37-L ADVANCED ENGINEERED COATINGS WITH EXTENDED DIE LIFE FOR TOOLING

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37.1 Project Overview and Industrial Relevance

Die coatings produced by physical vapor deposition (PVD) started being used in the die casting industry in the 1990s, but at that time the coatings were relatively simple in nature and tended to be used only to minimize soldering of the molten aluminum to core pins. Since then, die casters have developed more complex multi-layer coating architectures, and have also started to use the coatings for lube-free applications. However, factors that prevent the die cast aluminum alloys from sticking to the coatings are still not fully understood, and so optimum coating compositions have not yet been identified. In addition, die coating architectures need to be identified that will allow the coatings to last as long as the dies (~100,000 shots).

Coatings help prevent the aluminum castings from soldering to the die faces, allowing the amount of lubricants that are applied to the die to be reduced or even eliminated. Reducing or eliminating organic lubricants can significantly improve the quality of the die castings, allowing them to be used in new, higher performance applications. In addition, minimizing the use of lubricants will also reduce production costs arising from the purchase of the lubricants, the clean-up of effluents, and via an extension in die life, resulting in lower per-part costs. This project can lead to a significant improvement of the quality of die castings, allowing them to be used in higher performance applications, which is important for parts manufacturers, as die casting is normally the lowest cost approach to produce complex-shaped components from aluminum alloys.

37.2 Previous Work

A prior project was performed at the Colorado School of Mines (CSM) by Bo Wang [37.1]. As showed in Table 37.1, Bo Wang tested a variety of PVD coatings. The best coating identified in that project was AlCrN. Using this coating, a plant trial was performed at Mercury Castings, and it was possible to reduce the lubricant usage by 85%. The goal of this new project is to build on the research performed by Bo Wang, and achieve the complete elimination of conventional lubricants for the die casting process.

37.3 Recent Progress

37.3.1 Technical Approach

An enhanced laboratory test will be developed to test the level of adhesion between molten die casting alloys and substrate coatings. To ensure that the die casting process is accurately simulated, this test will include pressurization and/or fast filling of the molten aluminum against the substrate. A variety of coatings and coating architectures will be evaluated to determine those working layers (top layers) that exhibit no reaction, and ideally no wetting, against the molten aluminum alloy. In addition, the coating architecture (sub-surface layers) will be examined in detail, and the impact of coating architecture on coating durability will be evaluated in the laboratory. Finally, once the optimum coating architecture and working layer has been identified, these will be evaluated in a die casting production environment using in-plant trials.

37.3.2 Literature Review

As indicated above, Bo Wang identified that a working layer coating of AlCrN allowed a reduction of 85% of lubricant usage in a commercial aluminum die casting environment. One of the goals of the current project is to understand and characterize the mechanisms controlling wetting and adhesion of molten aluminum to the types of materials that would be used for coating die casting dies (normally ceramics such as AlCrN). Initially, this will involve a review of the technical literature in several related fields, including brazing, the dissolution of materials by liquid metals, and the wetting and reaction between ceramics by liquid metals. This should identify the best types of ceramic coatings to minimize wetting and soldering during die casting.

A relevant publication is a recent paper by Eustathopoulos [37.2], who reviewed factors controlling the wetting of ceramics. He noted that the wetting of a non-reactive liquid on a flat, smooth and chemically homogeneous solid surface is quantified by the value of Young's contact angle θ_Y. This is shown schematically in Figure 37.1. Wetting is characterized by a value of θ_Y less than 90º. Nonwetting is characterized by a value of θ_Y greater than 90º. The intrinsic contact angle θ_Y in a non-reactive solid-liquid system is given by the classical equations of Young and Young-Dupré (shown below, where the quantities σ_{SV} and σ_{LV} define the surface energy of the solid and liquid, respectively, and σ_{SL} the solid/liquid interface energy). Wa is the adhesion energy of the system defined as the energy required to separate reversibly a solid and a liquid having a common interface of unit area, creating two free surfaces, one solid-vapor and one liquid-vapor. Therefore, Wa is related to the surface energies of the system by $Wa = \sigma_{SV} + \sigma_{LV} - \sigma_{SL}$.

$$\cos\theta_Y = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}$$

$$\cos\theta_Y = \frac{W_a}{\sigma_{LV}} - 1$$

According to 2nd equation above, the intrinsic contact angle θ_Y in a non-reactive liquid/solid system results from two types of competing forces: (i) adhesion forces that develop between the liquid and the solid phases, expressed by the quantity of adhesion energy which promotes wetting, and (ii) cohesion forces of the liquid taken into account by the surface energy of the liquid σ_{LV} acting in the opposite direction (the cohesion energy of the liquid is equal to $2\sigma_{LV}$). Usually liquid metals are high surface energy liquids and these values reflect the high cohesion of metals due to their metallic (i.e., chemical) bonding.

Thus, according to 2nd equation above, good wetting (i.e., a contact angle of a few degrees or tens of degrees) of a liquid metal on a solid substrate can be observed if the adhesion energy is close to the cohesion energy of the liquid ($2\sigma_{LV}$). Eustathopoulos noted this is possible only if the interfacial bond is strong, i.e., chemical in nature [3]. He also noted that liquid metals wet ceramics such as carbides, nitrides or borides of transition metals because a significant part of the cohesion of these materials is provided by metallic bonds. These are the types of ceramic coatings currently used for die casting dies.

Among the solids that are not wetted by non-reactive liquid metals are the different forms of carbon, the ionocovalent oxides and the predominantly covalent ceramics with a high band gap like BN. In these non-wetting systems, adhesion is provided by weak van der Waals interactions. However, as noted later, this situation is complicated somewhat when reaction between the liquid and the substrate is considered. Eustathopoulos noted that, under the temperature and atmosphere conditions normally used in practice, liquid metals (Cu, Al, etc.) do not wet ionocovalent ceramics such as alumina, silicon carbide or graphite (see highlighted data in Table 37.2, extracted from the Eustathopoulos paper [37.2]). However, the situation may be more complex for Al-Si alloys such as A380 than for pure aluminum.

Eustathopoulos also addressed the impact of roughness on wetting. He noted that when $\theta_Y >> 90°$, wetting on high-roughness solids leads to the formation of "composite interfaces", partly solid–liquid and partly solid–vapor, (Figure 37.2a) resulting in contact angles θ well above θ_Y. In this case, even limited stress produced during cooling leads to detachment of the solidified metal from the substrate by a purely adhesive rupture. Figure 37.2a looks similar to several of the photographs from Bo Wang's thesis [37.1] for the rough AlCrN coatings.

Eustathopoulos noted that wetting in metal/metal and metal/ceramic systems is often accompanied by reactions at the solid–liquid interface. Two possible reactions can occur: (i) Wetting with formation of a new compound at the interface; (ii) Dissolutive wetting, with extensive dissolution of a solid in a liquid. Eustathopoulos noted that for many liquid metal–solid systems, the formation of a new compound is preceded by the dissolution of the solid in the liquid, which appears to be close to the behavior exhibited between liquid aluminum and un-coated H13 die steel from Bo Wang thesis [37.1].

37.4 Plans for Next Reporting Period

In the coming period, the review of the published literature will be continued to better understand the mechanisms controlling wetting of ceramics by liquid metals. In addition, another goal is to become more familiar with the die casting process and the test developed by Bo Wang [37.4], so that an improved adhesion test can be developed that better simulates the aluminum die casting process. However, preliminary experiments will be made using only a slight modification to Bo Wang's test, to allow the current author to become familiar with the pros and cons of this test. Results will be presented at the next meeting from this initial testing.

37.5 References

[37.1] Bo Wang, An Investigation of the Adhesion Behavior of Aluminum on Various PVD Coatings Applied to H13 Tool Steel to Minimize or Eliminate Lubrication During High Pressure Die Casting, PhD thesis, CSM, 2016

[37.2] Nicolas Eustathopoulos, Wetting by Liquid Metals—Application in Materials Processing: The Contribution of the Grenoble Group, Metals 5, 2015, 350-370

[37.3] D. Chatain, L. Coudurier and N. Eustathopoulos, Wetting and interfacial bonding in ionocovalent oxide-liquid metal systems, Revue Phys. Appl. 23, 1988, 1055-1064

[37.4] Bo Wang, Gerald R. Bourne, Andras L. Korenyi-Both, Alex K. Monroe, Stephen P. Midson, Michael J. Kaufman, Method to evaluate the adhesion behavior of aluminum-based alloys on various materials and coatings for lube-free die casting, Journal of Materials Processing Technology, 237, 2016, 386–393

37.6 Figures and Tables

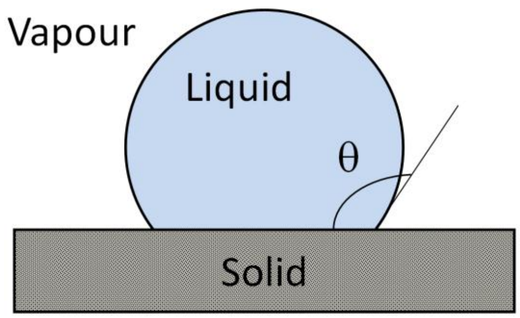

Figure 37-L.1: Definition of the equilibrium contact angle θ. For a flat, smooth and chemically homogeneous solid surface, θ is the Young contact angle θ_Y. [37.2]

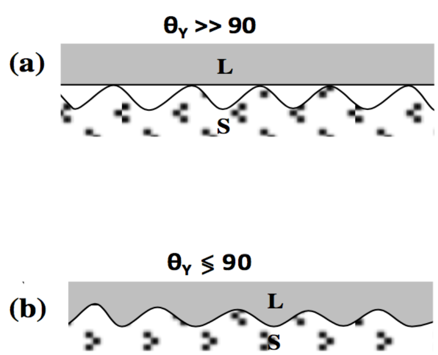

Figure 37.2. Microscopic configuration at solid/liquid interfaces: (a) For θY >> 90°, at microscopic scale, the liquid contacts the rough surface of the solid only at a few points. During cooling the solidified liquid detaches spontaneously from the solid; (b) For θY values lower than 90° or higher, but close to this value, an intimate contact exists at any point of the interface. [37.2]

Table 37.1 –The aluminum adhesion test results of one bare and twelve hard-coated H13 tool steel coupons along with the information on surface treatment, coating method, coating composition and thickness. [37.1]

#	Material	Supplier	Method & Treatment	Composition	Thickness [μm]	Breaking Strength [MPa]
1	AlCrN	1	CAE	$Al_{0.67}Cr_{0.33}N_x$	1.7	0
2	AlTiN	2	CAE	$Al_{0.68}Ti_{0.32}N_x$	1.5	0
3	CrWN	2	Nitriding + CAE	$Cr_{0.97}W_{0.03}N_x$	6.7	0
4	AlTiN	3	CAE	$Al_{0.62}Ti_{0.38}N_x$	3.3	0*
12a	AlCrN	5	Nitriding + CAE	—	—	0*
5	TiAlN	3	CAE	$Ti_{0.56}Al_{0.44}N_x$	1.8	0.01
12b	AlCrN	5	CAE	—	—	0.04
6	CrN	4	CAE + Fine Polish	CrN_x	4.4	0.07
7	H13	—	—	—	—	0.12
8	Cr	CSM	MS	Cr	2.2	0.12
9	CrWN	4	CAE + Fine Polish	$Cr_{0.95}W_{0.05}N_x$	4.2	0.26
10	CrN	5	Filtered CAE	CrN_x	5.0	0.78
11	TiN	CSM	MS	TiN_x	0.6	0.84
12	AlCrN	5	CAE + Fine Polish	$Cr_{0.54}Al_{0.46}N_x$	5.1	1.30
13	TiB_2	6	MS	TiB_x	1.5	2.54

CAE — cathodic arc evaporation
MS — magnetron sputtering
*— sample broke during handling
12a and 12b — same coating as #12 AlCrN, but received and measured later

Table 37.2: Wetting of different types of solids by non-reactive liquid metals at temperatures close to the metal melting point. The yellow highlight is provided by the current author [37.2]

Type of substrate	Type of interaction	θ (degrees)	Examples
Solid metals	Strong (chemical)	θ << 90°	Cu/Mo: 10°–30°
Semiconductors			Sn/Ge: 40°; Si/SiC: 35°–45°
Ceramics with a partially metallic character			Cu/WC: 20°; Au/ZrB_2: 25°
Carbon materials	Weak (physical)	θ >> 90°	Au/C: 120°–135°
Ionocovalent ceramics			Ag/Al_2O_3, Cu/SiO_2: 120°–140°; Au/BN: 135°–150°
Ionocovalent oxides	Moderate (chemical)	θ ≈ 90°	(Ag+O)/Al_2O_3; Al/Al_2O_3