Development of a Coating for Wear and Cracking Prevention in Die-Casting Dies by the Filtered Cathodic Arc Process

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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 fatigue 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^{o} 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 low-cycle 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_xC_y, TiN, TiCN, ZrN, VC and TiAlN [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^{o} C or 1300^{o} 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_7C_3, 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.

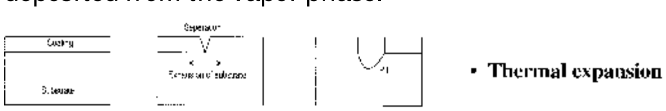

Figure 1: Schematic showing a probable mechanism of coating failure (Difference in coefficient of Thermal Expansion) [5].

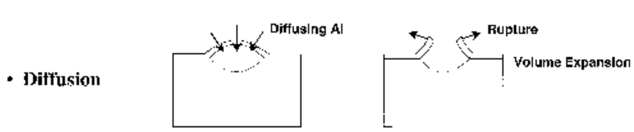

Figure 2: Schematic showing the probable diffusion mechanism of coating failure (Diffusion of metal) [5]

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]

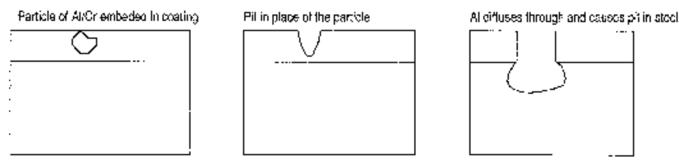

Figure 3: Failure due to embedded particle of Al/Cr, during coating Process [5].

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 voids 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.

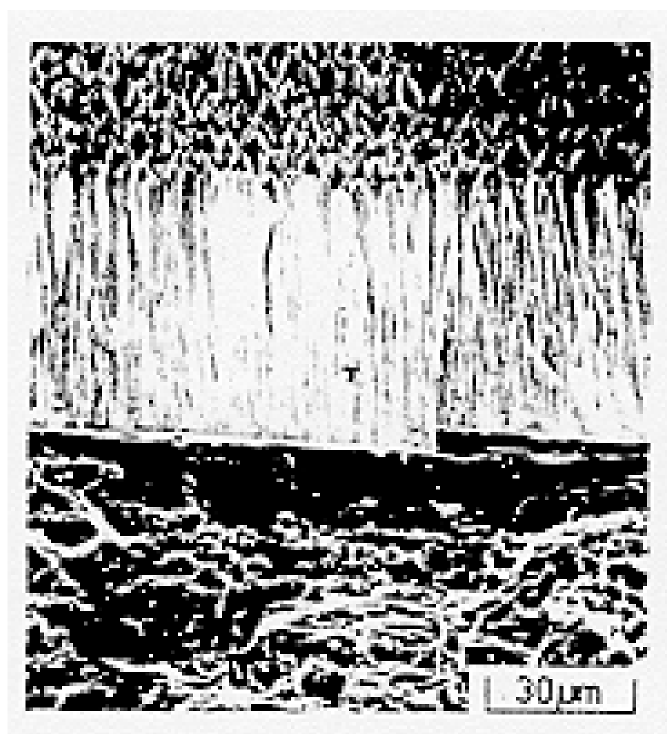

Figure 4: Columnar microstructure of PVD coatings. (Electron micrograph) [8]

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 metals [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).

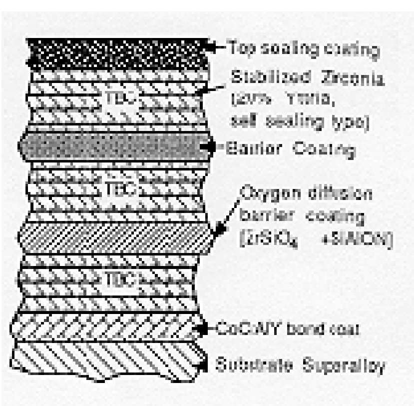

Figure 5: Structure of a typical multilayer coating (Thermal barrier coating) [9]

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.

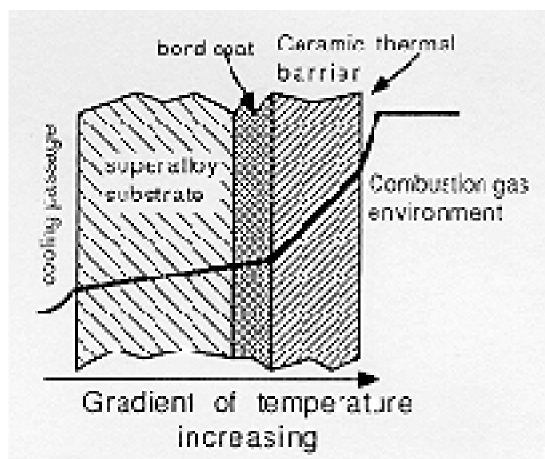

Figure 6: Thermal gradient in a typical multilayer coating system [9]

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 $600^{\circ}C$ [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 biased, significant ion implantation can be achieved.

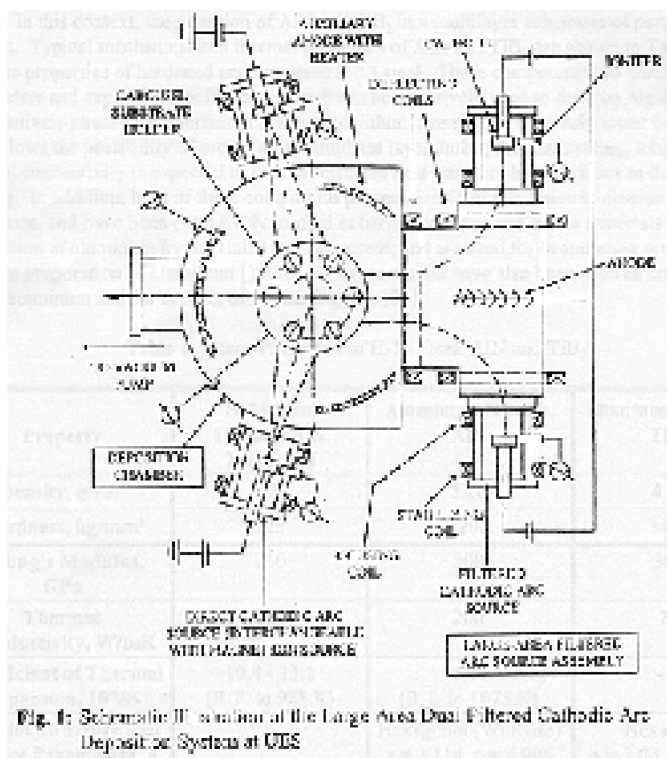

Figure 7: Schematic Illustration of the Large Area Dual Filtered Cathodic Arc Deposition System at UES.

Description of the coating process:

All the coatings were deposited in the filtered cathodic-arc 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 eliminates 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 $7x10^{-4}$ 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 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_2 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 failure 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:

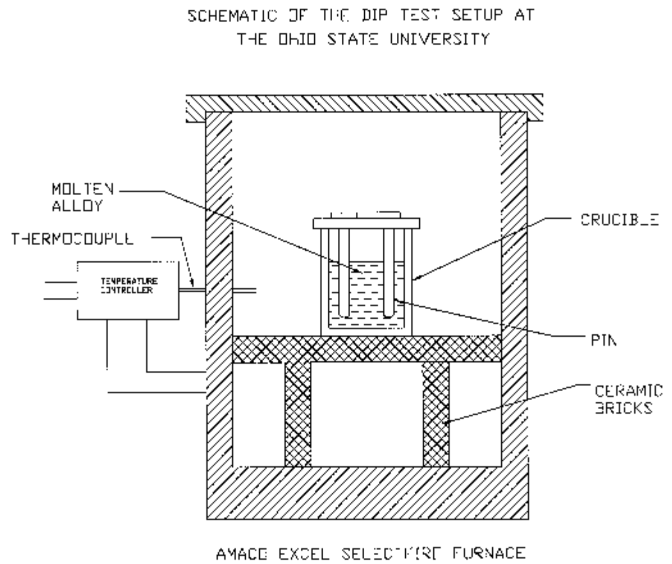

Figure 8: Schematic Illustration of the Accelerated Corrosion Test setup at The Ohio State University

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 10^{-4} 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.

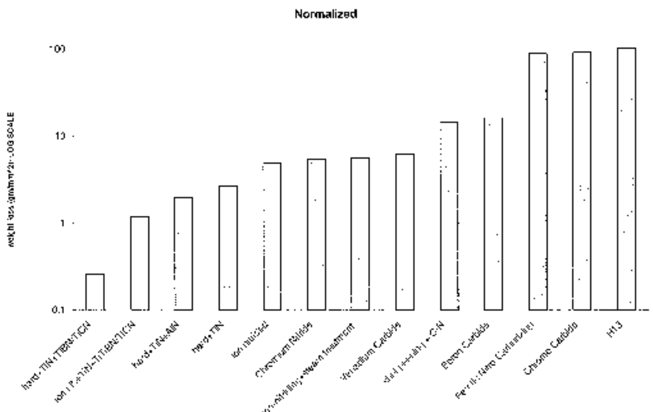

Figure 9: Performance of the TiN / TiBN / TiCN multilayer coatings as compared to other coatings. This graph has been normalized by assigning a value of 100 to H-13.

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.

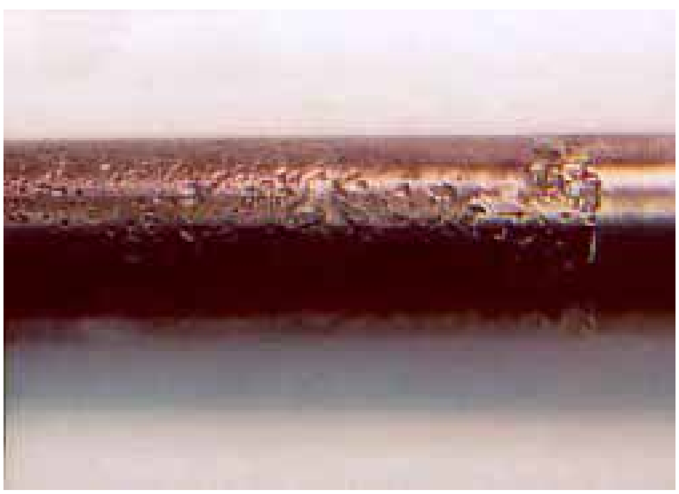

Figure 10: Uncoated H-13 pin after 2 hours at 680°C in molten aluminum A380.1 (1X)

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.

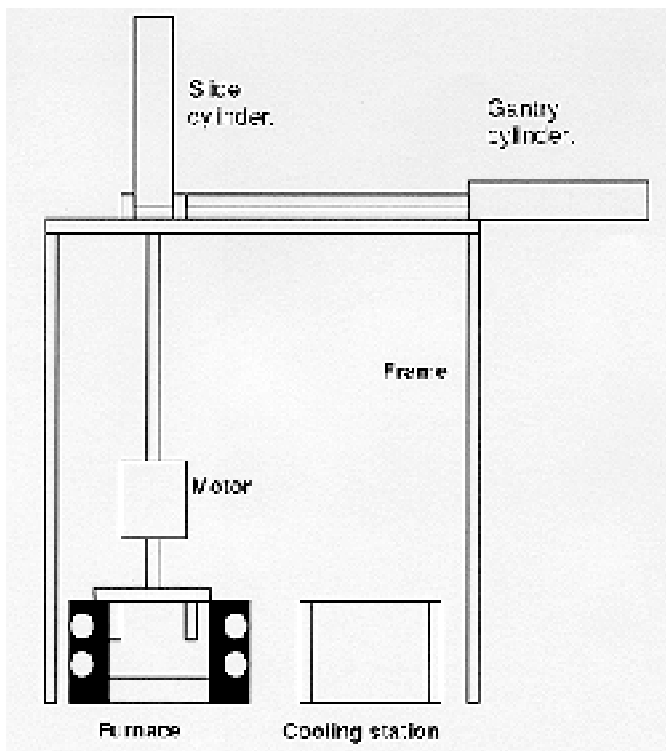

Figure 13: Geometry of the test coupon used for the thermal cycling tests. (Dimensions are in inches)

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.

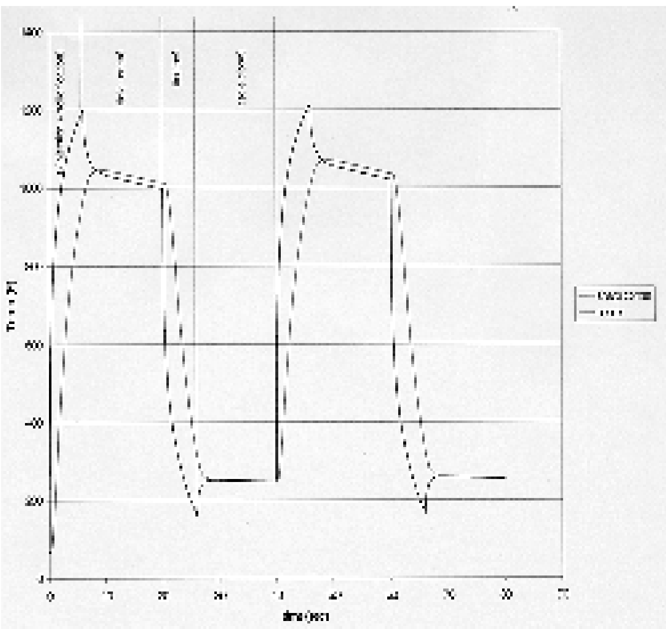

Figure 14: Thermal cycles obtained from DEFORM simulations.

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 1.

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(sec)	Heat transfer coefficients[12] (Btu/in^{2}sec.°F)
Cast metal injection	Dip in molten A380	t_{cav}	6	$1.35 * 10^{-2}$
Casting ejection (Die open)	Test pins in air	t_{air-1}	14	$8 * 10^{-6}$
Lubricant spray	Dip in lubricant solution	t_{lub}	6	$1.4 * 10^{-2}$
Die closing	Test pins in air	t_{air-2}	14	$8 * 10^{-6}$

Table 1: Cycle times during the Thermal Cycling tests.

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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.

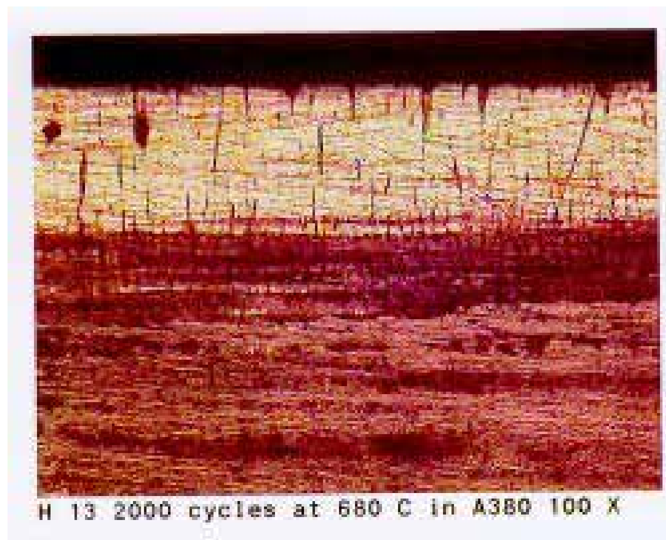

Figure 15: H-13 coupon after 2000 cycles (100X)

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.

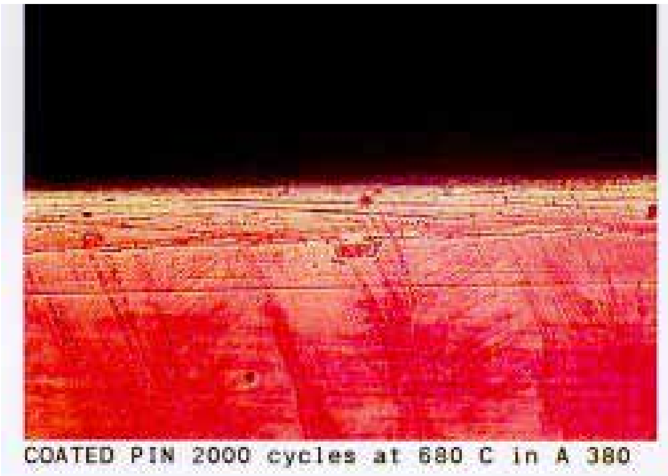

Figure 16: The coated coupon after 2000 cycles (100X)

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.

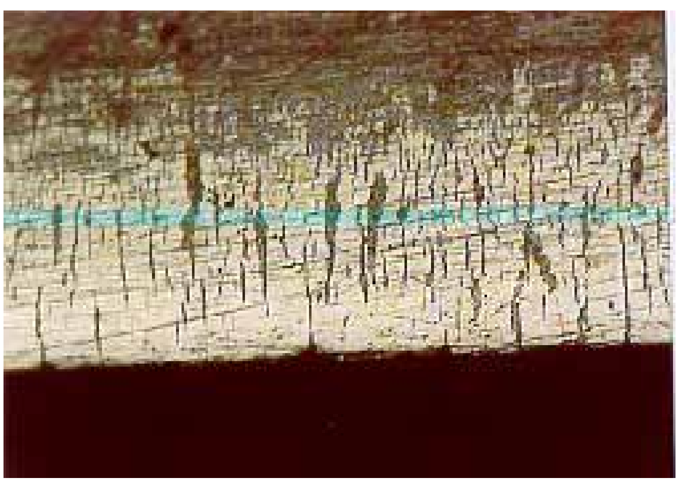

Figure 17: The H-13 coupon after 5000 cycles (100X)

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.

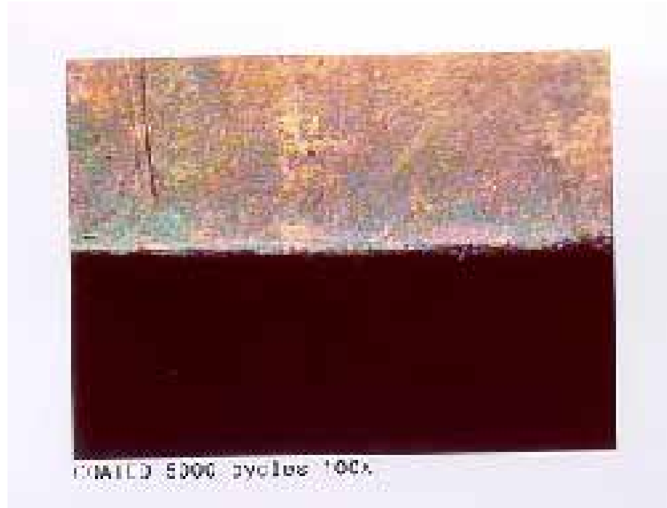

Figure 18: The coated coupon after 5000 cycles (100X).

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 Ion nitriding, 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 thermal 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 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 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:

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