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Dissolution and soldering behavior of nitrided hot working steel with multilayer LAFAD PVD coatings

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Abstract

Soldering and corrosive dissolution 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, these corrosive reactions result in core pin or sprue dissolution, and at the least, some soldered cast metal remains behind when the casting is ejected. The objective of this work was to explore the possibility of surface engineering of the die steel surface to reduce the dissolution and soldering tendencies of the surface. This paper presents a duplex surface treatment approach for dissolution resistance that consists of nitrided hot working die steel substrate coated 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.

Keywords: Nitrided hot working die steel substrate; Multi-layer titanium based coatings; Large area filtered arc deposition technique; Soldering in die casting

1. Introduction

Aluminum die-casting is a high volume manufacturing process hence downtime, scrap rate and cycle time play an important role in the economics of the operation. Two-thirds of the downtime during normal production is caused by die-related problems. Die soldering, the physiochemical interaction between the molten cast metal and the die surface, is a major contributor. It is responsible for the adhesion of the cast metal to the die surface, and the dimensional changes of this surface caused by dissolution. The adhesion of casting to the surface of the die, core pins and inserts makes ejection very difficult resulting in bent ejector pins and in heavily damaged castings. Fig. 1 shows an image of a core pin, which has strongly soldered to the casting. The core pin had to be broken to release the core from the casting. Note the heavy marks left by ejector pins on the cylindrical casting [1].

Evidence from production shows that the presence of an oxide layer or lubricant layer reduces the occurrence of adhesion [2]. An oxide layer is present on the die surface due to oxidation of the die steel during heating and water quenching (steam oxidation). Surface treatments and single layer PVD and CVD coatings have also been found to be effective in reducing the soldering tendency. However, single layers often fail due to pitting corrosion around the defects present in vacuum ion-plating, sputtering and arc deposition [1].

Soldering of the aluminum on the die surface will occur when the aluminum alloy melt has deficiency of iron. This melt then reacts with the iron-rich surface causing intermetallic formation and dissolution of the steel surface into the melt. Fig. 2 represents the inter-

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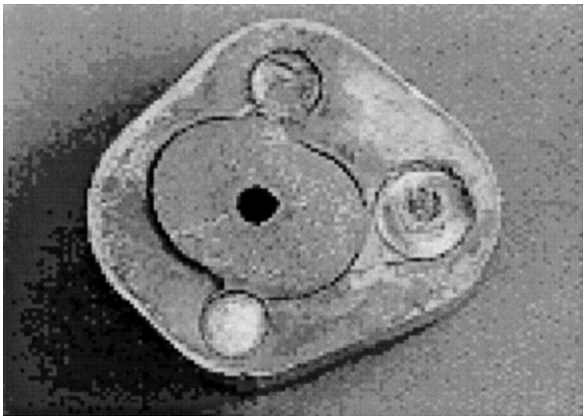

Fig. 1. Picture of a soldered pin.

metallic formed after dipping H13 steel in molten Al alloy melt for 5 h at 680°C [3]. Deposition of the aluminum on the die surface during the solidification process leads to solid-state diffusion between iron and the aluminum leading to chemisorption and adhesion. During a typical die casting cycle, the die surface is in contact with the molten metal for under 1 min, which implies that the formation of an intermetallic layer at the interface takes place in a short time.

The objectives of the present study were to develop multilayer die coatings with minimal defects, to evaluate these coatings for dissolution behavior with the help of accelerated corrosion tests, and to investigate the adhesive and chemisorption tendency by ejection tests on soldered casting.

2. Experimental procedure

Two tests were used to evaluate dissolution and adhesion behavior of the coated coupon surface in contact with liquid and solidifying molten aluminum alloy: accelerated corrosion test and casting ejection test.

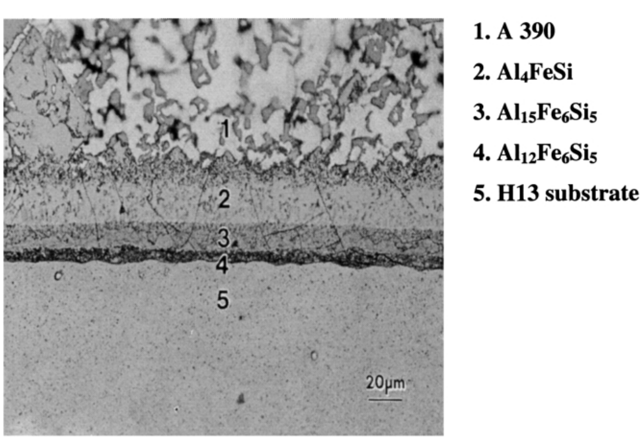

Fig. 2. Picture of the soldered intermetallic layers on a H13 pin.

2.1. Accelerated corrosion 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 (Fig. 3). The test procedure consists of dipping the test coupons in the aluminum alloy A 380 melt maintained at 680°C (1256°F). The dip timing of 2 h was used for all coupons to enhance the corrosion rate and weight loss. Fresh alloy was used for each round of tests. Several cylindrical coupons (pins) were loaded onto the fixture. A control pin, hardened H-13 pin, was used in each campaign so that results of different campaigns can be compared. After stipulated time, the pins were removed from the furnace and any aluminum adhering to the surface of the pins was leached using an 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 0.0001 g, and the weight loss per unit area was calculated. This weight loss is a measure of the dissolution characteristic of the pin surface.

2.2. Casting ejection tests

Molten aluminum has affinity for the steel surface, bare or coated H13 die steel. This affinity results in chemisorption and adhesion (welding) of aluminum on the pin surface. This adhered surface substantially increases the ejection force required to separate the casting from the die surface. A tribologically sound surface (well lubricated with no adhesion) will permit 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.

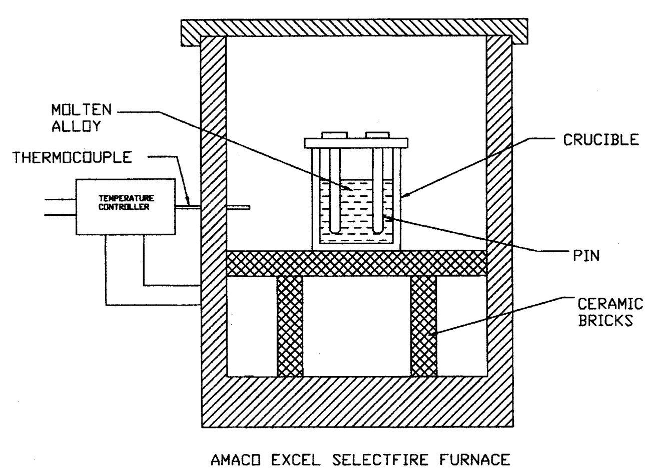

Fig. 3. Schematic illustration of the accelerated corrosion test setup at the Ohio State University.

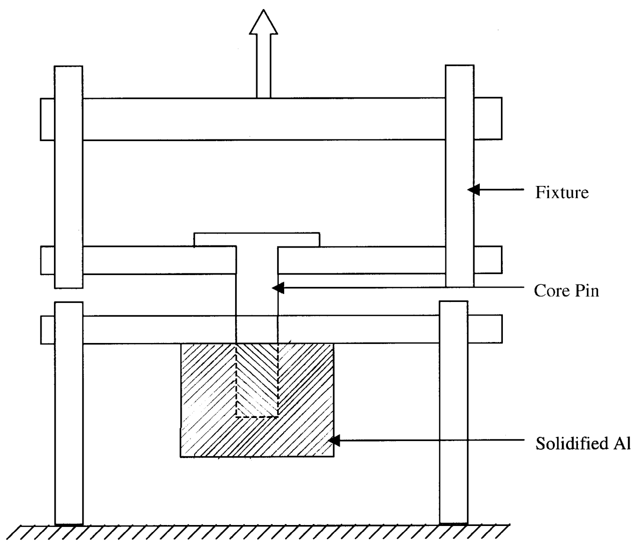

Fig. 4. Schematic of the ejection test set up.

From the fundamentals of tribology [4,5], the force required to break this bond, F_E, can be given by,

$$F_E = Fn^* \mu_a(W_{12}, H, \theta)$$

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, μ_a 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. 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).

The schematic of the test set up is as shown in Fig. 4. The approach consisted of solidifying a casting around a 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 constant depth. After a predetermined time, the melt solidified onto the dipped pin. This solidified cylinder (casting) was then pulled from the pin using a specially designed clamping mechanism, and the force of ejection was measured.

3. Coatings deposited by the LAFAD technique

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. While some have all the properties required for good corrosion, erosion and thermal fatigue resistance but have very poor bonding to the substrate. The recent trend has been to engineer the coatings to harness the best of each, and put it to work in a composite coating system.

3.1. LAFAD deposition technique

Thin hard ceramic coatings can be deposited in a variety of ways like plasma-assisted deposition, physical vapor deposition, chemical vapor deposition, pack cementation and other available techniques [6]. 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

Table 1
Relevant information about the coatings and surface treatments previously tested at the Ohio State University

Technique	Coating/surface treatment	Coating thickness	Hardness
Physical vapor deposition	CrN_x	6–8 μm	2500 HV
	Cr_xC_y	10 μm	1850 HV
	B_xC	2 μm	900 HV
Thermo-reactive deposition	VC	7–10 μm	3000 HV
Surface treatments	Ultraglow (Ion nitriding–)	0.15–0.20	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	6–8 μm	2500 HV
Substrate	H13	–	45–47 HRc

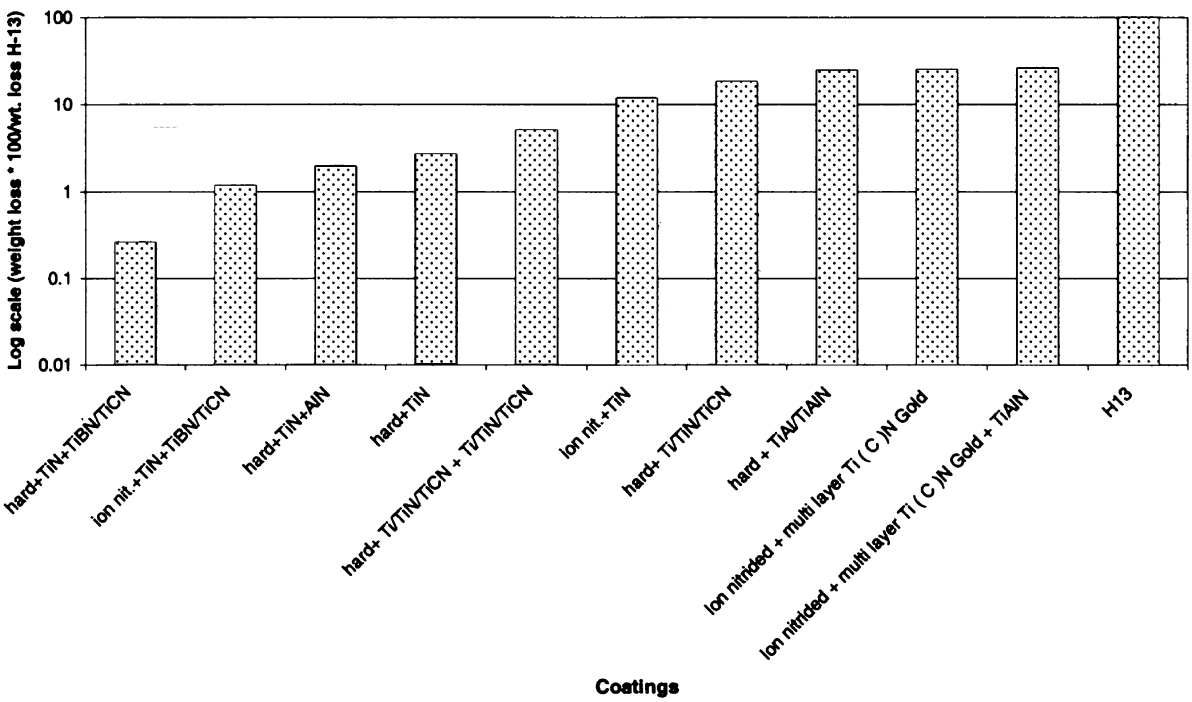

Fig. 5. The performance of all the LAFAD coating candidates as compared to H-13. The weight loss per unit area is represented on a log scale and normalized to 100 for H-13 [7].

use the capabilities of each. However, this multi-stage process requires recleaning 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 multi-layer coating and other surface modification steps in single, versatile deposition equipment.

Different multilayer coatings were deposited on H-13 steel substrates at UES, 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 [8,9]. This technique allows the plasma flux from

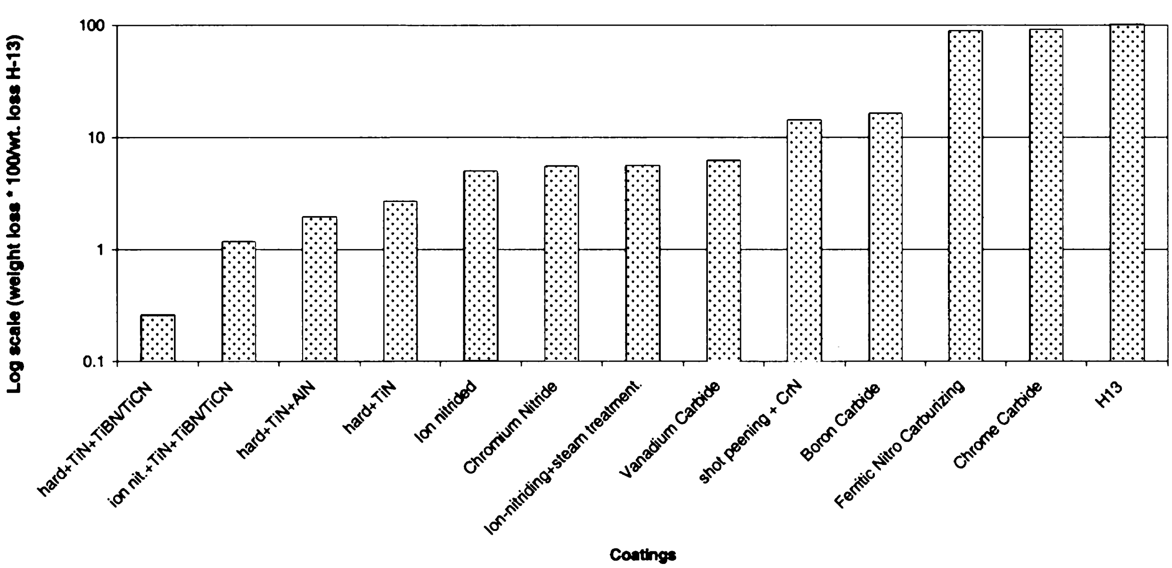

Fig. 6. Performance of the LAFAD multilayer coatings as compared to other coatings testes previously at the Ohio State University. This graph has been normalized by assigning a value of 100 to H-13. Weight loss per unit area is represented on a log scale [7].

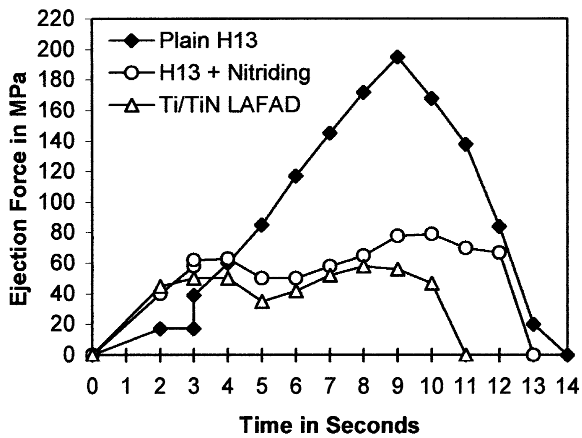

Fig. 7. The change in a force during ejection for the three surface treated coupons uncoated, nitrided and multilayer coated.

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 [10] and by Vetter and Perry [11] that the arc sources can be used to extract highly energetic electrons that ionize the gaseous plasma, such that the plasma envelope that completely surrounds 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 arc plasma generated by a patented electronic trigger and arc-spot control circuitry 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 [12]. The deposition chamber is evacuated to a pressure of 7×10^{-4} Pa prior to the introduction of gases such as argon or nitrogen for cleaning of the substrates prior to metal deposition. The pins to be coated are 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 filtering technique (magnetically modifying the path of the ions to reach the substrate) eliminates heavy pure metal droplets from depositing on the surface.

The Ti/TiN multilayer coatings were deposited using two Ti cathodes, in the filtered-arc mode. A thin (submicron) bond layer of Ti was used prior to the deposition of a multilayer of TiN and TiB_2 (using TiB_2 cathode). The following coating system candidates were developed for testing:

- A: Ion nitrided + filtered arc TiN coating;
- B: Pre hardened + filtered arc TiN coating;
- C: Ion nitrided + filtered arc TiN coating + filtered arc TiB_2;
- D: Pre hardened + filtered arc TiN coating + filtered arc TiB_2 coating;
- E: Pre hardened + filtered arc TiN coating + filtered arc AlN coating;
- I: Ion nitrided + multi layer Ti(C) N (gold colored);
- J: Ion nitrided + multi layer Ti(C) N (gold) + TiAlN;
- K: Pre hardened + Ti/TiN/TiCN;
- L: Pre hardened + Ti/TiN/TiCN + Ti/TiN/TiCN;
- M: Pre hardened + Ti/TiN/TiAlN;
- H13: Uncoated DME CX-25 M-3 core pin.

Coatings A through E had a thin transition layer of Ti between the substrate and the TiN layer.

3.2. Characterization of coatings

The coatings were characterized for thickness, hardness and adhesion. The thickness and structures of the layers were characterized by Calotest equipment. 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 thickness of ion nitriding was approximately 250 m, the total thickness of the multilayer coating was 3–4 m and the individual thickness of each layer was approximately 0.5–0.7 m. The Ti layer in the multilayer coatings was very thin with the thickness of 0.1 μm.

The hardness of ion-nitrided and coated H-13 pins was measured using a microindentor with loads of 25 and 50 g. Both coated and nitrided H13 steel showed hardness of approximately 11.9 GPa (1220 Vickers) as compared to 5.19 GPa (530 Vickers) for the H-13 steel substrate. Since the coating thickness or ion nitriding depth was in the range of 3–4 μm; the hardness values represent a composite effect of the coating and the substrate. The hardness values were measured on nanoindentor scale with the load of 5 mN and depth of indentation was 100 nm. The typical values for the

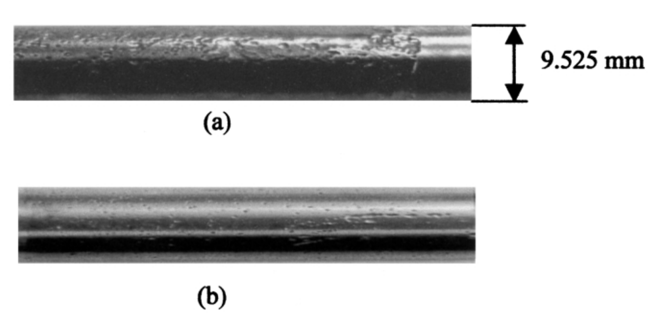

Fig. 8. (a) Uncoated H-13 pin after 2 h at 680°C in molten aluminum A380.1. (b) Ti/TiN coated pin after 2 h at 680°C in molten aluminum A380.1.

hardness on nano scale were 28–33 GPa for the multilayer coatings and the modulus was 250–300 GPa. The scratch adhesion tests using the CSEM tester indicated that the coatings cracked at loads of 40–60 N.

4. Evaluation of LAFAD coatings and discussions

Results from work done previously at the Ohio State University were used for comparison with the results from the current round of tests. Table 1 includes relevant information about the selected candidates. It indicates the various coating techniques, composition, thickness and hardness.

Fig. 5 shows the performance of all UES coatings as compared to H-13 [7]. The weight loss per unit area for the 2-h dip is represented on a log scale. The four best multilayer candidates were then compared to the previously tested surface coatings and treatments. Results of this comparison are plotted in Fig. 6, which shows that the performance of the LAFAD multilayers was significantly better as compared to the other coatings tested previously at the Ohio State University. This plot is normalized with respect to plain H-13 by assigning a value of 100 to it. The weight loss per unit area is represented on a log scale. The TiCN/TiBN/TiN multilayer on the hard steel substrate (HRC 50) performed the best with negligible weight loss.

Fig. 7 shows the plots for the ejection tests for multilayer coatings (Ti/TiN), nitrided pins and H-13 pins. It can be seen that multi-layer coatings show minimum ejection forces and thus the minimum adhesion tendency.

Optical examination of the uncoated H-13 pin shows that the outer surface has dissolved away due to heavy pitting and dissolution into the molten aluminum (Fig. 8a) while the multilayer-coated pin shows a low concentration of very small pits (Fig. 8b). 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.

5. Conclusions

The development of mutilayer LAFAD coatings and their evaluation in accelerated corrosion and casting ejection tests provided the following observations:

1. Soldering formation occurs due to the simultaneous diffusion and dissolution at the cast metal-die steel interface. The driving force for intermetallic formation is the compositional gradient and the temperature gradient. In these tests the temperature gradient was kept constant and hence, the results were a function of compositional gradient only.
2. The improvements in weight loss observed in the present work shows that the multilayer coatings are at least an order of magnitude better in preventing corrosion of the coated H-13 core pins as compared to all the other commercially available coatings and surface treatments previously tested.
3. It is also noted that 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.
4. Multilayer coatings also 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.

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