Soldering and Ejection Behavior of Duplex and Multilayer Filtered Arc PVD Coatings

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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.

Figure 2

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.[5,6] 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[7] and by Vetter and Perry[8] 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 TiB_2 (using TiB_2 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

- 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.[10] 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

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.[8] 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. From the fundamentals of tribology,[10] 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.[9] The thermal cycle was developed by simulating the actual die conditions using a commercial FEA software (DEFORM).[9,11] The thermal cyclic test is explained in detailed by Shivpuri, et. al. in a previous publication.[8] The test coupon is shown in figure 4. The flat surface of the coupon is for observing thermal fatigue cracking. The coupons were subjected to 3000 thermal cycles. They were cleaned with NaOH solution and examined optically after every 1000 cycles.

Figure 4

Results and Discussions

Results of Dip Test

A few results from work done previously at The Ohio State University[4] were used for comparison with the results from the current round of tests. Table 3 includes relevant information about the selected candidates. It indicates the various coating techniques, composition, thickness and hardness.

Table 3

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.[9]

Figure 5

Results of Ejection tests

Figure 6 shows the plots for the ejection tests for multilayer coatings (Ti/TiN), nitrided pins and H13 pins. It can be seen that multilayer coatings show minimum ejection forces and thus the minimum adhesion tendency.

Optical examination of the uncoated H13 pin shows that the outer surface has dissolved away due to heavy pitting and dissolution into the molten aluminum. The multilayer-coated pin shows a small concentration of very small pits. There is no observable damage to the edges of the pin. If these pits can totally be eliminated, the dissolution and adhesion performance of these coatings will further improve.

Figure 6

Result of Testing Thermal Cycling

Figure 7 shows the results of testing of multilayer coatings Ti/TiC, Ti/TiCN and Ti/TiAlN coated coupons. The Ti/TiC and Ti/TiCN coating candidates showed almost the same results. A lot of oxide seemed to have formed on the coated surfaces and small pits and pores were seen on both. After 1000 cycles, the coatings dissolved at some places while at other places the coatings were seen to have cracked and flaked, leading to soldering and removal of the coating. Some minute cracks, which might have formed in the substrate, were also observed around the pits in these coupons.

In the case of TiAlN coating, an oxide layer appeared but was thinner than that observed in any of the previous cases. This could be primarily due to rapid oxidation of the TiAlN surface to form hard and impermeable Al_2O_3, which prevented further oxidation. After testing, no crack network was observed on the flat surface on polishing. However, small cracks were seen forming on the edges of the coupon.

Figure 7

The cracking is found to be a substrate-driven phenomenon. Once the substrate cracks, it results in cracking of coating, and thus flaking and dissolution. The difference between the hardness of the substrate and coating is critical in removal of coating during early cycling. Therefore, to avoid this, an interface is required between the coating and the substrate that provide a gradual change in hardness. A duplex approach with ductile interlayer may work as desired under these conditions.

Figure 8 compares the duplex TiAlN coated coupon with shallow (type 1) and deep nitriding (type 2) before and after thermal cycling. After 1000 cycles, a large number of cracks were seen on the surface of coated sample with shallow nitriding. These were similar to those seen in the case of uncoated coupon with shallow nitriding. The width of the cracks was estimated to be about 15-20 microns. The cracks appeared to have started from the edges and propagated toward the surface. The cracks were seen to be much larger than the coating thickness of 2.5 microns. The behavior of the coated coupons with deep nitriding after testing was seen to be similar to that of the uncoated deep nitrided coupon. The cracks were seen to be wider (larger) and fewer than those seen on the shallow nitriding coupons.

Figure 8

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 Al_2O_3 on the TiAlN surface.[11] 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 wettability and thus, less adhesion of the cast metal on the coupon.

iv) During the thermal cycling tests, the nitrided coupons were observed to perform better than un-nitrided 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.

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Figure 1 – *Picture of a soldered pin.*

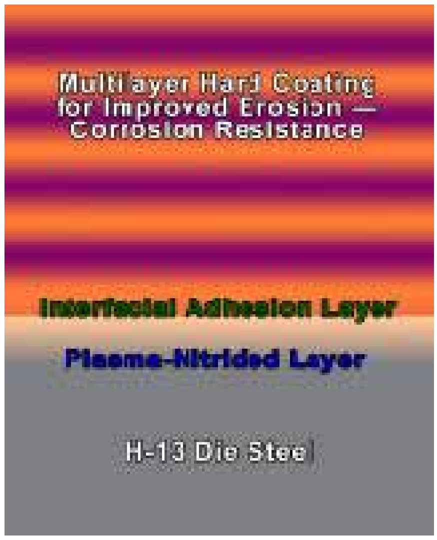

Figure 2 – *Schematic of multilayer coating system.*

S. No.	Coating
1	Ion nitrided + filtered arc TiN coating
2	Pre hardened + filtered arc TiN coating
3	Ion nitrided + filtered arc TiN coating + filtered arc TiB_2
4	Pre hardened + filtered arc TiN coating + filtered arc TiB_2 coating
5	Pre hardened + filtered arc TiN coating + filtered arc AlN coating
6	Ion nitrided + multi layer Ti(C)N (gold colored)
7	Ion nitrided + multi layer Ti(C)N (gold) + TiAlN
8	Pre hardened + Ti/TiN/TiCN (30°/3°)
9	Pre hardened + Ti/TiN/TiCN ([illegible]) + Ti/TiN/TiCN ([illegible])
10	Pre hardened + Ti/TiN/TiAlN
11	H13: Uncoated DME CX-25 M-3 core pin 45 – 50 HRc.

Table 1 – *Various multilayer coatings developed for resistance against soldering.*

Coating	Nano Hardness (GPa)	Elastic modulous(GPa)
TiN	32+ - 2	303+ - 15
TiCN(carbon rich)	33+ -2	255+ -11
TiCN (nitrogen rich)	32+ -1	253+ -6
CrN	24+-2	220+ -9
ZrN	29+ -2	216+-15

Table 2 – *Characterization of coatings.*

$$F_E = F_n * \mu\alpha \, (W_{12}, H, \theta)$$

where

- W12 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,
- θ is a function of surface roughness,
- F_E is the force of ejection and
- F_N is the force normal.

Equation 1 –

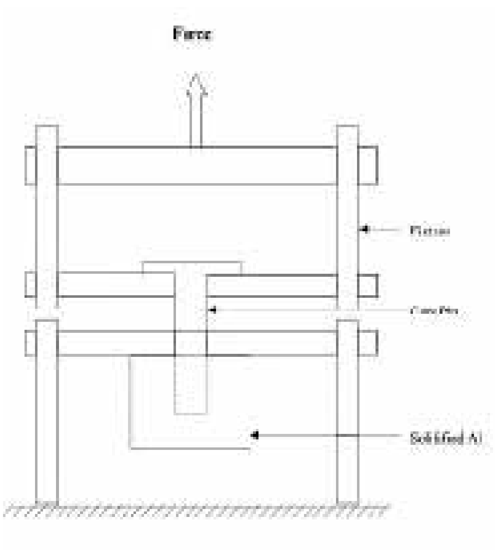

Figure 3 – *Schematic of the Ejection Test set up.*

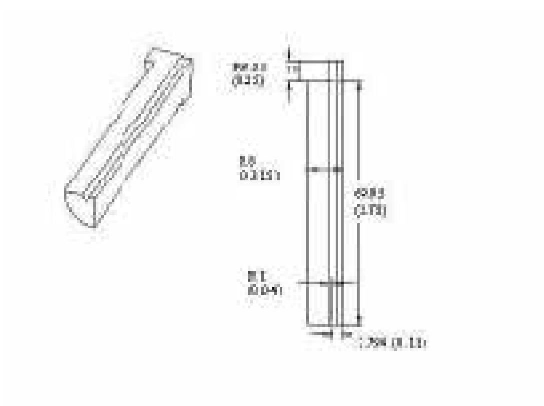

Figure 4 – *Geometry of the thermal cyclic test coupon.*

Technique	Coating/ Surface Treatment	Coating Thickness	Hardness
Physical Vapor Deposition	CrN_x	6-8 µm	2500 HV
	Cr_xC_y B_xC	10 µm 2µm	850 HV 900 HV
Thermo-Reactive Deposition	VC	7 – 10 µm	1000 HV
Surface treatments	Ultraglow (Ion Nitriding–)	0.15 - 0.20 mm (case depth)	697 - 1070 HV
	Ion Wear (Ion Nitriding - 2)	0.08 - 0.13 mm (case depth)	746 HV
	Ferro-Nitro-Carburizing	0.13-0.25 mm (case depth)	
Duplex	Shot Peening + CrN_x	6-8µm	2500 HV
Substrate	H13	-	45-47 HRc

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

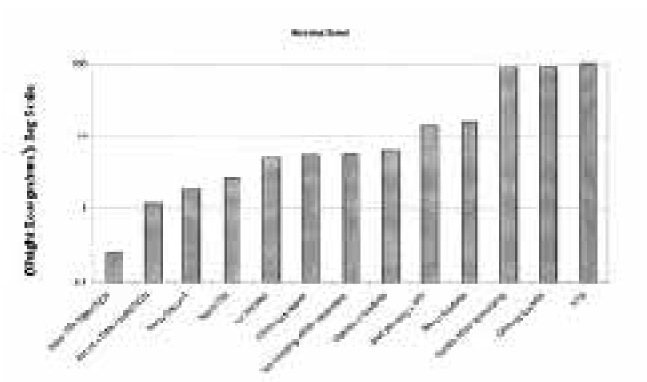

Figure 5 – *Weight loss of multilayer coatings compared to other surface treatments for a dip of two hours in A380 melts at 680°C. This graph has been normalized by assigning a value of 100 to H13. Weight loss per unit area is represented on a log scale.*

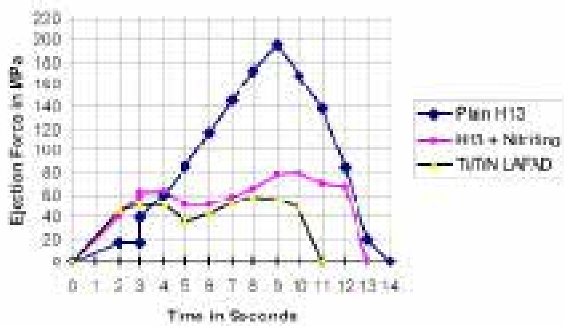

Figure 6 – *The change in a force during ejection for the three surface treated coupons uncoated, nitrided and multilayer coated.*

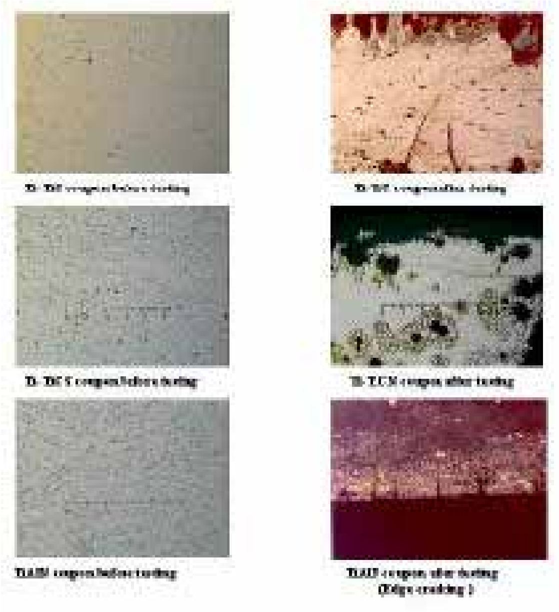

Figure 7 – *Surface characteristics of multilayer Ti/TiC, Ti/TiCN and Ti/TiAlN coated coupons before and after thermal cycling for 1000 cycles.*

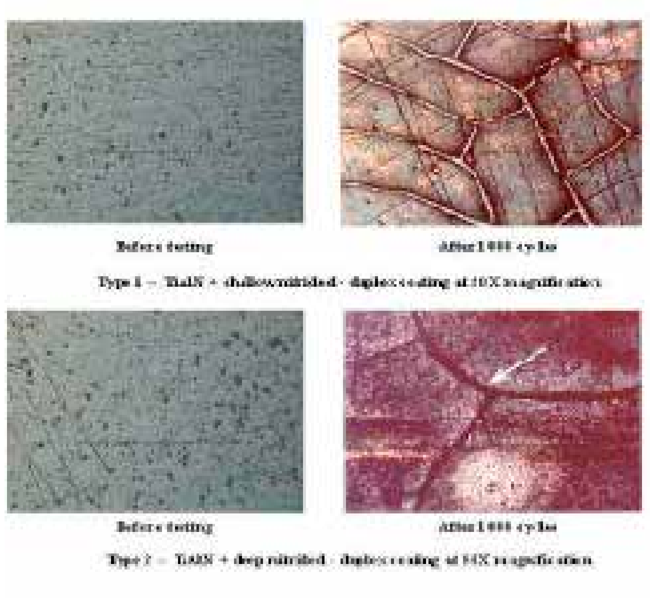

Figure 8 – *Surface micrograph (50 X) of TiAlN coatings with shallow and deep nitrided substrate.*