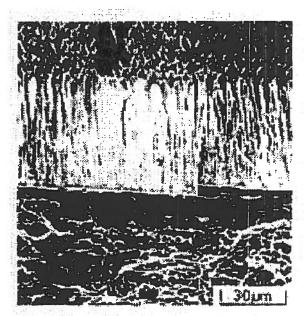


Figure 4: Columnar microstructure of PVD coatings. (Electron micrograph) [8]

#### **Multilayer Coatings**

Multilayer coatings have been developed on the philosophy of integrating the best properties from individual coatings into a single coating system. Some coatings have excellent resistance to molten aluminum but have poor thermal shock resistance. Others have good thermal fatigue resistance and excellent compatibility of the coefficient of thermal expansion with the substrate but have poor corrosion and erosion resistance. Some coatings have all the properties required for good corrosion, erosion and thermal fatigue resistance but have very poor bonding to the substrate. Recent trend has been to harness the best of everything and put it to work in a composite coating system. Composite coatings can be made up of two or more individual coating materials, either in a layer mode or in mixed mode. A special category of the mixed mode composite coatings is cermets i.e. they are made up of ceramics and metais [9]. Cermet coatings combine the heat resistance and strength of ceramics with the ductility and thermal conductivity of metals. [9]

A typical multilayer coating system generally consists of an interlayer of a compliant material between the substrate and the uppermost layer. (Figure 5) [9]. The uppermost layers are very hard and have excellent resistance to corrosion, erosion and abrasive wear while the interlayer provides a transition between the substrate and the outer layer. This interlayer may be a pure metallic layer or a layer of a composition similar to the outermost layer (as in functionally graded coatings/materials).



Figure 5: Structure of a typical multilayer coating (Thermal barrier coating) [9]

During thermal cycling, the single coatings fail due to a mismatch in the Coefficient of Thermal Expansion (CTE) as explained earlier. The critical issue of thermal fatigue/mismatch can be addressed as follows. Thermal fatigue has two components - the thermal component and the stress component. While the stress component can be partly mitigated by improving the hot yield strength of the substrate (through a variety of means like alloying, Ion implantation or through surface treatments like nitriding), the thermal component can be tackled by reducing the thermal gradient during the casting process by efficient heat management. The thermal mismatch/ thermal fatigue can be accommodated by providing a gradient through a tailored coating composition or through a multilayer coating (figure 6) [9]. Thus, a coating scheme that provides a way to create compliant interfaces to accommodate the mismatch stresses will go a long way in improving the thermal fatigue resistance of dies. Providing a gradient for coefficient of thermal expansion from the outer surface of the coated die to the substrate will reduce the thermal mismatch stresses, which are exacerbated due to repeated thermal cycling in use. At the same time, a coating that minimizes the tendency of soldering is desirable for reducing the down time between heats and extending the die life. A coating with high thermal conductivity would reduce thermal gradients by permitting efficient heat transfer from the hot to the cold locations.

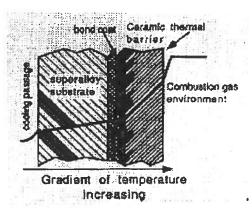


Figure 6: Thermal gradient in a typical multilayer coating system [9]

The materials for the individual layers in a typical multilayer coating system are chosen such that their lattice parameters, crystal structures and the thermal expansion coefficients are very nearly the same. These can effectively be used to develop highly coherent and relatively stress free interfaces between the layers. The

relatively low strength and low hardness intermediate layer provides strain compliance in thermal cycling while its high thermal conductivity provides excellent heat transfer characteristics to the multilayer coating. As always, the outermost layer, which has very good mechanical properties, takes the brunt of the die-casting process.

Apart from this, the tribological properties can markedly be improved by using multilayer coatings [10]. A reduced grain size and a correspondingly large number of interfaces will increase both the hardness and the toughness of the coatings. The relatively low compressive residual stress in the multilayer as compared to that in the single layers is also beneficial for adhesion of the coating. A multilayer coating will also have lower porosity than a single layer coating, since the open structure reaching from the surface to the substrate will be interrupted by repeated nucleation at the interface between sublayers [11].

The coatings can be deposited in a variety of ways like plasma-assisted deposition, physical vapor deposition and other available techniques. The multilayer coatings can be deposited in the same coating system (integrated process) for the ease of control of parameters, or in separate coating chambers to optimally use the capabilities of each. However, this process requires re-cleaning of the coated part and other considerations related to vacuum. It also adds to the cost of the process due to interruption and additional process steps. Therefore, it is desirable to have a process capability that permits design and deposition of multilayer coating and other surface modification steps in a single, versatile deposition equipment. The cost-effectiveness of a duplex or multistep process is determined by the performance improvement and productivity gains.

#### **Experimental Procedure**

#### **Deposition of Coatings:**

In the current system, H13 steel is the substrate, and TiN is the outer resistant layer with an intermediate transition layer of Ti. The intermediate Ti layer not only provides excellent adhesion to the surface but also establishes a gradient in the coefficient of thermal expansion from the substrate to the coating surface. Being softer than the coating itself, it also helps in accommodating the strains due to the difference in the coefficient of thermal expansion. This system shows considerable improvement in performance over that of the TiN coating only. Although TIN does not last long due to oxidation, above 600°C [1], the outer Ti-B-C-N chemistry was tried for protection against corrosion due to molten aluminum.

The various multilayers were deposited on H-13 steel substrates at UES, using a novel "filtered cathodic-arc deposition" system. The unique, patented design of the coating system allows the creation of a "plasma immersed" environment in the coating chamber by

manipulating the arc plasma jets using strategically placed scanning magnetic coils and auxiliary anodes [12-13]. This technique allows the plasma flux from different cathodes in a multi-cathode chamber to be uniformly mixed and enveloped around the part.

The large-area filtered arc cathodic arc deposition system at UES is shown schematically in Figure 7. It consists of three key components: direct arc sources, large area filtered arc sources and the auxiliary anode assembly. It has been shown by Gorokhovsky [14] and by Vetter and Perry [15] that the arc sources can be used to extract highly energetic electrons and used to ionize the gaseous plasma, such that the plasma envelope that completely surround the part can be created in the coating chamber. Using this technique, very high ion currents can be obtained as compared to the other PVD techniques such as EBPVD and sputtering. The high degree of ionization of the gaseous plasma permits ion saturation levels suitable for ion nitriding. Moreover, when the substrate is strongly blased, significant ion implantation can be achieved.

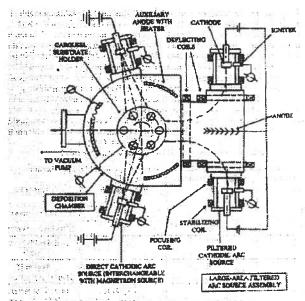


Fig. 1; Sohemasic Bustration of the Large Area Dual Filtered Cathodic Are Deposition System at UES

Figure 7: Schematic Illustration of the Large Area Dua! Filtered Cathodic Arc Deposition System at UES.

#### Description of the coating process:

All the coatings were deposited in the filtered cathodicarc deposition system at UES Inc. Titanium, aluminum and titanium diboride cathodes were during deposition. The arc plasma was generated by a patented electronic trigger and arc-spot control circuitry that effectively elim-

inates the tendency for the arc spot to be extinguished unpredictably, and provides a stable and continuous operation of the arc for an extended period. The deposition chamber was evacuated to a pressure of 7x10<sup>-4</sup> Pa prior to the introduction of gases such as argon or nitrogen for cleaning of the substrates or for metal deposition, respectively. The substrates were mounted on a variable speed substrate holder with double-planetary rotation capability, that can be biased to a desired voltage using either a bipolar DC pulse or RF power supply.

The TiN/TiCN/TiBN multilayer coatings were deposited using two cathodes, Ti and  ${\rm TiB_2}$  in the filtered-arc mode. A thin (sub-micron) bond layer of Ti was used prior to the deposition of a multilayer of TiCN (using Ti cathode) and TiBN (using TiB, cathode).

An important aspect of the coating deposition, and achievement of superior adhesion and surface finish, relates to the original surface finish of the substrate. Even an as-ground surface of the core pins (which are centerless ground to a fine finish) is sufficiently uneven at the nanoscale of the coating/substrate interface to offer sites for stress concentration. This then can lead to relatively easy fallure of the coating, sometimes merely due to thermal mismatch and internal stresses generated during deposition. When subjected to the harsh erosive/corrosive environment, such stress concentration sites become the preferred locations for the coating failure. Therefore, surface finish of the part being coated must be carefully considered. In the present work, it was found that polishing the substrate to remove surface irregularities was an important aspect of improved coating adhesion and performance.

#### Characterization of Coatings

The coatings were characterized for thickness, hardness and adhesion. The thickness and layer structures were characterized by Calotest equipment. The total thickness of the multilayer coating was found out to be 4.2 microns. Auger electron microscopy (AES) was used for compositional characterization. Hardness was measured using a microindentor and a nanoindentor on selected samples. Scratch tests were performed using a CSEM scratch-adhesion tester.

The hardness of ion-nitrided and coated H-13 pins was measured using microindentor with loads of 25 gm and 50 gm. Both, coated and nitrided H13 steel showed hardness of about 11.9 GPa (1220 Vickers) as compared to 5.19 GPa (530 Vickers) for the H-13 steel. Since the coating or ion nitriding was in the range of 3-4 mm; the hardness values represent a composite effect of the coating and the substrate. The surface hardness of the Ti/TiCN multilayer was measured at 21 GPa (2143 Vickers) and a modulus at 305 GPa. The scratch adhesion tests using CSEM tester indicated that the coatings cracked at loads of 40-60 N.

#### Accelerated corrosion evaluation:

SCHEMATIC OF THE DIP TEST SETUP AT THE OHID STATE UNIVERSITY

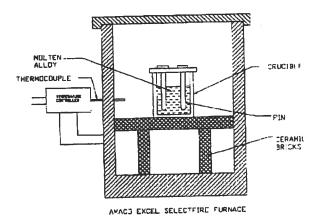


Figure 8: Schematic Hiustration of the Accelerated Corrosion Test setup at The Ohio State University

Accelerated corrosion evaluation for the coatings was carried out at The Ohio State University. Figure 8 shows the test setup for the accelerated corrosion tests. The weight loss from a test pin by dissolution in molten metal (Al) when the coated samples are dipped in molten aluminum for a predetermined length of time was used as a surrogate measure of the soldering resistance of the coating. The test pins were dipped in molten aluminum for a period of 2 hours along with an uncoated H-13 pin as reference pin. After removal from the melt, any aluminum adhering to the surface of the pins was leached using aqueous sodium hydroxide in an ultrasonic bath. After leaching, the pins were cleaned using a wire brush and the weight loss per unit area was found out using a Mettler AC100 weighing machine with a resolution of 104 grams. The results were compared to those from previous work done at The Ohio State University. Figure 9 shows the performance of the TiN/TiCN/TiBN coatings as compared to that of other coatings previously tested at The Ohio State University. Lower weight loss indicates a better performance. The plot is normalized with respect to H-13 by assigning a value of 100 to it. The weight-loss scale is plotted on a logarithmic scale and hence, the mulitlayer coatings have weight loss several orders of magnitude smaller than that of the plain H-13 pin.

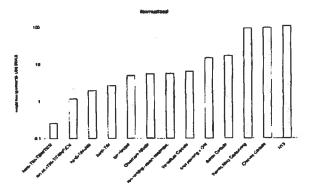


Figure 9: Performance of the TiN/TIBN/TICN multilayer coatings as compared to other coatings. This graph has been normalized by assigning a value of 100 to H-13.

Figures 10 and 11 show the surface condition of the pin as compared to a plain H-13 pin. It can be seen that the surface of the uncoated pin had dissolved away due to heavy pitting and attack due to molten aluminum while the coated pin shows a low concentration of very small pits. There is no observable damage to the edges of the pin.

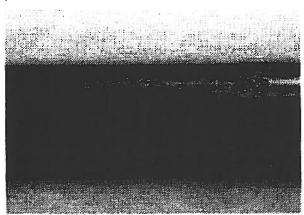


Figure 10: Uncoated H-13 pin after 2 hours at 680°C in molten aluminum A380.1 (1X)

#### **Thermal Cycling Tests:**

Figure 12: Schematic of the Thermal Cycling simulator at The Ohio State University [16]

The best coatings from the accelerated corrosion tests were tested in thermal cycling to evaluate their resistance to delamination and cracking due to thermal cycling. Figure 12 shows the thermal cycle simulator [16] at The Ohio State University, which was used for the tests. The simulator is a PLC controlled machine. Two pneumatically operated cylinders control the movement of the test

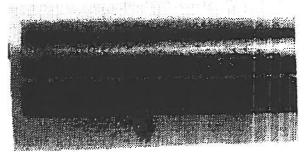


Figure 11: Multilayer Coated pin after 2 hours at 680°C in molten aluminum A380.1 (5X)

pins from the melt to the lubricant tank. It is also fitted with a motor that is used to rotate the pins in lubricant solution for effective cooling and for preventing vapor blanket effect during cooling. DME "CX 41 M-3" core pins were used as substrates for deposition of coatings. These pins were machined as shown in figure 13. This was done to study the effect of corner radii on cracking.

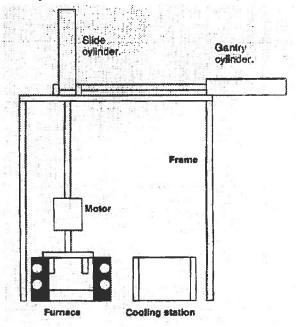


Figure 13: Geometry of the test coupon used for the thermal cycling tests. (Dimensions are in inches)

Our objective was to simulate most of the conditions in laboratory and study the behavior of the coatings in service. The test coupons were dipped in molten aluminum alloy A380.1 at a temperature of 680°C or 1256°F. They were then removed after a pre-set time and dipped in lubricant (1:40 Die Slick 2000: water) to cool the surface

down. The coupons were again dipped in molten aluminum. This cycle was repeated.

Timings for all the stages i.e. Dip time in aluminum, Time in air, Dip time in lubricant and Time in air were preset, so that we were as close to the actual conditions as possible. The thermal cycle used in the current round of tests was obtained by simulating the "surface temperature" of the samples from the cycle used by Prof. Jack Wallace at the Case Western Reserve University [17]. The time-temperature cycle for the tests was obtained from Heat transfer simulations using the FEM simulation software DEFORM. The time-temperature plot obtained from the simulations is shown in figure 14.

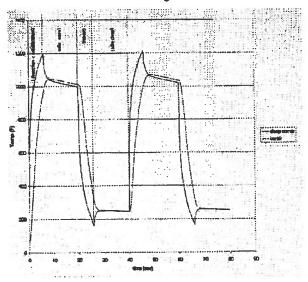


Figure 14: Thermal cycles obtained from DEFORM simulations.

This plot can be divided in 4 regions characterizing the 4 stages in the die casting cycle, namely:

- 1.Injection
- 2. Ejection (die open)
- 3.Lubricant spray
- 4.Die closing

During these stages the die surface experiences drastic changes in the heating/cooling cycle which are reflected as drastic changes in the slope of the time-temperature plot. The times for the 4 stages can be plotted from the given data. The respective times are shown on the table

During the thermal cycling tests, the H-13 sample initially showed very little visible damage to the surface due to soldering and corrosion. This was seen in the form of small pits on the surface and at the corners. During the first 50-100 cycles, some aluminum was observed to

Die casting cycle	Corresponding cycle on the thermal cycle simulator	Designation	Cycle times used(mc)	esefficients.  (Bin/m² sec.")
Out metal injection	Dip is moken A380	- Second	6	1.45 - 10"
Casting ejection (Die open)	Test pins in all	Tagne	14	8 * 1,18
Lubricam spray	Dip in lubricara	lare	6	14*10
Die closing	Test pins in sir	f <sub>ail</sub> z	14	4 - 11/4

Table 1: Cycle times during the Thermal Cycling tests.

Table 1: Cycle times during the Thermal Cycling tests.

be sticking on the test coupons when they were lifted from the molten aluminum crucible. Thereafter, very less or no sticking was observed, though the surface showed heavy buildup of oxide and lubricant layer.

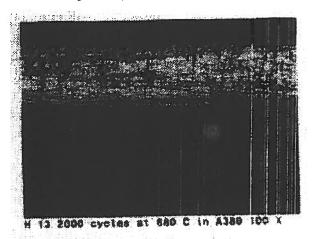


Figure 15: H-13 coupon after 2000 cycles (100X)

Figure 15 shows the H-13 coupon after 2000 cycles. Most of the cracks were observed at the sharp edge at the bottom and were seen to be originating from the sharp edge. The thin lines seen at 90° were from the 600 grit SiC paper used to remove the oxide and reveal these cracks. It may be noted that the cracks exhibit a tapering structure. They are quite wide at the edge and narrow towards the inside. This is evidence that the cracks are opening up. The formation of the oxide inside the cracks promotes the expansion of the cracks due to volume expansion during to the formation of oxide. Being wide at the edge makes them ideal sites for the initiation of corrosion and soldering due to molten aluminum. Figure 16 shows the coated coupon at the edge after 2000 cycles. There was no visible soldering or cracking observed at any of the edges.

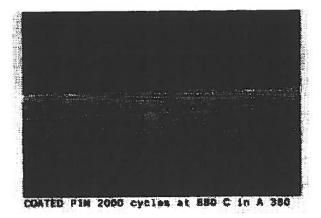


Figure 16: The coated coupon after 2000 cycles (100X)

Figure 17 shows the surface of the H-13 coupon after 5000 cycles. As can be seen, the size as well as the concentration of the cracks was observed to increase considerably. A lot of relatively small cracks were observed to be initiated on the surface itself as against those after 2000 cycles. Many of the old cracks were seen to have propagated further and increased in width resulting in an evident gap at crack initiation points at the edges of the coupon. Some corrosion was also seen on faces of the coupon in the form of small pits. Some pitting damage was also seen at the site of cracks on the edge of the coupon.

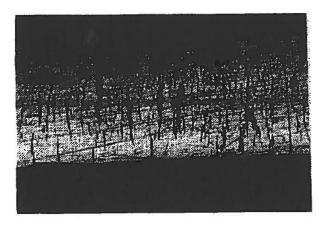


Figure 17: The H-13 coupon after 5000 cycles (100X)

Figure 18 shows the coated coupon after 5000 cycles. It can be observed that the coated pin shows very little damage to the surface and edges for a treatment similar to that of the uncoated pin. No visible cracking was observed on any of the edges. Some microscopic damage to the coating was seen at one of the edges of the pin in the form of very small pits and chipping of the coating.

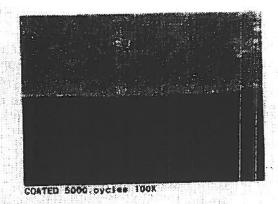


Figure 18: The coated coupon after 5000 cycles (100X)

#### Conclusions:

in the present study, multilayer coatings were deposited at UES Inc. using the 'Large-Area Filtered Cathodic Arc deposition System'. These coatings were evaluated at The Ohio State University using the accelerated corrosion evaluation tests and the results were compared with several other commercial coatings available namely lonnitriding, Chrome nitride, Vanadium carbide, Boron Carbide, Ferritic Nitrocarburizing, Chrome Carbide, Ion nitriding + steam treatment and shot peening + Chrome nitriding. The same coatings were evaluated using thermai cycling tests using cycles obtained by DEFORM simulations based on the cycles used by Prof. Wallace [17]. The multilayer coatings definitely show a significantly improved performance in the erosion/corrosion test against molten aluminum alloy, as compared to all the other commercially available coatings and surface treatments tested. The improvement observed in the present work shows that the current coatings are at least an order of magnitude better in preventing corrosion and failure of the coated H-13 core pins. It is also noted that a combination of ion nitriding and hard coating provides a much greater improvement of performance than simple hard coating. This is due to the improvement in the strength and surface hardness of the substrate as a result of ion nitriding.

During the initial 5000 cycles for the thermal cycling tests, the coating is seen to suppress cracking of the substrate, thereby delaying crack initiation and reducing the incidence of cracking. This is a very significant result, as it demonstrates the beneficial effect of a duplex treatment of die steel for combating two major causes of die fallure in the die casting application. The filtered cathodic arc deposition process used in the present study has demonstrated the capability of the technique to significantly improve the useful lifetime of the die casting dies.

#### Future work:

It should be noted that this work represents initial studies during the Phase I of the Department of Energy funded development program, and shows the feasibility of the duplex process, which combines a heat treatment step with a multilayer coating design. The current coating system definitely performs better than the plain H-13 coupon and has shown significant promise as an alternative to the existing single layer coatings used in the industry. Further work is aimed at detailed evaluation of the coating process and optimization of the composition and the deposition conditions of individual layers in the coating for a commercially viable process.

#### Acknowledgements:

The current study was supported by grants from the Department of Energy, Contract number DE-FG02-98ER82702. The substrate preparation and deposition work was carried out by Mr. Boris Brodkin, and analytical work was performed by Dr. A. K. Rai. Their enthusiastic support and assistance in this project is gratefully acknowledged.

#### References:

- 1. T. Aral, Transactions of 18th NADCA International Die-Casting Congress "Paper No. T95-102" (1995)
- 2. Shivpuri R., Y. L. Chu, K. Venkateshan, Conard J. R. K. Sridharan, Shamim M. and Fetherson R. P. " Evaluation of metallic coatings for erosive wear resistance in die casting applications" Wear, (1996) v.192, pp. 49-55
- 3. Rej D. J. and Alexander R. B., "Cost estimates for commercial plasma source ion implantation" Journal of Vacuum Science and Technology, B 12 (4), 2380-87 (1994)
- 4. Chellapilla S, Shivpuri R. and Balasubramaniam S., Proceedings of the NADCA conference
- on the many faces of Die-casting, Paper T97-101, 295 (November 1997)
- 5. Lakare A, Shivpuri R, and Gopal S.: "Evaluation of thin film coatings for erosive-corrosive wear prevention in die-casting dies": presented at The 12th International surface Modification Technologies Conference, 12-15 October 1998, Rosemount, Illinois
- 6. Gorokhovsky V. I. and Bhat D. G., "Principles and Applications of Vacuum Arc Plasma-assisted Surface Engineering Technologies," International Workshop on Surface Engineering and Coatings, National Aerospace Laboratories, Bangalore, India (June 1998).
- Aharonov R., Chellapilia S., Janoss B. and Shivpuri R., "An Investigation of The Corrosion of H13 Steel Coated With CrN: Effect
  Of Steel Surface Preparation," Paper presented at the International Conference on Metallurgical Coatings and Thin Films, San
  Diego, CA, April 12, 1999.
- 8.Rickerby D.S. and Matthews A. Advanced Surface Coatings: A Handbook of Surface Engineering, New York, Chapman and Hall, 1991, pp.- 11
- 9. Hocking M.G., Vasantshree V., and Sidky P.S. Metailic and Ceramic Coatings: Production, High Temperature Properties and Applications, New York, Longman Group UK limited and John Wiley and Sons Inc, 1989, pp.32, 312
- 10. Herranen M. et. al. "Corrosion behavior of Ti/TiN multilayer coated tool steel", Surface Coatings and Technology 99(1998) 191-
- 11. Rosbrook C. and Shivpuri R. "A Computer Aided Investigation of Heat Checking and Die Life Predictions in Die-Casting Dies", NADCA Conference at Cleveland Ohio, October 18-21; 1993
- 12. V. I. Gorokhovsky, U. S. patent 5,380,421 (1995)
- 13. V. I. Gorokhovsky, U. S. patent 5,435,900 (1995)
- 14. Gorokhovsky V. I., Polistchook V. P and Yartsev, Ivan M.: "Processes in a plasma arc installation for vacuum coating depositions. Part I: Plasma generation" Surface and Coatings Technology, (1993) v61 pp.101-107.
- 15. Vetter J. and Perry A. J., "Advances in cathodic arc technology using electrons extracted from the vacuum arc"; Surface and Coatings Technology, (1993) v61, pp. 305-308.
- 16. Nishant B. E. "An experimental set up for evaluating wear of core pins in die casting production" M. S. Thesis, The Ohio State University, 1998.
- 17. Benedyk J.C., Moracz D.J., Wallace J. F., "Thermal fatigue behavior of die materials for aluminum die-casting", 6th SDCE International Die-casting Congress", Cieveland, Ohio November 16-19, 1970; pp.187-206

# International Workshop On Surface Engineering and Coatings

June 25-30, 1998

EDITOR
INDIRA RAJAGOPAL
CO-EDITORS
K.S. RAJAM
R.V. KRISHNAN

National Aerospace Laboratories Bangalore 560 017



## **ALLIED PUBLISHERS LIMITED**

# **CONTENTS**

Pro	eface – Dr. R.A. Mashelkar	v
	Dr. C.G. Krishnadas Nair	vii
	Dr. R.K. Bhandari	ix
	Dr. T.S. Prahlad	xi
1.	Surface Engineering-A Broad Brush Picture	1
	S.R. Rajagopalan	
2.	Development and Applications of Chemical Vapor Deposited Polycrystalline Diamond  Lothar Schäfer	18
3.	Diamond Like Carbon for Window Applications (UV to IR)  R. Bhattacharyya	31
4.	Growth of Thick Film Diamond Using Direct Current (DC) Plasma Assisted Chemical Vapor Deposition (PACVD)  Jae-Kap Lee, Wook-Seong Lee, Kwang Young Eun and Young-Joon Baik	56
5.	Thermal Barrier Coatings: Life-Determining Factors and Failure Mechanisms  Shrikant V. Joshi	64
6.	Recent Innovations in Plasma Technology for Surface Modification S. Mohan	72
7.	Surface Engineering Activities at NAL Indira Rajagopal	86
8.	Plasma Immersion Ion Implantation at Elevated Temperatures  B. L. Mordike and C. Blawert	97
9.	CVD and PCD Diamond Cutting Tools for Advanced Manufacturing  Ajay P. Malshe	120

10	0. Studies on the Wear Behaviour of Thin Films and Coatings  E.S. Dwarakadasa	
11.	Setting up of an Advanced Heat Treatment Workshop  Maurice Grech	136
12.	Functional Plating M.K. Totlani, A.K. Grover, S.N. Athavale and A.L. Pappachan	151
13.	Functionally Graded Coatings  Lalgudi V. Ramanathan	160
14.	Surface Modification sing Laser and Plasma Technique to Make Corrosion and Oxidation Resistant Materials  A.S. Khanna	178
15.	Corrosion Behaviour of Magnesium-Based Metal Matrix Composite Produced by Powder Metallurgy Technique J. Idris, Y.C. Yaw and C.W. Chang	213
16.	Coatings and Characteristics of Ti-X-N By Plasma Enhanced Chemical Vapor Deposition Kwang Ho Kim and Bum Hee Park	236
17.	Plasma Source Ion Implantation Research in India P. I. John and S. Mukherjee	249
18.	Characteristics of Sputter Coated Copper Films on Silicon Wafer Thirumany Sritharan, Tan Heng Wei and Oh Joo Tien	271
19.	Laser Processing of Materials Susanne Mordike	289
20.	Electroless Nickel  K.S. Rajam	310
21.	Electroless Ni-P Plating-Problems and Opportunities  X. Chen and G. Qi	327
22.	Preparation and Characterisation of Carbon Nitride Films S. Xu, Yin-an Li and X.F. Chen	346

23.	Co-W Alloys for Replacement of Conventional Hard Cr. S. Eskin, O. Berkh, G. Rogalsky and J. Zahavi	364
24.	Principles and Applications of Vacuum Arc Plasma-Assisted Surface Engineering Technologies  Vladimir I. Gorokhovsky and Deepak G. Bhat	381
25.	Selecting Equipments and Coating for Speciality Engineered Surfaces in the Tooling Industry  K.V. Krishnamurthy	400
26.	Surface Characterisation of Coatings by Rutherford Backscattering Spectrometry (RBS)  Dinesh K. Sood	418
27.	Technology and Application of Soft, Hard and Superhard Coatings G. Erkens, T. Leyendecker, O. Lemmer, R. Wenke, S. Rambadt, H.G. Fub and M. Alunovic	433
28.	The Surface Modification of Biomaterials  R. Sivakumar	443
29.	Diamond and Diamond Like Nano-Composites  V.D. Vankar	465
	Author Index	467

# Principles and Applications of Vacuum Arc Plasma-Assisted Surface Engineering Technologies

Vladimir I. Gorokhovsky and Deepak G. Bhat!

Arcomac Plasma Processing Laboratory, Toronto, Ontario, Canada

> <sup>1</sup>UES, Inc., Dayton, Ohio, USA

#### **Abstract:**

Many advances have taken place in recent years in the technology of plasma-assisted surface treatment of materials. These advances have demonstrated the potential to significantly enhance the technological capabilities of such existing plasma-assisted heat treatment processes as ion nitriding and ion implantation, as well as to introduce new capabilities in the traditional plasma-assisted surface coating technologies, such as sputtering and evaporation.

The surface engineering science has evolved in recent years with a greater awareness of the environmental impact of industrial process technologies. More attention is now being given to the need for reduction in industrial waste stream, which has necessitated a departure from traditional process technologies. The vacuum arc plasma based surface treatments address these issues eminently, by adopting benign process techniques, which are environmentally friendly, at the same time commercially viable as a result of tangible improvements in process efficiencies.

The vacuum arc plasma-assisted processes are capable of providing solutions to a myriad of industrial technology needs. Some examples include: plasma-chemical treatments and ion etching, plasma spray and synthesis of ultrafine powders, plasma nitriding and ion implantation of industrial machinery parts, deposition processes for wear resistant and oxidation resistant hard coatings, and so on. Presently, it is incumbent upon the practitioner of these processes to rely on a number of different process technologies and equipment to meet the various needs. A universal process chamber which is capable of providing a combination of technological processes by suitable hybrid, modular system design, is therefore, expected to meet the requirements of a number of processes and industries.

The vacuum arc discharge plasma has been used successfully in the last two decades for depositing hard coatings for cutting tools and other tribological applications. The current technologies of evaporation, sputtering and cathodic arc deposition, although used widely and successfully in many industries, still suffer from certain limitations. This paper describes a new advance in the technology of cathodic arc plasma technology, which promises to eliminate many of the current barriers to successful application of physical vapour deposition techniques on a broad scale. The development of a large-area electromagnetic filter has essentially eliminated one of the

major drawbacks of the cathodic arc deposition technique, viz. the formation of macroparticles. The unique, patented design of the filter permits practically complete removal of macroparticles from the metal vapour flux entering the deposition chamber. The vacuum arc cathode is also a theoretically unlimited electron emitter. The paper describes how this capability can be used to enhance the efficiency of deposition processes, which suffer from low ionization efficiency. In addition, the possibility of using the versatile filtered cathodic arc technology for the improvement of traditional ion nitriding and implantation processes are briefly described. Several examples of the application of this technology are given, and features of commercially available deposition equipment, and its operational flexibility to meet a variety of needs, are described.

#### Introduction:

The technologies for surface modification of materials have witnessed a significant growth during the last decade. Prior to this period, many technologies were developed almost in isolation from other techniques, as researchers sought ways to improve the state of the art of available technologies by investigating modifications to the process hardware and control systems, use of better diagnostic tools, and so on. As these techniques became more sophisticated, reliable and cost-effective, a clear pattern emerged in the last decade that shifted the focus from isolated developments and/or improvements in a particular surface modification technique to a more synergistic approach, which sought to combine the advantages of more than one technique into a single process. This new direction in the technological developments is now rightfully called "surface engineering."

The field of surface engineering now encompasses not only individual deposition or surface modification processes, but also the aspects of process modeling, equipment modeling and design, properties of materials being modified, and the characteristics of the applications in which these modifications are being introduced. This "global" approach to technology development clearly has one significant benefit. The customer now finds that his requirements are addressed more fully because the developers of technology have begun to look at their technologies as engineering solutions to complex, interactive problems, and not simply ways of providing marginal benefits over a competitive process technology.

# Synergistic Aspects of Low Pressure Plasma Processes:

The recent developments in the surface engineering of materials show that the new techniques attempt to bridge the gaps which existed in the past between various methods. It is instructive to examine this aspect in terms of the operating process parameters for various surface engineering processes. Many surface modification techniques are available in the operating pressure range from atmospheric to low vacuum. These include plasma spray and atmospheric pressure chemical vapour deposition (APCVD), Low-pressure CVD (LPCVD), plasma-assisted CVD (PACVD), vacuum plasma spray, and some of the heat treatments such as ion plasma nitriding of steels. For the deposition of metallic and compound films and coatings on substrates, methods such as evaporation

and sputtering operate in the medium vacuum range, from 10<sup>-1</sup>-10<sup>-5</sup> Torr. Processes such as ion implantation and ion-beam assisted deposition operate in the high to ultra-high vacuum range. Figure 1 schematically shows the typical operating pressure ranges of various surface engineering methods.

While it is clear that many surface engineering methods are available, each one has its unique characteristics, advantages and disadvantages, and it is often not readily possible to combine two or more different processes in a simple, cost-effective manner. Figure 1 also shows that there is an overlap of operating pressure for many of these processes. However, there are other limitations which make it difficult to incorporate two different processes into a single process chamber for simultaneous operation. This can be understood by examining Fig. 2, which schematically shows the current-voltage characteristics of several types of low-pressure plasma processes. This diagram shows, for instance, that while the magnetron sputtering and cathodic arc evaporation techniques may overlap in terms of operating pressure, the two techniques have significantly different electrical characteristics, making it difficult to combine them in a single, duplex process. These two methods use different approaches to create a flow of coating material species. In the cathodic arc process, the flow of atomic species is created by evaporating from a target by means of cathodic arc spots. On the other hand, in magnetron sputtering (as also in diode and triode sputtering), the flow of atomic species is generated by sputtering the target by ion bombardment. To obtain a high rate of coating deposition, it is necessary to use sputtering ions with the maximum sputtering ability, such as Ar, Kr or other noble gases. In the vacuum arc process, the production of atomic species takes place by evaporating the target material by the arc discharge itself. The arc is self-igniting in the presence of metal vapour flow, and therefore, no other agent is required to sustain the arc. Similar comparisons can be made between other deposition processes as well.

Despite some fundamental differences in the operating characteristics of the various deposition techniques, recent trends in the physical vapour deposition technologies have shown an inclination towards combining such methods. A good example of this is the Arc-Bond Sputtering (ABS) technology introduced by Hauzer B.V. of the Netherlands in the early 1990's. In this method, the cathodic arc ionization is used for initial ion cleaning of the substrate and to deposit an initial bond layer of metal on the part. The arc cathodes are then withdrawn from the chamber. The operating pressure and other parameters are adjusted for magnetron sputtering, and deposition is carried out in an unbalanced magnetron sputtering mode. The technique works quite well for the deposition of hard coatings on tools, moulds and wear parts, and for many other applications. Similarly, the ion-beam assisted deposition methods (IBAD) utilize bombardment by ion beams during deposition to enhance the properties of films deposited by thermal or electron-beam evaporation techniques. These "hybrid" techniques provide many functional benefits; however, they also make the overall technological process quite complex and expensive.

Self-sustained and non-self-sustained high voltage discharge can be used for sputtering from targets or for ion bombardment of growing films. The self-sustained discharge can be of two types: normal and abnormal glow discharge, or magnetron discharge. The pressure range for these

discharges varies from about 100 Torr to about 0.1 torr for ion nitriding and ion etching processes, and from 0.1 Torr to 10<sup>-5</sup> Torr for sputtering sources and for biasing the substrate. A common disadvantage of using a dc negative bias for both sputtering and biasing the substrate is that plasma breakdown occurs when switching from the high-voltage-low-current mode to the low-voltage-high-current mode with several fast-moving cathodic arc spots on the surface of the substrate or biasing target. To avoid this undesirable effect, it is necessary to use passive or active arc suppression techniques. In the case of the passive technique, a high-speed electronic switch is used to turn off the power when arc breakdown is likely to occur. However, it is not a reliable method, and cannot prevent the appearance of arc spot craters. In the active mode, it is possible to use ac bias or to superimpose positive ac pulses with high repetition frequency to prevent arc breakdown.

Recent developments in power semiconductor devices makes it possible to produce compact bias power supply devices with a high frequency output signal. Some of these devices use a sine wave signal with a frequency from 1 to 100 kHz, while other devices using IGBT or MOSFET transistors provide a rectangular wave signal. These devices prevent arc breakdown by interrupting the high negative voltage bias with short positive pulses so that the negative voltage does not exist long enough to create the harmful type II or type III cathodic arc spots. In addition, the oscillating electromagnetic field in the vicinity of the substrates tends to neutralize the surface charge of the dielectric films, and thus protects the coating from breaking down.

#### Cathodic Arc Evaporation - Historical Background:

It is well-known that the cathodic arc deposition technology was first developed in the former Soviet Union. The first commercial coating system using this approach was named "Bulat" and was the basis of many subsequent developments in this technology. The "Bulat" patent [1], assigned to Sablev and co-workers at the Kharkov Physical Technical Institute in Kharkov, Ukraine, was purchased by a company in New York in early 1980s, leading to the birth of a company called Multi-Arc, Inc.

The history of the development of cathodic arc evaporation is quite interesting. The original impetus for the development of this technology came from the work initiated in late 1960s and early 1970s at several Soviet research institutes, working almost independently of one another. There were three premier institutes in the former Soviet Union, engaged in the research on vacuum arc plasma pumping technologies. These institutes were: Kurchatov Institute of Atomic Energy, Moscow, Russia; Kharkov Physical Technical Institute, Kharkov, Ukraine, and the Efremov Institute for Electrophysical Equipment, St. Petersburg (formerly Leningrad). The work at these institutes was aimed at developing pumping systems for large installations, such as accelerators, large vacuum furnaces and other applications of critical interest to the Soviet Military and Space programs.

At the Kharkov Institute, Sablev, Romanov, Andreev and others were developing vacuum arc plasma pumping techniques and equipment, using titanium cathodes because of their excellent

gettering properties. According to popular legend, a tool was accidentally left in the vacuum chamber for several days, and was exposed to the Ti<sup>+</sup> and N<sup>+</sup> plasma, which caused the formation of a gold-coloured coating on the tool. The researchers discovered that the tool was quite hard. They immediately put several tools in the chamber, and coated them with this gold coating, and found that the tools performed extremely well in machining. Sablev and his colleagues immediately began working on a deposition system, incorporating cylindrical titanium cathodes, and developed the first cathodic arc deposition system. The discovery of this new technology quickly led to further development work on cathodic arc deposition techniques at other Soviet research institutes engaged in the vacuum arc plasma technology development.

In the cathodic arc process, a high-current-low-voltage arc spot moves at a high velocity around the cathode surface, igniting other arc spots in its wake. Typical lifetime of an arc spot is on the order of ~ 10 ns, and the spot moves at a speed of ~ 10 m/s. The voltage in the arc spot is about 20V, while currents as high as 500A can be sustained. There are two types of arc spots: type I, which are sometimes called fast spots, and type II, which are called slow or thermal spots. Type I spots exist for a very short time (about 10-100 ns to 1 ms-microsecond) and produce very small (about several nm) craters which are not important for most applications. They move with very high speed. The erosion rate for Type I spots is negligible. The lifetime for Type II spots or thermal spots can reach 1 ms (millisecond), and they can move with a velocity of about 1- 10 m/s (depending on the target material, arc current, gas, pressure, etc.). The erosion rate G for type II spots can be determined as:

$$G = \rho I$$

where I is arc current in amperes, and  $\rho$  (mg/coulomb) is the characteristic constant which determines how many grams of target material will be transferred with 1 coulomb of electrical charge. Usually this value ranges between 10 and 50 micrograms. For titanium it will be 20  $\mu$ g in nitrogen atmosphere.

The arc spot moves in the direction of decreasing arc voltage, which means that the anode should ideally face the cathode for a stable condition. It is often necessary to confine the arc spot and control its movement so as to maintain a continuous arc excitation mode. Several methods have been used to achieve this purpose. These include using the chamber itself as the anode [1], use of an insulated metal screen or grooves along the side edge [2], a magnetic field [3-5], a ring with high magnetic permeability [6], a ring with high electrical conductivity [7], and a boron nitride ring [8]. In all these cases, the purpose is to confine the arc to the cathode surface and to achieve uniform target erosion. Karpov [9] recently reviewed the developments in cathodic arc sources. Figure 3 shows the first cathodic arc sources due to Sablev and Snaper [10], and one of the sources developed by Karpov [9]. The cathodic arc deposition process was first commercialized in the U.S. by Multi-Arc and Vac-Tec in the early 1980s for the deposition of hard coatings for tools and dies, and for decorative applications.

# Development of Filtered Cathodic Arc Deposition Technology:

The vacuum arc discharge plasma has been used successfully in the last two decades for the deposition of hard coatings for cutting tools and machine parts. In this process, a jet of a highly ionized metal plasma, flowing from the cathodic arc spot transfers coating material from the target to the substrate surface. A significant disadvantage of this method is the formation of droplets, also known as macro-particles, in the cathodic arc jets, which limit the application of the process to surface coatings that do not require high precision or surface finish. These particles also deleteriously influence critical properties of the coatings. For instance in the case of TiN coating on cutting tools, the presence of titanium particles in the coating compromises the hardness and wear resistance of the coating.

One of the first macroparticle filters was based on the plasma-optical principle, and was described by Aksenov, et al [11]. It was a quarter-torus cylindrical electromagnetic plasma guide, and was based on the torus-type plasma traps, which were developed for the controlled nuclear fusion apparatus such as the Stellarator in the U.S. and the Tokamak in the former USSR. The filter removed the macro-particles and achieved deposition rates for titanium metal films up to 40  $\mu$ m/hr, but could operate only with small cathode targets and could not be scaled up due to the difficulty of scaling up the cylindrical magnetic coils. The macro-particle filters available in the market today are based on this original work, and suffer from the same limitations. Several macroparticle filter designs for cylindrical cathodes are shown schematically in Fig. 4 [9].

The cylindrical cathodic arc filters used in Bulat-type deposition equipment are limited in the practical size to which they can be scaled up. Vac-Tec in the U.S. used rectangular sources to overcome the scalability problems associated with the Aksenov design. These rectangular sources used boron nitride sheets to insulate the cathode, in order to prevent the arc from shorting to the housing. This allowed Vac-Tec to scale up the deposition systems up to a point, but led to another instability problem caused by the arc evaporation of boron nitride in the superimposed magnetic field. This destroyed the source and thus limited its applicability.

Up to now, the commercially available filtered arc sources can only provide a limited deposition area. The CAF-38 source, for instance, consists of a cylindrical plasma guide tube of 10 cm internal diameter, which provides a plasma beam diameter of about 50 mm. Using magnetic rastering, this source can cover a maximum of about 150 mm coating area [12]. Filtered arc sources produced by CSIRO in Australia are based on the design of sources used in Russia in the 1970s, and provide a 50 mm coating area, with a deposition rate of about 1 μm/hr for the TiN coating. Another disadvantage of the existing state-of-the-art filtered arc source technology is the relatively low level of ionization of reaction gas, such as nitrogen or oxygen. In comparison with the nearly 100% ionization of metal plasma, the gaseous plasma ionization is less than 1%. The degree of ionization of the gaseous component decreases with increasing gas pressure, especially for reactive gases, as a result of decreasing cathode erosion rate [13, 14]. Martin, et al [15] showed recently that significant

improvement of coating properties can be achieved by gaseous ion-assisted filtered arc deposition (FAD), in which the ratio of metal to gaseous ions can be controlled.

These limitations of the conventional macroparticle filters were addressed by Gorokhovsky, by developing an innovative rectangular electromagnetic filter, leading to several Russian patents in 1980. This basic design was later patented in the U.S. [16]. The initial filter design was used for the deposition of DLC coatings on a variety of substrates and applications. These included laser mirrors, ball bearings for navigational gyroscopes used in the aircraft and the SS-20 missiles, cutting tools, magnetic heads of recording devices, automotive piston rings, mechanical joints, surgical and microsurgery tools, and so on.

The large-area dual filter arc source developed by Gorokhovsky uses a rectangular plasmaguide chamber with two rectangular coils installed on the opposite sides. Two cathodic arc sources with rectangular or circular target are installed on the side walls of the plasma-guide chamber surrounded by rectangular deflecting coils. A dynamic magnetic field is applied to repel the arc from the edges, and imposes a transverse field at high switching frequency to make the arc run continuously around the target by the use of multiple magnetic coils placed around the rectangular target.

The principle of the Large Area Filtered Arc Deposition (LAFADTM) is shown in Fig. 5. In this design, two cylindrical or rectangular vacuum arc sources are placed opposite each other, and separated by an anodic baffle plate. The source uses superimposed deflecting magnetic field to turn the metal ion flow 90° into the deposition chamber. A series of advanced static and dynamic magnetic stabilizing coils provide improved steering of the cathode spots, and to reduce the reflection of ions at the entrance of the filter. A set of scanning magnetic coils allows the ion plasma jet to be swept in the vertical direction so as to cover large surface areas. This advanced filtered design provides practically droplet-free coating on large areas, ranging from about 250 mm in width to heights on the order of 300 mm to 2 m or more.

The filtered arc source allows deposition of droplet-free coatings by deflecting the plasma flow along the curvilinear magnetic lines of force towards the substrate, while the droplets, having straight trajectories, are captured on the baffles. Thus, a fully ionized flow of metal plasma is directed to the substrate. The vacuum arc cathode is also a theoretically unlimited electron emitter, thus providing an efficient source of high-density electron current. In this mode, it facilitates the generation of a uniform, high-density plasma cloud in the process chamber. This results in a "plasma-immersed" environment, which provides a uniform condition for plasma ion etching, ion nitriding, low energy ion implantation and plasma-assisted chemical vapour deposition.

The filtered arc plasma contains a fully ionized flow of target metal vapour, and a relatively highly dissociated, ionized and activated reactive gas. This leads to a maximum fluence of bombarding ions with a small energy deviation. As a result, it is possible to produce metastable coatings with highly disordered structures, with unique properties. Examples of coatings deposited using the filtered arc sources are given later.

# Surface Engineering Using Vacuum Arc Plasma Processes:

In the PVD processes, the important characteristics of the ionized particles generated in the plasma are: charge, degree of ionization and kinetic energy of atomic particles. In this regard, the cathodic arc processes offer the most advantage, since the arc plasma permits the formation of multiply-charged ions, unlike most other PVD processes, such as evaporation and sputtering. The ionized fraction in the plasma also depends on the cathode material and operating pressure.

The ion energy at the substrate can be increased by applying a negative bias to accelerate the positive ions. The substrate bias cannot be increased beyond a certain value, since at high bias potential, self-sputtering results in no net deposition. When judiciously applied, bias-induced bombardment of substrate by highly charged ions causes diffusion of the ion species into the substrate, thereby providing a strong transition interface for the growing film. The temperature of the substrate also increases as a result of bombardment, a factor which must be taken into account for substrates prone to microstructural and dimensional changes under such conditions.

The vacuum arc plasma can operate over a wide pressure range, from about 50 torr to about 10<sup>-5</sup> Torr. Thus, in the high pressure range, arc plasma can enhance gaseous plasma-immersed processes such as PACVD, and glow-discharge ion nitriding. It is possible to superimpose a vacuum arc plasma source in a typical PACVD or ion nitriding chamber and coupled to the existing plasma process to enhance ionization efficiency and deposition rates. Similarly, in the low vacuum range from 10<sup>-2</sup> to 10<sup>-4</sup> Torr, where many direct deposition processes operate (e.g. thermal and e-beam evaporation and sputtering), superimposed vacuum arc plasma can enhance these processes by improving deposition rates and microstructure. In the medium to high vacuum range (> 10<sup>-5</sup> Torr), arc plasma environment can be used to enhance processes such as Ion-beam assisted deposition (IBAD) and ion implantation, and especially the emerging plasma source ion implantation (PSII).

These benefits are derived as a result of the high degree of ionization provided by the vacuum arc plasma. The high energies of the ionized species in the arc plasma also permit very efficient plasma cleaning of the surface, thereby providing a very high degree of adhesion of the growing film. This aspect has been beneficially utilized in a limited way in the Hauzer Arc-Bond Sputtering system (operating at the Titan Industries Watch Factory in Hosur, Tamil Nadu, India). The LAFADTM design permits a very high ion current density in the plasma, which has been measured at about 10 mA/cm² for deposition of TiN. This value is nearly an order of magnitude higher than the best current densities reported for various arc sources [9]. In the following section, some examples are given to illustrate how the vacuum arc plasma source can be used to enhance the conventional PVD techniques.

## Comparison of Low Pressure Arc Processes with Other PVD Methods:

<u>Electron Beam Evaporation</u>: The e-beam PVD method provides the maximum rate of deposition of metallic coatings, using powerful electron guns. At the same time, this process results in a coating microstructure that is highly columnar, rough and porous. Another disadvantage of the e-beam method is the limited ability to deposit compound coatings, because of the tendency for dissociation under the influence of the electron beam. The e-beam apparatus is also prone to damage in the reactive environment necessary to produce oxide coatings.

Improvements in the e-beam PVD techniques have recently been introduced in which RF or arc discharge is superimposed on the evaporated metal flux. Ion bombardment during deposition permits significant improvement of microstructure and adhesion of the deposited film. The critical parameter in this regard is the ion-to-atom arrival ratio  $r_i$  (=  $q_z/q_o$ , where  $q_z$  and  $q_o$  are concentrations of charged and neutral particles). This ratio is significantly improved by the superimposed RF or arc plasma excitation, which ionizes the metal and gaseous vapour and assists in the dissociation of molecular species. These methods have been used for improved deposition of hard carbon films [17, 18] and cubic boron nitride [19].

The density of ion saturation current coming to the substrate from the plasma can be calculated from the famous Bohm equation:

$$J_i~\sim~0.6 n_e e (kT_e/m_i)^{0.5}$$

where  $n_e$  is electron density (equal to ion density in a quasi-neutral plasma environment),  $T_e$  is the electron temperature, k is the Boltzmann constant and  $m_i$  is the mass of ions. In the arc plasma, the value of electron density can be several orders of magnitude greater than for glow discharge (Fig. 2), while the electron temperature is usually the same, about 1-3 eV. Therefore, in an arc discharge it is possible to reach a much higher level of ion bombardment current on the substrate surface: about  $0.1\text{--}10 \text{ mA/cm}^2$ , as compared to  $< 0.01 \text{ mA/cm}^2$  for RF or DC glow discharge. Therefore, arc discharge-enhanced e-beam evaporation occurs at a higher rate while maintaining the same level of ionization. In other words, it is possible to increase the deposition rate significantly - by a factor of 100--1000 or more - without altering the basic characteristics of the process. Typically, ion bombardment energy on the order of 50--100 eV is necessary to prevent the development of columnar morphology by increasing the surface mobility of atoms, which can be readily achieved by arc plasma enhanced evaporation.

Sputtering Processes: These processes rely on the bombardment of sputtering gases such as Ar' to remove atoms from the surface of the cathode and to transport them into the plasma environment. The efficiency of sputtering, or sputtering yield, is usually quite poor. For instance, the sputtering of metal targets by powerful DC magnetrons may provide a deposition rate on the

order of 1.0  $\mu$ m/hr for stationary substrates, while the sputtering of ceramic and non-conductive targets using RF magnetrons is as low as 0.001-0.01  $\mu$ m/hr. These rates are often not very cost-effective for applications such as thermal barrier coatings.

Improvements in the sputtering process efficiency have been achieved by pulse bias (DC and RF), which can improve deposition rates as well as microstructure. Kelly, et al [20] used DC pulse biasing to deposit AlO<sub>x</sub> films in a reactive atmosphere. One problem with the sputtering of insulating materials is that the process is quite sensitive to both gas pressure and composition, as well as the tendency for arcing of the target due to the formation of an insulating film on the target surface. Thus, frequent ion cleaning of the target is required. The unbalanced magnetron sputtering provides significant improvements in plasma density, but the value of the parameter r<sub>i</sub> still does not exceed 10-20%, and the plasma penetration is still too low to prevent the shadow effect on 3D surfaces.

Another factor to consider is the fact that the plasma cloud propagates from the target towards the substrate merely by diffusion, and reduces the ionization rate dramatically by recombination processes. By contrast, deposition in a cathodic arc plasma environment in which the average ion velocity can reach as high as 10<sup>6</sup> cm/s, the highly ionized metal vapour is transported to the substrate practically without losses. The primary disadvantage of the cathodic arc process is the formation of the droplet phase, which in some cases can reach as high as 50% of the eroded material. Even with this limitation, the arc plasma process provides a much more efficient deposition of material as compared to sputtering.

A simple calculation can be used to illustrate the efficiency of the cathodic arc deposition process. For titanium, the typical erosion rate is estimated to be on the order of 2-4x10<sup>-5</sup> g/coulomb. For an arc source with a 100 A current, this results in a flux of about 0.002-0.004 g/s of titanium vapour. Assuming that about 50% of the metal flux is lost due to macroparticles, and that all the ionized species are completely transferred to the substrate, it gives a mass deposition rate of about 0.001-0.002 g/s. For a surface area of 1 m², this translates to a deposition rate of about 2-4 A/s, or about 1 µm/hr. In reality, it has been found that the large-area filter design permits nearly 80% or more of the metal flux to be ionized and transferred to the substrate. The dual rectangular filter design of the LAFAD™ system provides comparable rates of deposition, allowing this source to be used for applications where high deposition rates and adhesion are important. This source provides maximum ratio of ionized to neutral species, and can be used in combination with a sputtering source with proper shielding.

Ion Cleaning, Ion Implantation and Ion Nitriding: It is clear from the foregoing discussion that any glow discharge plasma processes can be enhanced by the vacuum arc plasma environment. As shown in Fig. 1, the vacuum arc plasma operates over a wide range of pressure, and can be adapted to different surface engineering environments. This is true also of the ion cleaning, nitriding and implantation processes. The impulse glow-discharge plasma nitriding is already established as a state-of-the-art heat treatment process for many industrial applications. New applications are being

International Workshop on Surface Engineering and Coatings NAL, Bangalore, India, June 25-30, 1998

developed for ion implantation technology based on the plasma source ion implantation (PSII), which is also referred to as plasma-immersed ion implantation (PIII).

The high ionization efficiency of the cathodic arc plasma can be effectively combined with these processes to enhance the properties of engineered surfaces. Using a shielded cathodic arc target, high ion current densities on the order of 10 mA/cm² can be achieved at the substrate surface in the pressure range of 10<sup>-4</sup> to 10<sup>-2</sup> Torr. In this pressure range, a number of deposition processes operate, as shown in Fig. 1, and can be significantly enhanced by this capability.

#### Examples of LAFAD™ Coatings:

Some examples of coatings deposited by large-area filtered cathodic arc deposition technique are shown in Table 1. These examples are merely illustrative, and give some idea about the range of coatings, which can be deposited by this technique. As can be seen, the LAFAD<sup>TM</sup> technique is applicable to a variety of coating requirements, from microelectronics to turbine blades. It has been used successfully for applications in a variety of industrial applications. These applications are listed in Table 2.

#### **Conclusions:**

In the foregoing, a broad overview of the various physical vapour deposition methods was provided, with a particular emphasis on the newly developed advanced filtered cathodic arc deposition technology. The highlights of the large-area filtered arc deposition (LAFAD™) technique were described, and the significant advantages and applications of this technique over other conventional PVD methods were pointed out. It is suggested that the unique technological features of the vacuum arc plasma processes, viz. a wide operating pressure range, permits incorporation of this technology in conjunction with other PVD processes, for synergistically improving and extending the applicability of other processes in a hybrid deposition technology configuration.

#### References:

- 1. I. P. Sablev, et al, U.S. Patent 3,793,179 (1974).
- 2. A. A. Plyutto, V. N. Ryzhkov and A. T. Kapin, Soviet Physics, JETP, 20, 328 (1985).
- 3. H. Wroe, U.S. Patent 2,972,695 (1958).
- 4. I. P. Sablev, et al, U.S. Patent 3,783,231 (1972).
- A. A. Andreev and A. A. Romanov, U.S. Patent 4,512,867 (1981).
- 6. C. F. Morrison, U. S. Patent 4,448,659 (1983).
- 7. R. Buhl and Ch. Hasler, DE Patent 370,745 (1987).
- 8. W. M. Mularie, U.S. Patents 4,559,121, 4,559,125 (1983).
- 9. D. A. Karpov, Surface and Coatings Technology, 96, 22-33 (1997).
- 10. A. A. Snaper, GB Patent 1,263,830 (1969); U. S. Patent 3,625,848 (1971).
- A. Aksenov, V. A. Belous, V. G. Padalka and V. M. Khoroshikh, Soviet Journal of Plasma Physics, 4, 425 (1978).
- D. Baldwin and S. Falabella, Technical Proceedings of the Annual Meeting of Society of Vacuum Coaters, 1995.
- V. N. Zhitomirsky, U. Kinrot, B. Alterkop, R. L. Boxman and S. Goldsmith, Surface and Coatings Technology, 86-87, 263, 1996.
- V. I. Gorokhovsky, T. Kurtinina and D. Otorbaev, in Collection of Scientific Papers on Wear Resistant and Protective Coatings (M. A. Voronkin, Ed.), Institute of Superhard Materials, Academy of Sciences of the UkrSSR, Kiev, 1989 (in Russian).
- P. J. Martin, A. Bendavid, T. J. Kinder and L. Wielunsky, Surface and Coatings Technology, 86-87, 271, 1996.
- 16. V. I. Gorokhovsky, U.S. Patents No. 5,380,421 and 5,435,900 (1995).
- 17. R. Buhl, E. Moll and H. Daxinger, U.S. Patent 4,448,802 (1984).
- V. I. Gorokhovsky, V. P. Polistchook and I. M. Yartsev, Surface and Coatings Technology, 61, 101-114 (1993).
- M. Murakawa and S. Watanabe, Surface and Coatings Technology, 43-44, 128-136 (1990).
- P. J. Kelly, O. A. Abu-Zeid, R. D. Arnell and J. Tong, Surface and Coatings Technology, 86-87, 28-32 (1996).

International Workshop on Surface Engineering and Coatings NAL, Bangalore, India, June 25-30, 1998

Table 1: Examples of Coatings Deposited by LAFAD™ Process

Application	Coating	Characteristics
Antifriction Coating	TiN + DLC	5 μm thick coating on Al-Si alloy joints.
		Coefficient of friction < 0.1; On hardened
		steel parts, Coefficient of friction < 0.02
Thermal Barrier Coating	Alumina + NiCrAlY	Multilayer coating, 20-25 µm thick, with a
on Turbine Blades		uniform, microcrystalline structure;
		Thickness variation < 40% over entire
		surface
Cutting Tools	Alumina on TiN-	Alumina coating thickness = 0.5 μm,
	coated Cemented	Microhardness = 2,500 kg/mm <sup>2</sup> , Tool life ~
	Carbide	2-3 times better than PVD TiAIN coating
Cutting Tools	TiN	Ultrafine-grained (crystallite size ~ 100 nm)
		structure with hardness ~ 35 GPa;
		Conventional TiN shows columnar structure
		with hardness ~ 20-25 GPa.
Silicon Wafers	As doped Si	Ultrafine conductive functional coating
		Thickness ~500-1000 Å,
		Roughness, Rz~100 Å
Hard Disk Drive	DLC	Highly dense (D = $4.0 \text{ g/cm}^3$ at ion energy ~
		50-70 eV), Microhardness = 15-25 GPa,
		Electrical Resistivity = $10^{-6}$ - $10^{-10} \Omega$ -cm.

#### Table 2: Applications of LAFAD™ Technology

#### **CUTTING AND FORMING TOOLS**

- ♦ Indexable Inserts
- ♦ Conventional Round-shank Tools
- ◆ Printed Circuit Board Drills
- ♦ Die-casting Dies and Moulds
- ♦ Knives, Saw Blades

#### **ELECTRONICS**

- ♦ Photovoltaic (Solar) Coatings
- Hard Disks and Magnetic Heads
- ♦ Conductive Photolithographic Coatings
- Heat Sinks and Heat Spreaders
- ♦ Flat Panel Displays
- ♦ Large IC Substrates
- ♦ Sensors

#### **AUTOMOTIVE**

- Piston Rings
- Engine Valves and Components
- ♦ Decorative Trim

#### **BIOMEDICAL**

- Surgical and Microsurgery Tools
- Dental and Orthopædic Implants

#### **DECORATIVE COATINGS**

- Coatings for Glass and Ceramics
- Cutlery, Chrome Replacement
- ♦ Artificial Jewelry
- Furniture Hardware and Trim
- ♦ Fixtures and Appliance Parts

#### **AEROSPACE**

- ♦ Turbine Blades
- ♦ Compressor Blades
- ♦ Bearings
- ♦ Mechanical Linkages

#### **OPTICS**

- ♦ Infrared Optics
- ♦ Laser Mirrors
- ♦ X-ray Windows
- ♦ Fiber Optics

#### MACHINE COMPONENTS

- ♦ Joints and Linkages
- Sliding and Rotating Parts
- ♦ Bearings
- ♦ Corrosion Control Coatings

International Workshop on Surface Engineering and Coatings NAL, Bangalore, India, June 25-30, 1998

#### LOG (PRESSURE, TORR)

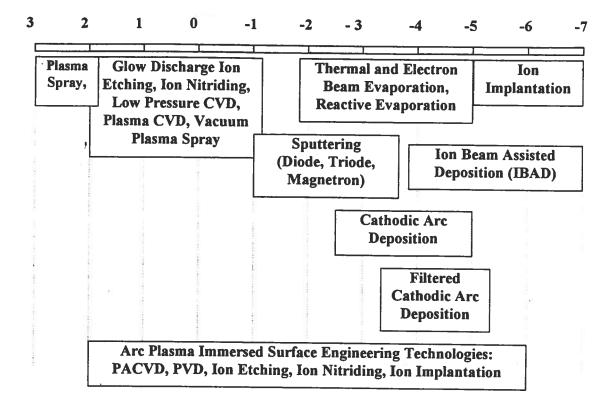


Figure 1: Operating Pressure Ranges for Various Surface Engineering Processes

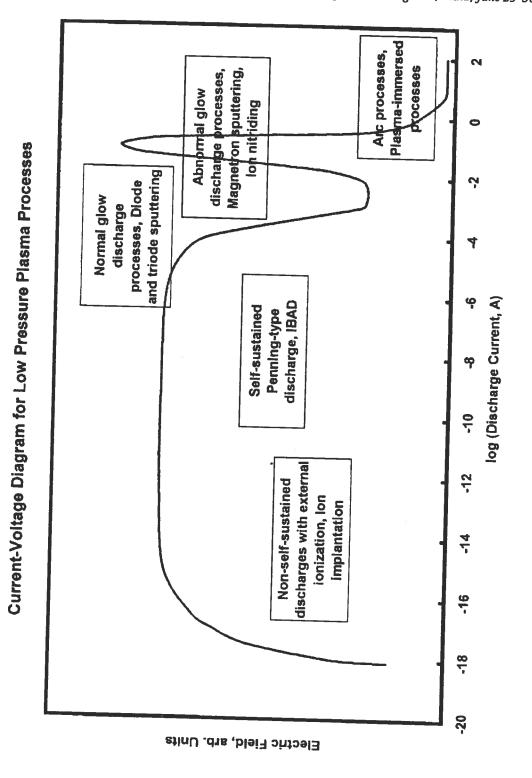


Figure 2: Current-Voltage Characteristics of Low Pressure Plasma Processes.

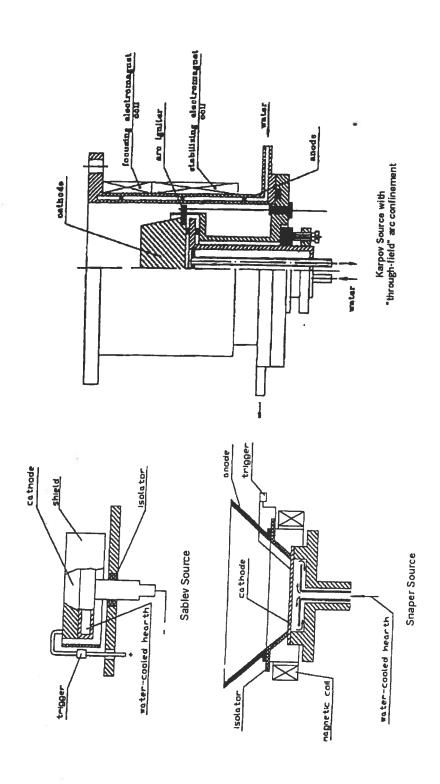
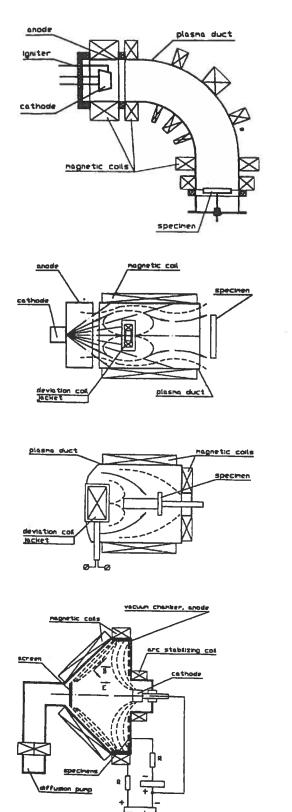
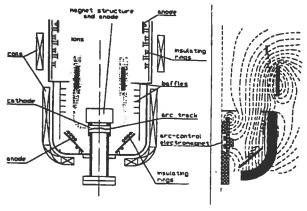


Figure 3: The original cathodic arc sources due to Sablev [1, 4], and Snaper [10]. The source by Karpov [9] provides a means for controlled motion of the cathode spot for uniform erosion and utilization of the cathode.

# International Workshop on Surface Engineering and Coatings NAL, Bangalore, India, June 25-30, 1998





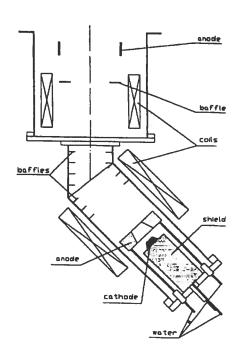


Figure 4: Schematic illustrations of some macroparticle filter designs (adapted from Karpov [9]).

Legend: <u>Top left</u>: Aksenov filter;

<u>Middle left</u>: Magnetic Island filter;

<u>Bottom left</u>: ExB filter; <u>Top right</u>:

"Dome" filter; <u>Middle right</u>:

"Knee" filter.

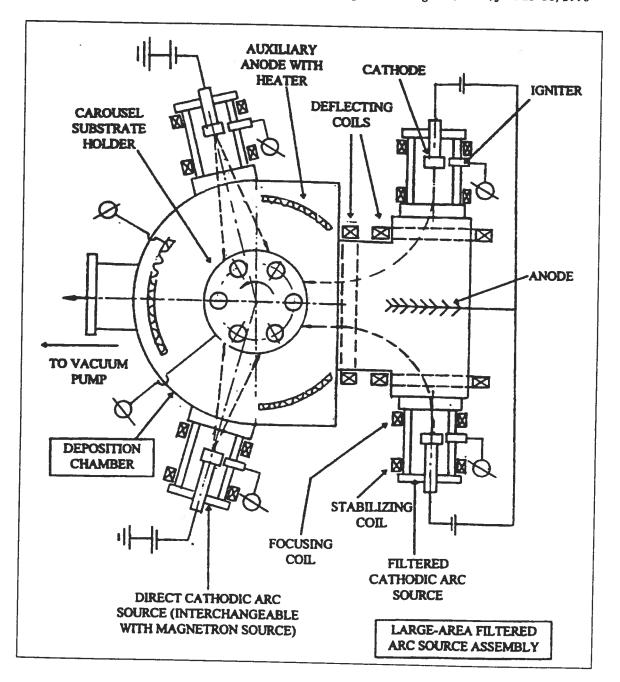


Figure 5: Schematic illustration of the Large Area Filtered Arc Deposition (LAFAD<sup>TM</sup>) apparatus, showing the arrangements of direct and filtered arc sources, auxiliary anode assembly and substrate holder.