Abstract
Soldering, washout and thermal fatigue are the primary causes of die non-performance in permanent mold and die casting production of net shape parts for the transportation industry. At worst, corrosive reactions between the liquid metal and die steel result in core pin or sprue dissolution, and at the least, some soldered cast metal remains behind when the casting is ejected. This paper presents a duplex surface treatment approach for dissolution resistance and improved ejection that consists of nitrided hot working die steel substrate followed by multi-layer titanium-based coatings applied by the Large Area Filtered Arc Deposition technique. The dissolution behavior of the coating candidates is evaluated by measuring weight loss after dipping them in molten aluminum for a predetermined time. Results are compared with those of single layer coatings and surface treatments. The chemisorption and adhesion behavior is evaluated by measuring ejection force of the soldered material. The duplex coating is found to significantly reduce both the dissolution and adhesion tendencies of the coated steel surface. This paper also includes thermal cycling results for the selected duplex coatings, which indicate that the duplex approach needs further refinement before it can be used for improvement in thermal fatigue resistance.

Introduction
Die soldering is primarily responsible for the adhesion of the cast metal to the die surface. The adhesion of the casting to the surface of the die, core pins and inserts makes ejection very difficult, resulting in bent ejector pins and for heavily damaged castings. Figure 1 shows an image of a core pin, which was so strongly soldered to the casting that it had to be broken to release the core from the casting. Note the heavy marks left by ejector pins on the cylindrical surface of the casting.1

Figure 1
According to the Al-Fe phase diagram, at high temperatures Al can dissolve a small amount of Fe (around 2% at 700°C or 1202°F). The Al-Si-Fe eutectic reaction occurs at the composition of about 0.8% Fe. Theoretically, when Fe is allowed to somewhat above this amount, the supersaturated molten metal exhibits little or no tendency to dissolve die steel while the two materials are in intimate contact. For this reason, most aluminum die casters desire alloys which contain between 0.8 and 1.1%Fe. However, as the iron content increases above 1.2%, the larger amount, size and shape of the plate-like iron constituent does impair mechanical properties. Sludging becomes more likely, introducing several problems. Fluidity and casting characteristics are also adversely affected.2

Soldering of the aluminum on the die surface occurs when the molten aluminum reacts with iron rich die surface causing intermetallic formation and dissolution of the steel surface into the melt during cavity filling.3 During the solidification state, solid-state diffusion between iron and the hot aluminum leads to chemisorption and adhesion. In a typical die casting cycle, the die surface is in contact with the molten metal for under a minute, which implies that the formation of an intermetallic layer at the interface takes place in a short time.

Surface treatments and single layer Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) coatings have been found to be effective in reducing this soldering tendency. However, single layers often fail due to pitting corrosion around the pinhole and macro-particle defects present in coating deposited by the vacuum ion-plating, sputtering and arc deposition.4

The objectives of the present study were to develop multilayer and duplex (coating + surface treatment) die coatings with minimal coating defects and a (aluminum to steel) diffusion resistant surface treatment and then to evaluate these coatings for –

1. Dissolution behavior with the help of accelerated corrosion dip tests.
2. Adhesive and chemisorption behavior by ejection tests.
3. Heat checking behavior by thermal cycling tests.
Multilayer coatings have been developed on the philosophy of integrating the best properties from individual coatings into a single multilayer coating system. Some layers of this system would have excellent resistance to molten aluminum but have acceptable thermal shock resistance. Others have good thermal fatigue resistance and excellent compatibility of the coefficient of thermal expansion with the substrate, but have acceptable corrosion and erosion resistance. Some may 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 engineer the coatings to harness the best of everything, and put it to work in a composite coating system. A schematic of a multilayer system is shown in Figure 2. This paper presents an approach to design and evaluate these coatings for die casting applications.

Deposition Of Duplex and Multilayer Coatings

LAFAD Deposition Technique

Different multilayer coatings were deposited on H13 steel substrates at UES Inc., using a novel “Large Area Filtered Arc Deposition (LAFAD)” system. This 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. This technique allows the plasma flux from different cathodes in a multi-cathode chamber to be uniformly mixed and enveloped around the part. The system at UES consists of three key components: direct arc sources, large area filtered arc sources and the auxiliary anode assembly. It has been shown by Gorokhovsky and by Vetter and Perry that the arc sources can extract highly energetic electrons, which can be used to ionize the gaseous plasma. This plasma envelope completely surrounds the part during deposition process chamber. Using this technique, very high ion currents can be obtained as compared to the other PVD techniques such as Electron Beam Physical Vapor Deposition (EBPVD) and sputtering.

Coatings Tested

• For protection against soldering

The Ti/TiN multilayer coatings were deposited using two Ti cathodes, in the filtered-arc mode. A thin (sub-micron) bond layer of Ti was used prior to the deposition of a multilayer of TiN and Ti sub-micron (using Ti cathode). Coatings A through E had a thin transition layer of Ti between the substrate and the TiN layer. Table 1 gives the various coating system candidates developed for protection against soldering.

Table 1

<table>
<thead>
<tr>
<th>Coating System</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ti/TiN</td>
</tr>
<tr>
<td>B</td>
<td>Ti/TiCN</td>
</tr>
<tr>
<td>C</td>
<td>Ti/TiAlN</td>
</tr>
</tbody>
</table>

• For protection against thermal fatigue

The coupons were nitrided to two different case depths, 150 microns (shallow nitrided) and 350 microns (deep nitrided), to study the effect of case depth on the initiation and propagation of thermal fatigue cracks during thermal cycling. The multi-layer coatings evaluated were Ti/TiC, Ti/TiCN and Ti/TiAlN. In duplex coating, the test coupons (H13) were first nitrided and then coated with TiAlN.

Characterization of Coatings

The selected coatings were characterized for thickness, hardness, and adhesion. The thickness and layer structures were characterized by Calotest equipment. The total thickness of the multi-layer coating was found out to be 4.2 microns. Auger electron microscopy (AES) was used for compositional characterization. The hardness of ion-nitrided and coated H13 coupons was measured using microindentor with loads of 25gm and 50gm. 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 H13 steel substrate. Since the coating or ion nitriding was in the range of 3-4µm, the hardness values represent a composite effect of the coating and the substrate. The surface hardness of the multi-layer coatings was in the range of 20 to 40 GPa (2143 Vickers for Ti/TiCN) and a modulus of approximately 300 GPA. The scratch adhesion tests using (Scanning Electron Microscope) CSEM tester indicated that the coatings cracked at loads of 40-60 N. The properties of various coatings are shown in Table 2.

Table 2

<table>
<thead>
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<th>Coating System</th>
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<tbody>
<tr>
<td>A</td>
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<tr>
<td>C</td>
<td>Ti/TiAlN</td>
</tr>
</tbody>
</table>

Experimental Procedure

Three tests were used to evaluate dissolution, adhesion behavior and thermal cycling behavior of the duplex-coated coupon surface in contact with liquid and solidifying molten aluminum alloy. These were the accelerated corrosion dip, casting ejection and thermal cycling tests.

Accelerated Corrosion Dip Test

The soldering resistance of a coating can be evaluated by its dissolution rate: mass loss of the coated coupon dipped in molten aluminum alloy for a predetermined length of time. The test procedure consists of dipping the test coupons for a predetermined time in the aluminum alloy A380 melt maintained at 680°C (1256°F). A dip timing of two hours was used for all the coupons to enhance the weight loss. The accelerated corrosion test equipment is explained by Shivpuri, et al. in a prior publication. Fresh alloy was used for each round of tests since the melt quality gets affected due to dissolved Fe from the core pins and oxidation of Al at the melt surface. Several cylindrical coupons (pins) were loaded onto the test fixture. The coupons used were DME CX 25 H13 core pins of hardness 47-50HRc, 3/8in. in diameter and 3 in. in length in each campaign so that results of different campaigns can be compared. After a stipulated time, the pins were removed from the furnace and any aluminum adhering to the surface of the pins was leached using aqueous solution of sodium hydroxide in an ultrasonic bath. After removal of aluminum, the pins were cleaned with a wire brush to remove any oxide or other residue. The pins were then weighed using a Mettler AC 100 weighing machine with a resolution of 0.0001gm, and the weight loss per unit dip area was calculated.

Ejection Tests

The soldered surface substantially increases the ejection force required to separate the casting from the die surface. A tribologically-sound surface (well lubricated with no adhesion) permits clean/low force ejection of the casting. Adhesive strength between a die casting alloy and die steel is related to the soldering tendency of the two materials.
the fundamentals of tribology, the force required to break the soldering bond, \( F_e \), is given by:

**Equation 1**

The normal component of the force depends on the differential contraction of the casting with respect to the pin and the taper angle on the pin (in this experiment, this angle was kept to be “zero” to enhance the ejection force). A schematic of the ejection test set up is as shown in figure 3. The test procedure consisted of solidifying a casting around coated pin, and then pulling the casting from the pin using a fixture mounted on an MTS machine. This force of separation is a measure of the adhesive tendency of the casting to the pin surface. A small crucible was used as a mold for the casting process. A measured amount of A380 was melted in this crucible and the coated pin was dipped to a fixed depth. After a predetermined time, the melt solidified onto the dipped pin. This solidified cylinder (casting) was then ejected from the pin using a specially designed clamping mechanism and the force of ejection was measured.

**Figure 3**

Thermal Cycling Test

The thermal cycling tests were carried out on the thermal cycle simulator at the Ohio State University. The thermal cycle was developed by simulating the actual die conditions using a commercial FEA software (DEFORM). The thermal cyclic test is explained in detail by Shivpuri, et al. in a previous publication.

**Results and Discussions**

Results of Dip Test

A few results from work done previously at The Ohio State University were used for comparison with the results from the four best multilayer candidates were then compared to the previously tested surface coatings and treatments. Results of this comparison are plotted in figure 5, which shows the performance of the LAFAD multilayer was significantly better as compared to the other coatings tested previously at The Ohio State University. This plot is normalized with respect to plain H13 by assigning a value of 100 to it. The weight loss per unit area is represented on a normalized scale. It may be noted that the TiN/TiBN/TiCN multilayer on the hard steel substrate (HRC 50) performed the best with negligible weight loss.

**Table 3**

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Weight Loss (1000 cycles)</th>
</tr>
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<tbody>
<tr>
<td>Ti/TiC</td>
<td>10</td>
</tr>
<tr>
<td>Ti/TiCN</td>
<td>8</td>
</tr>
<tr>
<td>Ti/TiAlN</td>
<td>5</td>
</tr>
<tr>
<td>H13</td>
<td>12</td>
</tr>
</tbody>
</table>

**Equation 1**

\[
F_e = \frac{\rho V}{\pi r^2} \left( 1 - \frac{r}{R} \right)
\]

where \( \rho \) is the density of the casting material, \( V \) is the volume of the casting, \( r \) is the radius of the casting, and \( R \) is the radius of the pin. The thermal fatigue behavior of duplex coating seems to be dominant by the behavior of the substrate. In both cases, oxidation and soldering were seen to be less than that seen in the case of pure nitriding, which can be attributed to the formation of \( \mathrm{Al}_2\mathrm{O}_3 \) on the TiAlN surface. Therefore, once
optimized with a ductile interlayer, this duplex approach is probably a better approach to counter both heat checking and soldering at the same time.

**Conclusions**

The development of multilayer LAFAD and duplex coatings and their evaluation in accelerated corrosion, casting ejection and thermal cycling tests provided the following observations:

i) The improvements in weight loss shows that the multilayer coatings are at least an order of magnitude better in preventing soldering of the coated H13 core pins as compared to all the other commercially available coatings and surface treatments previously tested. The best results were observed in TiN + TiBN/TiCN multilayer coatings.

ii) A combination of ion nitriding and hard coating (Duplex approach) 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 well as diffusion behavior provided by ion nitriding.

iii) Multilayer coatings provided much lower forces in the ejection tests; this was due to the higher surface energies, low wettabiltiy and thus, less adhesion of the cast metal on the coupon.

iv) During the thermal cycling tests, the nitried coupons were observed to perform better than un-nitried coupons. The multilayer coating did not prove effective without a good interface. With nitriding, these coatings were seen to suppress cracking of the substrate, thereby delaying crack initiation and reducing the incidence of cracking. However, once the cracking initiated, the behavior of the substrate dominated.

v) With the duplex approach, the number of cracks was reduced with increase in crack depth. The depth of the crack can also be reduced if a ductile interlayer could be placed between the coating and the substrate.

vi) With this duplex approach, the filtered cathodic arc deposition process has demonstrated to be a possible technique to significantly improve the useful lifetime of the die casting dies.

**References**


Table 2 – Characterization of coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Nano Hardness (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>32 ± 2</td>
<td>303 ± 15</td>
</tr>
<tr>
<td>TiCN (carbon rich)</td>
<td>31 ± 2</td>
<td>255 ± 11</td>
</tr>
<tr>
<td>TiCN (nitrogen rich)</td>
<td>32 ± 1</td>
<td>253 ± 6</td>
</tr>
<tr>
<td>CrN</td>
<td>24 ± 2</td>
<td>220 ± 9</td>
</tr>
<tr>
<td>ZrN</td>
<td>29 ± 2</td>
<td>216 ± 15</td>
</tr>
</tbody>
</table>

Equation 1 –

\[ F_E = F_n \cdot \mu \alpha (W_{12}, H, \theta) \]

where

- \( W_{12} \) is work of adhesion (dependent on the surface energies and tribological state of the surface),
- \( H \) is the hardness of the softer material,
- \( \mu \alpha \) is the adhesion component of friction,
- \( \theta \) is a function of surface roughness,
- \( F_e \) is the force of ejection and
- \( F_N \) is the force normal.

Table 3 – Relevant information about the coatings previously tested at The Ohio State University.

Figure 3 – Schematic of the Ejection Test set up.

Figure 4 – Geometry of the thermal cyclic test coupon.

Figure 5 – Weight loss of multilayer coatings compared to other surface treatments for a dip of two hours in A380 melts at 680°C. This graph has been normalized by assigning a value of 100 to H13. Weight loss per unit area is represented on a log scale.

Figure 6 – The change in a force during ejection for the three surface treated coupons uncoated, nitrided and multilayer coated.
Figure 7 – Surface characteristics of multilayer Ti/TiC, Ti/TiCN and Ti/TiAlN coated coupons before and after thermal cycling for 1000 cycles.

Figure 8 – Surface micrograph (50 X) of TiAlN coatings with shallow and deep nitrided substrate.