Characterization of large area filtered arc deposition technology: part II — coating properties and applications

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Abstract

A dual-filtered cathodic arc deposition process was used to synthesize a variety of hard coatings on polished substrates, using large-area filtered-arc deposition (LAFAD) technology. The surface morphology showed that the coatings were free of macro defects or inclusions, and there was no degradation of the initial surface finish. Mechanical properties of the coatings deposited were measured by a nanoindentation technique. A duplex (heat treatment + deposition) process was used to deposit a unique multilayer hard coating on H-13 steel core pins used in aluminum die-casting application. Extensive characterization of the coated pins showed that the coating improved the erosion/corrosion resistance, as well as thermal cracking resistance, of the steel by nearly one order of magnitude over commercially used PVD coatings. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vacuum arc; Filtered arc; Multilayer; Die-casting dies; Hardness; X-Ray diffraction (XRD)

1. Introduction

The filtered cathodic arc deposition process is known to provide a significant advantage over the conventional cathodic arc process, in that macroparticles can be effectively removed using electromagnetic filtering techniques. The unique advantages and features of the LAFAD technology were described in Part I of this paper and elsewhere. The filtered cathodic arc deposition technology is of great interest and relevance to a number of industrial applications due to the fact that highly adherent, droplet-free coatings with unique microstructure and properties can be obtained by this method. Of particular interest in this regard are decorative coatings, cutting tool coatings, coatings for medical and surgical tools, and tribological coatings for ultra-smooth applications, such as hard disc drives and read/write heads in recording systems.

In the present work, a number of different coatings were deposited on substrates of steel, silicon, and tungsten carbide, using the LAFAD universal surface engineering system. The purpose of the work was to deposit hard coatings for a variety of industrial applications, and to compare them with commercially used coatings. The coatings were characterized by various techniques, and the performance of selected coatings in the pressure die-casting application was evaluated against...
commercial coatings being used in this application, using laboratory simulation of erosion/corrosion and thermal fatigue conditions.

2. Experimental details

2.1. Substrate materials

Highly polished steel (440C, H-13, M50) discs and silicon wafers were used as substrate materials. The substrates were cleaned ultrasonically in acetone and isopropyl alcohol before placement into the deposition chamber. 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 bipolar DC pulses or an RF power supply.

2.2. Deposition of coatings

All the coatings were deposited in the LAFAD system. Cathodes of titanium, chromium and zirconium were used during deposition of various coatings. The arc plasma was generated by primary cathodic arc sources of LAFAS plasma source, having an electronic trigger and arc spot magnetic steering circuitry that effectively eliminates the tendency of the arc spot to be extinguished unpredictably, thereby providing a continuous and stable operation of the arc for an extended period [3]. The deposition chamber was evacuated to a pressure of $7 \times 10^{-4}$ Pa prior to the introduction of gases, such as argon, nitrogen and methane.

In the study of the die-casting application, highly polished ($R_a < 50$ nm) coupons of H-13 steel, which is commonly used for manufacturing die-casting dies, was used as a substrate. In the simplest case of a Ti/TiN multilayer system, TiN was the outer layer, with an intermediate transition layer of Ti. The intermediate Ti layer not only improves adhesion to the substrate, 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 strains due to the difference in the coefficient of thermal expansion, which are induced during the casting process. In our work, we also deposited a multi-component alloy coating, based on a Ti–B–C–N system, for protection against corrosion due to molten aluminum. Titanium, aluminum and titanium diboride cathodes were used during deposition. TiN–TiCN–TiBN multilayer coatings were deposited using two cathodes, Ti and TiB$_2$, in the filtered-arc mode. A thin (sub-$\mu$m) bond layer of Ti was used prior to the deposition of a multilayer of TiCN (using Ti cathode) and TiBN (using TiB$_2$ cathode).

The coating process consisted of sputter cleaning, deposition of a metal bond layer, followed by deposition of the multilayer coating. The substrates were cleaned in Ar plasma, aided by electrons from the arc sources, for 3–5 min at a working pressure of $6 \times 10^{-2}$ Pa, and a substrate bias of $-400$ V (RF). The initial metal bond layer was deposited at a working pressure of $6 \times 10^{-2}$ Pa and a substrate bias of $-60$ V (RF). The deposition time for the bond layer was varied, depending on the total coating thickness.

TiN, CrN and multilayer coatings were deposited employing Ti and Cr cathodes, respectively, in filtered arc sources in a nitrogen atmosphere. Titanium carbonitride (TiCN) coating was deposited using Ti cathodes in a mixture of nitrogen and methane. Carbon and nitrogen content in the TiCN coating was varied by adjusting the flow rates of nitrogen and methane gases. Multilayer Ti/TiCN coating was deposited by switching the atmosphere from argon to methane/nitrogen mixture. In the case of TiN/CrN multilayer coating, one chromium target and one titanium target were used in the filtered-arc mode, and the arc evaporation was alternately switched from one to the other at fixed time intervals. Typical working pressure, substrate bias, and substrate temperature for these coatings were in the ranges $10^{-2}$–$10^{-1}$ Pa, $-40$–$-100$ V (RF) and 350–400°C, respectively.

2.3. Characterization and testing

The coatings were characterized by a variety of techniques. The chemical composition was determined by Auger electron spectroscopy (AES). AES analysis was performed with a Varian model 981-2707 Auger electron spectrometer. A 5-kV electron beam was rastered over an area of $0.1 \times 0.1$ mm$^2$. The electron beam current was 1 $\mu$A. There was a modulation voltage of 10 eV peak-to-peak on the CMA. The vacuum chamber was backfilled with argon to a pressure of $7 \times 10^{-3}$ Pa, and a Varian model 981-2043 ion gun operating at 2 kV was used for sputtering. Quantification of the AES data is based on sensitivity factors determined from binary and elemental standards, including graphite, Si$_3$N$_4$, TiO$_2$ and chromium metal. The overlapping N KLL and Ti LMM spectra were resolved using methods developed previously [4,5]. Ball cratering of one of the samples was accomplished using a 3-cm ball coated with a slurry of 0.3 $\mu$m alumina powder. The dimensions of the crater were measured using a Tencor Alpha-Step 200 profilometer. After the sample was prepared, an AES depth profile was obtained by scanning the electron beam across the crater, as described previously [6].

In one instance, glow-discharge optical emission spectroscopy (GD-OES) was used to determine the compositional modulation of a nanolayered TiN/CrN coating. The phase identification and crystallographic
Fig. 1. AES depth profile analysis of filtered-arc TiN coating. The high level of carbon is believed to be introduced from the back-streaming of oil vapors from the diffusion pump.

Fig. 2. AES depth profile analysis of filtered-arc CrN coating.
orientation were carried out by X-ray diffraction (XRD), and the coating thickness was measured by the ball wear-scar (Calotest™) technique. Optical microscopy was used to evaluate the coating morphology. Coating adhesion was determined by the CSEM Revetest™ automatic scratch adhesion tester. The scratch rate was 1 mm min⁻¹, and the normal loading rate was 20 N min⁻¹. The maximum load used was 100 N. The critical loads at failure were determined according to both acoustical and optical criteria.

The hardness and elastic module of various coatings over a range of loads were measured using microhardness testers, as well as a Nanoindentor II™ hardness tester in the constant displacement mode with a Berkovich indenter tip. Various coatings deposited in this work were also characterized by the ‘work of indentation’ method [7,8], to determine the coating-only hardness from a range of hardness measurements on coated samples. This method involves indenter a coated substrate through the film to measure the composite hardness of the coating/substrate system. The method then proceeds to fit a model curve to the entire set of data, from which the intrinsic hardness of the coating can be extracted as a fit parameter. The substrate hardness can be determined separately, or from high-load indentation tests.

In the case of specimens used in the evaluation of coating performance in the pressure die-casting application, specialized erosion/corrosion and thermal fatigue tests [9] were carried out. In brief, the weight loss of a test pin by dissolution, 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 alloy A380 for a period of 2 h, along with an uncoated H-13 pin as a reference sample. After removal from the melt, any aluminum adhering to the surface of the pins was dissolved in aqueous sodium hydroxide in an ultrasonic bath. The pins were then cleaned using a wire brush and the weight loss per unit area was calculated. The results were compared with those obtained on commercial PVD coatings and surface treatments used in the die-casting application. In the thermal cycling test, specially designed H-13 pins were coated, and then dipped in a bath of molten aluminum alloy A380 for a few s, removed and sprayed with a water/lubricant mixture to quench the surface, and again dipped in the melt. The total cycle time per cycle was approximately 40 s. Tests were conducted for a total of 5000 cycles, and the samples were examined at pre-determined intervals of 1000, 2000 and 5000 cycles for evaluating the damage.

Fig. 3. GD-OES analysis of nano-layered filtered-arc TiN/CrN coating, showing the well-modulated compositional variation between CrN and TiN.
3. Results and discussion

3.1. Chemical composition

The AES profile of a TiN coating is shown in Fig. 1. It is evident that Ti and N are distributed homogeneously throughout the coating thickness, and the Ti/N atomic ratio is close to unity. Note that ~12–15% carbon was also observed in the TiN coating. This carbon is believed to have been introduced from the back-streaming of diffusion-pump oil during deposition, and demonstrates the powerful gettering properties of Ti vapor in the vacuum arc process. Fig. 2 shows the AES depth profile of the CrN coating. It is evident that Cr and N are distributed homogeneously throughout the coating, with the atomic Cr/N ratio close to unity. Fig. 3 shows the GD-OES depth profile analysis of a TiN/CrN multilayer coating. The uniform, repetitive layers of the two films can be very clearly observed, indicating the capability of the technique to deposit nano-layered film structures in a controlled manner. The AES depth profile of a TiCN coating with ~25 at.% nitrogen is shown in Fig. 4.

3.2. Phase analysis

The phase analysis results of filtered-arc TiN and CrN coatings deposited on steel are summarized in Table 1, which also shows powder diffraction data for these two compounds for comparison. The XRD pattern of TiN coating on steel substrate shows a very strong (111) preferred orientation. Generally, TiN coatings deposited by CVD and PVD show a (111) orientation, although such strong texture is not typically observed [10,11]. The XRD pattern of a CrN coating indicates a pure cubic CrN phase with a (200) preferred orientation. Typically, arc ion-plating results in a preferred (200) orientation at low substrate bias (~100 V), (111) at low nitrogen pressure (<5 mtorr) and high

<table>
<thead>
<tr>
<th>Coating</th>
<th>Observed values</th>
<th>hkl</th>
<th>Powder values</th>
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<tbody>
<tr>
<td></td>
<td>d-spacing (Å)</td>
<td>Intensity (%)</td>
<td>d-spacing (Å)</td>
</tr>
<tr>
<td>TiN</td>
<td>2.468</td>
<td>100</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>311</td>
</tr>
<tr>
<td></td>
<td>1.236</td>
<td>10.4</td>
<td>222</td>
</tr>
<tr>
<td>CrN</td>
<td>2.4427</td>
<td>7</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>2.1058</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>1.4329</td>
<td>2.5</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>311</td>
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<td></td>
<td>1.1715</td>
<td>4.6</td>
<td>222</td>
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<tr>
<td></td>
<td>1.0503</td>
<td>1.0</td>
<td>400</td>
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<tr>
<td></td>
<td>1.0138</td>
<td>1.3</td>
<td>331</td>
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</table>
substrate bias (\( > -120 \text{ V} \)), and (220) at high pressure (\( > 5 \text{ mtorr} \)) and high substrate bias (\( > -120 \text{ V} \)) \[12\]. In the present work, a bias voltage of \(-40 \text{ V}\) was used at a nitrogen pressure of less than 1 mtorr. The cubic (f.c.c.) structure of CrN coating is also evident from the selected-area diffraction (SAD) pattern of the film deposited on a silicon substrate, as shown in Fig. 5.

### 3.3. Mechanical properties

The nano-indentation hardness results for TiN, TiCN and CrN are summarized in Table 2. Ultra-low load hardness measurements on thin films should be viewed with some caution, since it is often not possible to compensate completely for indentor tip bluntness and film elasticity effects. It is believed that the high hardness of the PVD films is a result of a dense and fine-grained microstructure, and concomitant high residual compressive stress in the coating. At the same time, the dependence of the measured hardness value on the applied load, and the relative hardness of the substrate are well known. It has been suggested that the nano-indentation values typically overestimate the actual values of the film hardness \[13\]. An example of the typical response of the coating in a micro-and nano-indentation hardness test using a Vickers pyramid indentor is shown in Fig. 6. The test was conducted on a hardened and tempered M-2 steel sample, coated with a \( \sim 4\mu \text{m} \)-thick filtered-arc TiN film. The hardness data, plotted as a function of the relative indentation depth (RID) parameter, clearly show that the nano-indentation hardness values are significantly higher than the micro-indentation values. This is typi-

<table>
<thead>
<tr>
<th>Coating</th>
<th>Nano-hardness (GPa)</th>
<th>Young’s modulus (GPa)</th>
</tr>
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<tbody>
<tr>
<td>TiN</td>
<td>31.8 ± 1.9</td>
<td>303 ± 15</td>
</tr>
<tr>
<td>TiCN_{0.3}</td>
<td>33.3 ± 1.4</td>
<td>255 ± 11</td>
</tr>
<tr>
<td>TiCN_{0.7}</td>
<td>31.8 ± 0.5</td>
<td>253 ± 6</td>
</tr>
<tr>
<td>CrN</td>
<td>24.2 ± 1.6</td>
<td>220 ± 9</td>
</tr>
</tbody>
</table>

### Table 3

Micro-indentation hardness data for various filtered-arc PVD coatings, measured by the ‘work of indentation’ method*.

<table>
<thead>
<tr>
<th>Sample/coating</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>Heat-treated M-2 steel</td>
<td>8.6 ± 1.1</td>
</tr>
<tr>
<td>FA-TiN</td>
<td>24.9 ± 0.6</td>
</tr>
<tr>
<td>FA-TiCN</td>
<td>51.6 ± 2.6</td>
</tr>
<tr>
<td>FA-CrN</td>
<td>26.8 ± 4.3</td>
</tr>
<tr>
<td>FA-TiCN/TiN</td>
<td>45.4 ± 1.7</td>
</tr>
</tbody>
</table>

*Data courtesy of J. Tuck, Oxford University, UK.
Fig. 6. Composite nano- and micro-indentation hardness of filtered-arc TiN coating on M-2 steel substrate (data courtesy of J. Tuck, Oxford University, UK).

Critical failure loads for the aforementioned coatings in the scratch test were in the range of 35–70 N. A typical acoustic emission–load graph for the TiN coating is shown in Fig. 7, indicating a failure load of ~70 N. This value is higher than the values typically obtained on PVD coatings in general, and approaches values observed on CVD TiN coatings on cemented carbide substrates [10]. Thus, it can be seen that the filtered-arc process can provide a very high degree of adhesion, in part due to the high level of ion bombardment achievable in this process.

Fig. 7. Revetest™ scratch test data for filtered-arc TiN coating on steel, showing excellent coating adhesion to the substrate.
4. Coatings for die-casting dies

This application provides a particularly aggressive environment for a protective coating, including erosion/corrosion from the molten metal at high pressure, and severe thermal cycling, leading to thermo-mechanical fatigue failure [15,16]. 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 the as-ground surface of the core pins (which are centerless ground to a fine finish) is uneven at the nanoscale of the coating/substrate interface, and offers sites where there is sufficient stress concentration under the aggressive thermal fatigue conditions. This can then lead to relatively easy failure of the coating, sometimes merely due to thermal mismatch and internal stresses generated during deposition and/or in service. When subjected to the harsh erosive/corrosive environment, such stress concentration sites become the preferred locations for coating failure. Therefore, surface finish of the part being coated must be carefully considered. A detailed study of this aspect by Aharonov et al. [17] has also corroborated the effect of surface finish on the coating performance in this application. In the present work, it was found that polishing the substrate to remove surface irregularities improved coating adhesion and performance. The deposition of an initial thin, metallic, bonding film prior to the deposition of the hard coating was aimed at further improving the compliance of the multilayer structure under harsh thermal-cycling conditions. This coating system shows considerable improvement in the performance of coated components as compared to substrates coated with typical PVD TiN, even though it has been suggested that the TiN coating typically does not last long, due to oxidation at temperatures above 600°C [18].

An example of a multilayer TiN/Ti coating is shown in Fig. 8. The total thickness of the coating was found to be 5.8 μm. The hardness of ion-nitrided and coated H-13 pins was measured by micro-indentation at loads of 25 and 50 g by placing the indentation through the
coating. Both coated and ion-nitrided H-13 steel showed hardness of approximately 11.9 GPa (1220 kg mm$^{-2}$) as compared to 5.19 GPa (530 kg mm$^{-2}$) for the uncoated H-13 steel. Since the thickness of the coating and ion-nitrided layer was in the region of 5–6 and 20–30 μm, respectively, the hardness values represent a composite effect of the coating and the substrate. The surface hardness of the Ti/TiCN multilayer was measured as 21 GPa (2143 kg mm$^{-2}$) with a modulus of 305 GPa by nano-indentation. The scratch adhesion tests indicated that the coatings cracked at loads of 40–60 N.

The results of weight loss experiments from the erosion/corrosion test in molten aluminum alloy are shown in Fig. 9. The plot is normalized with respect to the weight loss of an uncoated H-13 pin, by assigning this a value of 100, and the results are plotted on a logarithmic scale. Lower weight loss indicates a better performance. The multilayer coatings show a weight loss which is nearly two orders of magnitude smaller than that of the uncoated H-13 pin. Fig. 10 shows the surface condition of the coated pins as compared to an uncoated H-13 pin. It is evident that the surface of the uncoated pin has dissolved away due to heavy pitting.

Fig. 10. Appearance of uncoated and multi-layer TiN/TiCN/TiBN-coated H-13 pins after 2 h at 680°C in molten aluminum A380 alloy: a,b – uncoated H-13 pins; c,d – H-13 pins with multi-layer LAFAD coatings. Sample pin diameter 12.2 mm (1/2 in.).

Fig. 11. Appearance of uncoated and multi-layer TiN/TiCN/TiBN-coated H-13 Pins after thermal cycling in molten aluminum A380 alloy for several cycles. (a) Uncoated pin after 2000 cycles; (b) uncoated pin after 5000 cycles; (c) coated pin after 2000 cycles; and (d) coated pin after 5000 cycles.
and attack by 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.

The best coatings from the accelerated corrosion tests were tested in thermal cycling to evaluate their resistance to delamination and cracking. Fig. 11 shows the surface of the H-13 test pins after 2000 and 5000 cycles. It can be observed that a number of cracks were developed perpendicular to the edge of the square pin, due to thermal cycling. Several small cracks were formed on the surface of uncoated pin after 2000 cycles. During further cycling, many of these cracks were found to have propagated further, and increased in width. Some corrosion was also observed on faces of the coupon, in the form of small pits. Some pitting damage was also observed at the site of cracks on the edge of the coupon. In contrast, the multilayer-coated pins showed very little damage to the surface and edges, even after 5000 cycles. No visible cracking was observed on any of the edges. Some microscopic damage to the coating was evident at one of the edges of the pin, in the form of very small pits and chipping of the coating.

5. Conclusions

In the present study, single and multilayer coatings were deposited using the large-area filtered cathodic arc deposition (LAFAD) technique. The dual rectangular filter design of the LAFAD system provides rates of deposition comparable with single conventional cathodic arc source, allowing this source to be used for applications where high deposition rates and adhesion are important. The mechanical properties measured for the filtered-arc coatings show values superior to other, conventional PVD coatings. The multilayer coatings deposited by this technique showed a significantly improved performance in the erosion/corrosion test against molten aluminum alloy, against all the other commercially available coatings and surface treatments used for comparison in this work. This result is attributed to the improved adhesion, wear resistance and thermal cycling resistance of the coatings deposited in the duplex ion nitriding + deposition mode. During the thermal cycling tests, the multilayer coating was shown to suppress cracking of the substrate, thereby delaying crack initiation and reducing the incidence of cracking. This demonstrates the beneficial effect of a duplex treatment for die steel to combat two major causes of die failure 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 die-casting dies.

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