Introduction

The utility of hard tribological coatings based on transition nitrides (e.g., CrN, TiAlN, CrAlN, etc.) as protective layers on various forming tools (e.g., die and its components used in high pressure die casting) has led to improvements in increased die life, reduced machine down time, and improved product quality. Moreover, recent advances in the coating design made it possible to obtain nanoscale multilayer and nanocomposite coatings that exhibit outstanding multifunctional properties to meet a wide range of demands including high hardness, good toughness, chemical inertness, and good thermal stability, in comparison to traditional monolithic/single phase coatings.1,2

Besides the coating architecture design, the deposition technique has strong effects on the structure and properties of the coatings. So far, traditional physical vapor deposition techniques, including continuous dc magnetron sputtering (dcMS), pulsed dc magnetron sputtering (PMS), cathodic arc evaporation (CAE), and ion plating have been the major techniques used for the die casting surface engineering.

As compared to the evaporation techniques, the ions generated in the magnetron sputtering plasma can be controlled to bombard the growing film surfaces with tailored energies, which increase the adatom mobility and favor the growth of metastable phases in a non-equilibrium condition. It can be foreseen that an even greater advantage can be achieved if the target material itself is ionized. Unfortunately, the ionization degree of the deposition materials in the dcMS and PMS plasmas is very low (<5%).

The CAE technique has been a primary competitor to sputtering over the past twenty years. Originally developed in the Soviet Union, CAE quickly gained acceptance as an industrial process because of its low cost of implementation using low voltage and high current power suppliers in the 1980’s. CAE is an evaporation-like process in which a high current (hundreds of amperes) dc arc is struck on a metallic cathode surface, where the arc interacts with the cathode surface vaporizing the cathode materials with a high power density at the contact point.3 Due to a high-power density on the arc electrodes, the CAE process is characterized by a combination of a high deposition rate and a high degree of ionization of evaporated species, which makes this process a versatile deposition technology for producing well adherent and dense metal and compound films such as TiN, CrN, Ti-Al-N and their variants for industrial applications.

The main disadvantage of CAE deposition is the production of macroparticles due to the high power density on the cathode. These macroparticles become embedded in the films with a typical size from 0.2 to several micrometers (µm). These macroparticles are undesirable since they will degrade the uniformity of the film surface and impair the quality and properties of the deposited coatings. The macroparticle emission from the cathode spot can be greatly reduced or removed from the arc plasma by several approaches during plasma transport to the substrate, of which a magnetic filter with a positive bias has been the most successful that is known as filtered cathodic arc deposition (FCA). However, the FCA process is limited by its poor thickness uniformity resulting in difficulties to deposit multilayer films, and it will only work with limited coating materials.4

MPP Magnetron Sputtering

In an effort to improve the quality and adhesion of the coatings, considerable interest has been focused on the development of new magnetron sputtering deposition techniques for obtaining high density and ionization degree plasmas to match the CAE process in recent years. The high power pulsed magnetron sputtering (HPPMS) (also known as high power impulse magnetron sputtering (HiPIMS)) by Kouznetsov and co-workers5 and modulated pulsed power (MPP) magnetron sputtering by Chistyakov and co-workers6 are the most recent of these developments. The HPPMS/MPP techniques are aimed at obtaining a high ionization degree of the target species by using a pulsed, high peak target power density applied to the target for a short period of time. In HPPMS/MPP, the average thermal load on the target is kept low by operating the target with a pulsed high peak power density (e.g. 1-3 kWcm-2) for a short period of time (100-500 µs) and a low duty cycle (1-10%). A considerably larger fraction of ionized target species can be created by the high probability for ionizing collisions between the sputtered atoms and energetic electrons. These large number of metallic ions not only can densify the coating by the enhanced ion bombardment, but also can be utilized to pre-clean the substrate at the beginning of the film growth, thereby enhancing the bonding strength between the coating and the substrate.7
As shown in Figure 1, the difference between the Kouznetsov version of HPPMS/HiPIMS and the Chistyakov version of MPP techniques is basically in the magnitude, duration, and shape of the high power pulses. With the Kouznetsov technique, a single short high power pulse, on the order of 100–150 µs in duration is applied to the sputtering cathode, and the magnitude of the peak pulse power density is on the order of 1.0 to 3.0 kW cm⁻² in order to achieve a high degree of ionization of the sputtered material. With the MPP technique, the pulse length can be as long as 3,000 µs, and the peak power density is typically in the 0.5 to 1.5 kW cm⁻² range. The most important feature of the MPP technique is that the MPP pulse shape can be arbitrarily tailored into a multistep pulse. This characteristic of the MPP technique provides a much more flexible deposition process compared to the traditional HPPMS/HiPIMS technique.

The different pulse shapes and parameters between the HPPMS/HiPIMS and MPP techniques are attributed to their different plasma properties and deposition rates. The preliminary plasma characterizations of the MPP plasma of the Cr and Ta materials have confirmed that even though the peak target power in MPP is not as high as it is in the HPPMS, the MPP technique still produces a high degree of ionization of the sputtered target atoms. Unlike the traditional HPPMS plasma, which contains a wide range of ion energy distributions (e.g. up to 100 eV), the metal ions in a MPP plasma exhibited low ion energies in the range of 2–30 eV without the presence of the high energy ions, e.g. as detected in the PMS plasma (small insert in Figure 3a).

In the following sections, the great potentials and advantages of using the MPP technique for the die surface engineering will be illustrated using technical examples.

**MPP Plasma Characteristics**

The ion mass distributions (IMD) of the positive ions in the discharge plasmas during MPP magnetron sputtering of a Cr target in pure Ar and Ar/N₂ atmospheres have recently been determined using an electrostatic quadrupole plasma mass spectrometer (EQP) and compared with the plasma properties obtained using dcMS with similar average target powers and deposition conditions. Significant increases in the number of both target material (Cr) and gas (Ar) ions for an MPP plasma compared to a dcMS plasma were demonstrated for different average target powers (Figure 2).

Further plasma diagnostics of the MPP plasma using the EQP for the ion energy distributions (IED) of the positive ions has also demonstrated that a considerably larger fraction of ionized target species (Cr as an example) can be created in MPP as compared to traditional dcMS and PMS (as shown in Figure 3a and 3b). Additionally, the ions in a MPP plasma exhibited low peak ion energies in the range of 2–30 eV without the presence of the high energy ions, e.g. as detected in the PMS plasma (small insert in Figure 3a).

In the following sections, the great potentials and advantages of using the MPP technique for the die surface engineering will be illustrated using technical examples.

**Dense Nanostructure of the MPP Coatings**

The large number of target ion species in the MPP plasma can provide a more effective momentum transfer to the growing film compared to that in the traditional magnetron sputtering conditions, in which most of the ion species are from the inert gas. The highly ionized MPP plasma favors a high surface mobility of the condensing species, resulting in the growth of fully dense coatings without voids or porosities.

In our early work, an optimized surface engineering coating system based on CrN/AlN nanoscale multilayer design has been developed and shown great improvements in hardness, wear resistance, and thermal resistance as compared to traditional die coatings and surface treat-
Figure 4 – Cross-sectional SEM images of the CrN/AlN nanoscale multilayer films deposited by (A) dcMS and (B) MPP techniques. (The small insert TEM image shows that the modulation period of CrN/AlN nanolayers is 2.8 nm in this case)

Figure 5 – Optical images of an 80 µm thick α-Ta coating deposited using MPP showing a good homogeneity of the coating coverage on the side orthogonal to the target.14 (from reference 14 with permission, IEEE)

Figure 6 – (A) a 20µm CrN coating (10 µm/hr) deposited on 4x6 inch steel substrate; (B) cross-sectional SEM image of a 55 µm CrN coating (10 µm/hr)12 (from reference 12 with permission, Elsevier); and (C) cross-sectional SEM image of a 100 µm Ta coating (16 µm/hr).14 (from reference 14 with permission, IEEE)

Conformal Coating Depositions

It is always a challenge to coat complex shaped substrate/components in most PVD processes due to the line-of-sight limitation. However, the surface engineering of the die and die components surfaces generally requires a good step coverage and uniformity of the coatings. As the deposited species are largely metallic ions in the MPP plasma, it is possible to control the metal ion trajectory by biasing the substrate to improve the step coverage and achieve good deposition rate on the surface placed at an angle to the target. Recently, Lin et al.14 have deposited an 80 µm α-Ta coating on a steel substrate placed with one side facing the target surface and the other side orthogonal to the target. As shown in Figure 5, the thickness of the coating on the orthogonal side is 65 µm, which is of 81% of the thickness of the coating deposited on the side facing the target (80 µm). Considering the large thickness of the coating, the good homogeneity achieved by MPP is a direct consequence of the high ion fraction of sputtered species being controlled by the bias on the substrate.

Nanostructured Thick Coatings

The thickness of traditional magnetron sputter deposited coatings is often limited by the residual stresses that build up in the coating during the deposition, which are directly affected by the ion energy and ion flux arriving at the substrate.15 The MPP process is similar to the CAE process in that it produces a large flux of ionized target species but without the macroparticles. The large number of metallic ions arriving at the substrate also means that a lower substrate bias voltage can be used during deposition, which reduces the stress and damage in the deposited coatings. Therefore the MPP technique has the potential to be the source of ionized atoms that can be used to produce coatings with controlled orientations and minimal residual stress. If the stress can be kept low, e.g., less than −5GPa in compression, it is
possible to deposit dense coatings on the order of 50 µm in thickness or greater, which up to now, has been very difficult to do with magnetron sputtering.

Recently, 20-100 µm thick CrN, Cr2N, Ta conformal coatings have been successfully deposited using MPP at high deposition rates (e.g. 10 µm/hr for the CrN, 15 µm/hr for the Cr2N and 16 µm/hr for Ta). These thick coatings showed excellent adhesion and uniformity (Figure 6a), and extremely dense microstructures and fine grain sizes (Figure 6b and 6c). The residual stresses (σ) of these thick coatings are relatively low, in the range of -2 GPa to -5 GPa.

On account of their dense microstructures, the thick MPP coatings also exhibited excellent adhesion and mechanical properties. Progressive scratch tests performed on the 55 µm CrN coating showed no coating failure at a maximum load of 100 N (Figure 7a). The adhesion of the thick MPP Ta coatings has been further evaluated using the Rocalwell C indentation (HRC) using a 150 kg load. Figure 7b shows the SEM image of the 100 µm Ta coating surface after the HRC test. No coating cracking or delamination can be observed. The excellent adhesion of the thick MPP coatings is attributed to the low residual stress in the coatings and the strong bonding force between the coating and the substrate, which benefit from the enhanced ion bombardment from the highly ionized MPP plasma.

**Excellent Oxidation Resistance**

Since the die and die components are operated at high temperatures (e.g. 700 °C for the Al high pressure die casting), the thermal stability and oxidation resistance of the die coatings are critical. They are largely dependent on the microstructure, texture and residual stress of the coatings, which are strongly affected by the sputtering technique. Figure 8 shows a comparison of the CrN coatings deposited using the dcMS and MPP techniques after annealing at 900 °C. The porous dcMS CrN film was significantly oxidized (Figure 8a). On the other hand, the dense MPP CrN film effectively reduced the inward and outward diffusion rates of the ion species. After annealing at 900 °C, the MPP CrN film maintained an extremely dense structure with minimum damage from the oxidation (Figure 8b).

Another technical example is shown in Figure 9. A thick MPP CrN/AlN nanoscale multilayer coating was annealed in the ambient air at 900 °C and 1000 °C. The as-deposited film exhibits a face center cubic structure (circle symbol) with a strong cubic (c-) (220) peak and weak c(111) and c(200) peaks. After annealing at 900 °C, no crystal structure changes were observed in the coating. However, the diffraction peaks shifted toward the standard positions due to the stress and defect relaxations at elevated temperatures. After annealing at 1000 °C, no oxide peaks were observed in the coating. The coating maintained a strong c(220) peak with the development of a small amount of hexagonal (h-) Cr2N and h-AlN phases (Figure 9). These observations have demonstrated the excellent oxidation resistance and
thermal stability of the CrN/AlN coatings deposited using the MPP technique.

**Summary**

Recent developments for MPP magnetron sputtering have been briefly discussed in this paper. These include the MPP plasma properties, the improvements in the density and adhesion of the coatings, and the important advances in the high rate deposition of high quality thick coatings. These developments have greatly broadened the capabilities and applications of magnetron sputtering for increasing the life time and practical performance of the die and die components. The new MPP magnetron sputtering technique can also be used in new applications, such as new wear resistant coatings on piston rings, cutting tool coatings, aerospace and ground transport vehicle corrosion resistant and oxidation resistant coatings, and aggressive environment applications such as combustion and chemical processing systems.

**About the Author**

Dr. Jianliang Lin earned his Ph.D. in Materials and Metallurgical Engineering from the Colorado School of Mines (CSM). Now he serves as the Director in the Advanced Coatings and Surface Engineering Laboratory (ACSEL) at the CSM. Dr. Lin has been working actively for the North American Die Casting Association (NADCA) in the past 10 years and has been recognized for his contribution to the advancement of die casting surface engineering. His research activities focus on plasma thin film depositions, the development of multifunctional tribological superhard nanocomposite and superlattice coatings, 'smart' coatings, and recently the HPPMS and MMP techniques.

**References**


