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

by
Bo Wang
A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

Golden, Colorado
Date ____________

Signed: _______________________
Bo Wang

Approved: _______________________
Dr. Michael J. Kaufman
Thesis Advisor

Approved: _______________________
Dr. Gerald R. Bourne
Thesis Advisor

Golden, Colorado
Date ____________

Approved: _______________________
Dr. Angus Rockett
Professor and Head
Department of Metallurgical and Materials Engineering
ABSTRACT

The development of hard coating compositions and architectures that reduce or eliminate the need to lubricate die casting dies, core pins and inserts during high pressure die casting has been investigated in detail. Initially, two conventional methods for determining wetting and adhesion properties were examined, namely, the dipping test and the sessile drop test. It is shown that neither of these tests generated reliable wetting/adhesion results. For the dipping test, the aluminum adhesion to uncoated steel pins was strongly influenced by the physical shrinkage of the aluminum alloy upon solidification and cooling. For the sessile drop tests, the contact angle could not be measured accurately due to the tenacious oxide scale on the liquid aluminum surface, which prevents the aluminum from spreading and wetting the substrates; this was the case regardless of the environment (inert gas or high vacuum) used.

Based on the ineffectiveness of these conventional tests, a new test, referred to as the aluminum adhesion test (AAT), was developed with the goal of quantitatively measuring the aluminum adhesion to various uncoated and PVD-coated H13 steel substrates. The coatings that were tested using the AAT were divided into four groups: (1) those that had no adhesion strength (e.g., AlCrN, AlTiN and CrWN), (2) reactive metals (e.g. chromium) that either dissolve into the liquid aluminum or react to form intermetallics, (3) those with surface properties that result in nanoscale mechanical interlocking that result in the highest aluminum adhesion (e.g., TiB₂), and (4) those with intermediate adhesion strengths. This latter group includes most of the ceramic coatings having dense microstructures, which, although chemically inert, exhibit a range of adhesion strengths.

It was shown that, for all of the non-sticking coatings studied, the AlCrN coating appeared to be the best candidate because of its oxidation resistance at and above typical die casting temperatures. Consequently, the sticking behavior of various AlCrN coatings was examined as a function of coating chemistry (Al/Cr ratio), surface oxide layer, and surface roughness. It is shown that the Al/Cr ratio is less important than surface roughness/topography. Finally, in-plant die casting trials were conducted on the optimized AlCrN coatings and the results of these trials will be described in some detail.
ACKNOWLEDGEMENTS

I would like to express my deep appreciation to my advisors Dr. Michael Kaufman and Dr. Gerald Bourne for their support, guidance and critical advice through the research work. I felt lucky to have them as advisors, and I learned a lot about physical metallurgy and advanced electron microscopy techniques from them. The endless questions from Dr. Kaufman inspired and motivated me to study harder to better understand fundamental knowledge of materials science. I would also thank to my thesis committee members: Dr. Steve Midson, Andy Korenyi-Both, Dr. David Olson, and Dr. Graham Mustoe. I cannot imagine how I could have completed my Ph.D. without their valuable advice and support. I would also like to thank Dr. Robert Schulz and Sylvio Savoie from THE ALUMINIUM RESEARCH CENTRE – REGAL, Canada, for their help with the sessile drop test experiments. In addition, I would like to thank Nathan Worts, Dr. Erica Block and Dr. Jeff Squier for their help with the femtosecond laser work. Finally, I would like also thank to my two industrial mentors Steve Udvardy (NADCA) and Paul Rudnik (Plansee) and all of the companies and individuals for providing me the materials and coatings.

All the work in this thesis was performed through the Center for Advanced Non-Ferrous Alloys (CANFSA) and the Advanced Coatings and Surface Engineering Laboratory (ACSEL) in the Department of Metallurgical & Materials Engineering (MME) at Colorado School of Mines (CSM). I am grateful to all of the faculty, staff and fellow students at for their friendship and support.

The financial support of American Metal Casting Consortium’s (AMC) Casting Solutions for Readiness (CSR) program is also acknowledged. CSR is sponsored by the Defense Logistics Agency (DLA) Troop Support, Philadelphia, PA and the DLA Research & Development (R&D) Office, Ft. Belvoir, VA.

Many thanks to the Li Foundation for the fellowship that supported my Ph.D. studies at CSM.

Finally, I would like to express my deepest appreciation to my loving family and my wife Rongrong Wei for their solid support, encouragement and love.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................... iii

ACKNOWLEDGEMENT ......................................................................................................... iv

LIST OF TABLES .................................................................................................................. viii

LIST OF FIGURES ................................................................................................................. ix

CHAPTER 1: INTRODUCTION ........................................................................................................ 1
  1.1 Motivation ......................................................................................................................... 1
  1.2 Hypothesis ......................................................................................................................... 1

CHAPTER 2: LITERATURE REVIEW ........................................................................................... 3
  2.1 High Pressure Die Casting ............................................................................................... 3
  2.2 Casting Alloys and Die Materials ..................................................................................... 5
  2.3 Die Failure Modes ............................................................................................................ 7
  2.4 Surface Engineering for Die Protection .......................................................................... 9
  2.5 Die Coating Methods ...................................................................................................... 10
    2.5.1 Thermo-Reactice Diffusion (TRD) ............................................................................. 10
    2.5.2 Chemical Vapor Deposition (CVD) .......................................................................... 11
    2.5.3 Physical Vapor Deposition (PVD) ............................................................................ 11
  2.6 Structure Zone Diagram for PVD Coatings ..................................................................... 17
  2.7 Growth Defects in PVD Coatings .................................................................................. 22
  2.8 Failure Modes of Die Coatings ...................................................................................... 24
  2.9 Wettability and Adhesion ............................................................................................... 25
  2.10 Review of Past Work ..................................................................................................... 28
    2.10.1 Methods for Wettability/Adhesion Evaluation ......................................................... 28
    2.10.2 Development of Die Coatings .................................................................................. 30

CHAPTER 3: EXPERIMENTAL PROCEDURES ......................................................................... 32
  3.1 Dipping Test ...................................................................................................................... 32
  3.2 Sessile Drop Test ............................................................................................................. 33
  3.3 Liquid Adhesion Test ...................................................................................................... 34
    3.3.1 Equipment and Materials ......................................................................................... 36
    3.3.2 Test Procedures ...................................................................................................... 38
  3.4 Coating Deposition ........................................................................................................ 42
  3.5 Surface Texture Treatment Using Femtosecond Laser ..................................................... 44
  3.6 Characterization Technologies ....................................................................................... 45
### LIST OF TABLES

Table 2.1 – Typical times for aluminum high pressure die casting [7] ................................................. 4
Table 2.2 – Comparison of properties of hard coatings produced by conventional magnetron sputtering (MS) and cathodic arc evaporation (CAE) ........................................................................ 12
Table 3.1 – Powder materials used for the dipping test ........................................................................ 32
Table 3.2 – Composition of the two A380 aluminum alloys used for the aluminum adhesion tests ........................................................................................................................................ 37
Table 3.3 – Composition of H13 tool steel used for aluminum adhesion tests .................................. 37
Table 3.4 – Information about the thirteen types of specimens used for the aluminum adhesion tests ................................................................................................................................. 38
Table 3.5 – Deposition parameters for the #8 Cr and #11 TiN coatings using MPP .......................... 43
Table 3.6 – Deposition parameters for the single/compound-sputtered CrN and AlCrN coatings using MPP ........................................................................................................................ 43
Table 3.7 – Data for the Al$_{60}$Cr$_{40}$N coating measured by X-ray diffraction method (MA60C40_1) ................................................................................................................................. 46
Table 6.1 – 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 ................................................................. 61
Table 7.1 – Comparison of the AlCrN coatings #1 and #12 provided by Supplier 1 and Supplier 5 ........................................................................................................................................ 86
Table 7.2 – Surface roughness of the samples tested by aluminum adhesion test .............................. 92
Table 7.3 – Deposition conditions and properties of AlCrN coatings prepared by compound sputtering using the MPP power supply on various AlCr alloy targets .................................................................................. 94
Table 7.4 – The Al/(Al+Cr) ratios on coating surface and thickness of oxygen-rich layers for various treated the #1 AlCrN coating coated-coupons along with their aluminum adhesion conditions ......................................................................................... 101
Table 8.1 – Composition of the A362 aluminum alloy used for the in-plant trials [wt.%] ............... 121
LIST OF FIGURES

Figure 2.1  The typical process chain for a high pressure die casting cycle [5]................................. 3
Figure 2.2  Schematic illustration of high pressure die casting: (a) melt pouring and (b) cavity filled and casting produced [4]........................................................................................................ 4
Figure 2.3  Photograph of a typical lube spray for aluminum high pressure die casting ................. 5
Figure 2.4  Al-Si binary phase diagram (partial composition range) [9].......................................... 5
Figure 2.5  Soldering sample in die casting: (a) a soldered core pin showing cast alloy build-up and (b) a cross section showing the presence of a soldering intermetallic layer. [4].............................................................................. 8
Figure 2.6  Typical appearance of erosion on H13 tool steel pin surfaces [12]. .............................. 8
Figure 2.7  A comparison of the magnetic configuration and plasma confinement in conventional, unbalanced and dual-magnetron closed-field systems [43]..................... 13
Figure 2.8  A comparison of duty cycle as function of peak power density of DCMS, PDCMMS, MPPMS and HiPIMS [55]................................................................. 15
Figure 2.9  Classic 90° duct filter developed by Aksenov and co-workers [59] consisting of: 1-cathodic arc source, 2-plasma duct, 3-insulator, 4-coils, 5-soildenoid, 6-vacuum chamber, 7-insulators, and 8-substrate. ........................................................................ 16
Figure 2.10  Top view of linear filtered arc system developed by Gorokhovsky [57]: two direct non-filtered arc sources (a and b), two filtered sources (d and e), and coils (f and g). .................................................................................. 16
Figure 2.11  Surface conditions of the TiN coatings deposited by arc techniques (a) with filter and (b) without filter [58]............................................................................................................. 17
Figure 2.12  Structure Zone Diagram developed by Movchan and Demchishin (MD model) for the evaporation coatings at various substrate temperatures [63]......................... 18
Figure 2.13  SEM fracture cross sections and surface views of chromium, copper and aluminum coatings (2A-2F, and 2G-2I) deposited at various substrate temperatures and argon pressures used to develop the Structure Zone Diagram of Thornton as seen in Figure 2.15 [60]...................................................................................... 19
Figure 2.14  SEM fracture cross sections and surface views of aluminum, copper and molybdenum coatings (3A-3F) deposited at various substrate temperatures and argon pressures used to develop the Structure Zone Diagram of Thornton as seen in Figure 2.15 [60]...................................................................................... 20
Figure 2.15  Structure Zone Diagram (SZD) developed by Thornton for metal films sputtered at various substrate temperatures and argon pressures [60]........................................ 20
Figure 2.16  Structure Zone Diagram developed by Anders applicable to energetic deposition as a function of the generalized homologous temperature, the normalized kinetic energy flux, and the net film thickness [64].......................................................... 21
Figure 2.17  Types of nodular and flake growth defects in hard coatings prepared by physical vapor deposition (PVD) [68]................................................................................................. 23
Figure 2.18  Types of cavity growth defects in hard coatings prepared by physical vapor deposition (PVD) [68]................................................................. 23
Figure 2.19  Sketched steps for soldering process on coated core pins [21]................................................. 24
Figure 2.20  Photograph of negative draft or undercut formed on a solder core pin [21]......................... 25
Figure 2.21  Liquid droplets on solid surface: Young Model (left), Wenzel state (middle), and Cassie–Baxter state (right) [78]. ......................................................... 26
Figure 2.22  SEM micrographs of the laser textured Type 316L stainless steel surfaces and corresponding photographs of 3 μL water droplets on surfaces [81]. ................................. 27
Figure 2.23  Ejection test developed by Terek: test pins, schematic diagram and major results [91] .................................................................................................................. 30
Figure 2.24  Optimized die coating architecture proposed by Moore and co-workers [14]................. 31
Figure 3.1  Schematic diagram of the sessile drop equipment at the Colorado School of Mines. ...................................................................................................................... 33
Figure 3.2  Schematic diagrams and photographs of the sessile drop equipment with a higher vacuum capability: drawings of (a) the apparatus and (b) the sample holder, and the apparatus photographs (c-d) .................................................................................. 34
Figure 3.3  Schematic of the aluminum adhesion test consisting of six steps: (1-2) tube placement on coupon surface, (3) liquid alloy pouring and impingement, (4) alloy solidification, (5) tube removal and (6) tensile test ......................................................... 35
Figure 3.4  Photographs of the small amount of A380 aluminum alloy and its oxide scales remained in the alumina crucible after the majority of the alloy was poured out during the aluminum adhesion test: (a) alloy left in the crucible, and (b) alloy removal from the crucible. ........................................................................................................ 35
Figure 3.5  Boron nitride tube: (a) solid 3D drawing, (b) transparent 3D drawing, (c) 2D drawing, and (d) machined tube photograph ........................................................................... 36
Figure 3.6  Drill bushing: (a) photographs with special labels, (b-e) steps for drill bushing use .................................................................................................................. 39
Figure 3.7  Pin (top left), top fixture (top right) and bottom fixture (bottom middle): (a) solid 3D drawing, (b) transparent 3D drawing, and (c) the 2D drawing ......................... 40
Figure 3.8  Schematic drawing (a) and photograph (b) of the novel set of pin fixtures ........................................... 40
Figure 3.9  Photographs of the A380 aluminum alloy adhered bare H13 tool steel coupon: (a) before and (b) after the mechanic test ................................................................. 41
Figure 3.10  Temperature vs. time curves for the aluminum adhesion test on an uncoated H13 coupon: (a) entire test, (b) greater detail at the A380 pouring stage, and (c) greater detail at the 15 minute holding stage after pouring ........................................................................ 42
Figure 3.11  Schematic diagrams of laser surface texture on the polished H13 tool steel coupon with a total of nine of the 5 mm × 5 mm patterns. The inset indicated each pass of the laser probe (solid arrows), and the total 3 passes scanning from the top to the bottom, then to the top again and back to the bottom (short dashed-line arrows) ........................................................................................................ 44
Figure 3.12  Plot of lattice parameters as a function of sin²γ for the Al₆₀Cr₄₀N coating measured by X-ray diffraction (MA60C40_1) ........................................................................... 47
Figure 3.13  Drawings of the Calo test after a ball crater is formed on a single-layer coating: (a) top-view, and (b) cross-section view. ........................................................... 50

Figure 3.14  The 3D plot of the #1 AlCrN coating characterized by optical profilometry. ........... 50

Figure 3.15  Adhesion strength quality (HF 1-HF 6) based on the delamination and crack network after Rockwell C indentation test [99]. .................................................. 51

Figure 4.1  Photographs of the uncoated steel pins dipped in the A380 aluminum alloy for one minute: (a) before the test, (b) after the test and (c) after KOH cleaning; and sixty minutes: (d) before the test, (b) after the test and (f) after KOH cleaning ......... 53

Figure 4.2  Photographs of the two steel pins painted with powder materials before (a) and after (b) the dipping test. .................................................................................. 53

Figure 4.3  Schematic diagram of aluminum adhesion showing three possible types of behavior for uncoated steel pins: (I) no pits or chemical reactions, (II) pits, and (III) chemical reaction with formation of continuous reaction layer (soldering)........... 54

Figure 4.4  Schematic diagram of the two modes for a steel pin painted with powder materials before and after the dipping test: (I) powder material is inert to liquid aluminum; and (II) powder material is reactive with liquid aluminum. ...................... 55

Figure 5.1  Sessile drop tests of a small A380 aluminum alloy cube on a Type 304 stainless steel coupon at various temperatures: (a) 550°C, (b) 750°C, (c) 800°C, (d) 950°C, (e) 1050°C and (f) 1200°C. ........................................................................ 56

Figure 5.2  Sessile drop tests of a small piece of aluminum on polished H13 tool steel coupon at various temperatures: 460°C, 650°C, 700°C, 750°C, 800°C, and 850°C (measured contact angle is on the image right) ............................................................. 57

Figure 5.3  Schematic diagram of the evolution of oxide scale on the aluminum alloy surface in the sessile drop equipment. Note: at elevated temperatures, either hemi-spherical alloy surface is obtained or faceted liquid alloy or depending on the thickness of oxide scale on liquid alloy surface. ............................................. 59

Figure 6.1  Photographs of the bare H13 tool steel coupon with adhered A380 aluminum alloy (a) before and (b) after the mechanical test, and (c) the load as function of time curves. ........................................................................... 62

Figure 6.2  Photograph of the cold mount sample (a) and (b)-(f) cross-sectional SEM backscattered electron images (BEIs) of the interface between the A380 aluminum alloy and a bare H13 tool steel coupon ........................................... 62

Figure 6.3  Cross-sectional SEM backscattered electron images (BEIs) of the interface between the A380 aluminum alloy and a bare H13 tool steel coupon and the EDS mapping at the two interfaces between: (a) A380 aluminum alloy and the composite layer, and (b) dense layer and H13 tool steel substrate. ................. 64

Figure 6.4  Cross-sectional SEM backscattered electron image (BSE) and bright-field TEM image of the interface between the A380 alloy and a bare H13 coupon and the corresponding electron diffraction images of the locations of a, b and c. (red rectangle area is the FIB lift-out area for the TEM foil) .................................................. 66

Figure 6.5  Binary Al-Fe equilibrium phase diagram [104]. ...................................................... 67

Figure 6.6  Backscattered electron (BSE) image of the crack zone at the interface between the A380 aluminum alloy and the bare H13 tool steel coupon and schematic diagram of the phase distribution at the interface. .............................................. 67
Figure 6.7  SEM image of fractured cross-section of the as-deposited chromium coating (a) and light optical microscopic image of the interface between the adhered A380 aluminum alloy and the reacted chromium coated H13 tool steel substrate (b). 68

Figure 6.8  Binary Al-Cr equilibrium phase diagram [104] ............................................................... 69

Figure 6.9  SEM image of the chromium-coated H13/A380 interface (a) along with the EDS maps (b) and line scan data (c). The red arrow in the SEM image indicates where the line scan was taken and the scan direction. ................................................................. 70

Figure 6.10  Photographs of the #1 AlCrN-coated H13 tool steel coupon provided by Supplier 1 for the aluminum adhesion test: (a) as-received state before the test, (b) and (c) after the test ........................................................................................................ 70

Figure 6.11  SEM image of the fractured section of the #1 AlCrN coating and the EDS elemental maps ......................................................................................................................... 71

Figure 6.12  Optical microscope images of the pattern on the as-deposited #1 AlCrN coating after the Calo grinding test: (a) low magnification (5×) and (b) high magnification (50×) ......................................................................................................................... 71

Figure 6.13  X-ray diffraction patterns of the bare H13 tool steel and the #1 AlCrN coating before and after the aluminum adhesion test (AAT) .............................................................................................................................. 72

Figure 6.14  X-ray diffraction patterns of the as-deposited #1 AlCrN coatings supplied by Supplier 1 and the same coatings after annealing at different temperatures ........................................................................ 73

Figure 6.15  SEM images of the plan-view of the #1 AlCrN coatings supplied by Supplier 1: (a) as-deposited, and after annealed at (b) 800°C , (c) 900°C and (d) 1000°C. 74

Figure 6.16  Pin-on-disk results for the #1 AlCrN coatings supplied by Supplier 1 using WC and Si₃N₄ balls: (a) coefficient of friction as a function of number of cycles, and (b) wear rate. ................................................................................................................... 74

Figure 6.17  Photograph of the #13 TiB₂-coated coupon after aluminum adhesion test ............ 75

Figure 6.18  Cross-sectional SEM images of the TiB₂ coated H13 tool steel coupon: (a) as-deposited coating, and (b) area exposed to ambient atmosphere at 700° C. ...... 75

Figure 6.19  Cross-sectional SEM images of the interface between A380 aluminum alloy and TiB₂ coating at the sticking area of H13 tool steel coupon prepared by cross-section polisher: (a) low magnification image, (b) high magnification, and (c) enlarged image of the interface ........................................................................ 76

Figure 6.20  SEM image of the sticking TiB₂ sample foil prepared by FIB (a), and bright-field TEM of the alloy-TiB₂ interface (b).................................................................................................................. 77

Figure 6.21  EDS spectrum from Particle 2 in Figure 6.20 .......................................................... 77

Figure 6.22  Bright-field TEM image of the A380 TiB₂ interface (a), and microdiffraction patterns (b) from four different zone axes, namely, [011], [121], [112] and [031] of particle 1, and three different zone axes: [001], [013] and [112] from particle 2 ......................................................................................................................... 78

Figure 6.23  Bright-field TEM images of the A380-TiB₂ interface. Image b is from the square red box shown in image a. ................................................................................................................... 79

Figure 6.24  Bright-field TEM image of the A380-TiB₂ interface and the elemental X-ray maps of aluminum, oxygen, magnesium, titanium, boron, silicon and iron measured using EDS. .......................................................... 79
Figure 6.25 Cross sectional SEM images of the #10 CrN-coated sample at the interface with the solidified alloy at three various magnifications. .......................................................... 80

Figure 6.26 Bright-field TEM image (a and b) of the #10 CrN-coated sample provided by Supplier 5 at the interface of the solidified alloy and the coating along with the selected area electron diffraction pattern (SAED) from the twinned particle. The SAED (c) is taken from the area circled in the middle image down to zone axis of [101]. ............................................................................................................ 81

Figure 6.27 Bright-field TEM image (a) of the #10 CrN-coated sample at the interface of the solidified alloy and the coating. The microdiffraction pattern (b) was taken from one of the small particles at the interface and was indexed as a <112> zone from spinel. .................................................................................................................. 81

Figure 6.28 Bright-field TEM image and elemental x-ray maps of the interface between the A380 aluminum alloy and the coating for the #10 CrN-coating after the aluminum adhesion test (scale bar: 200 nm). ......................................................................................... 82

Figure 6.29 Elemental line scans across the aluminum alloy/coating interface of the #10 CrN-coating.................................................................................................................. 82

Figure 6.30 SEM images of the cross-section through the interface between the alloy and the AlCrN coating (Supplier 5) at a low magnification (a) and a high magnification (b) .................................................................................. 83

Figure 6.31 Bright-field TEM images of the interface between the AlCrN coating from Supplier 5 and the adhered A380 aluminum alloy at a low magnification (a) and a high magnification (b) .................................................................................. 84

Figure 6.32 Bright-field TEM image and elemental x-ray maps of the interface between the AlCrN-coated H13 steel from Supplier 5 and the A380 aluminum alloy after the AAT .............................................................................................................. 84

Figure 6.33 Elemental line scan across the interface shown in Figure 4.31 (left dark side is AlCrN coating, right light side is A380 aluminum alloy). .................................................................................. 85

Figure 7.1 Ternary Al-Cr-N equilibrium phase diagram at 1000°C [105] .......................................................................................................................... 87

Figure 7.2 SEM images of the thirteen coated samples (#1 - #13) tested using the aluminum adhesion test in (a) plan-view and (b) 45°-tilt view. .......................................................................................... 88

Figure 7.3 Cross-sectional SEM images of compound-sputtered CrN, Al_{50}Cr_{50}N, Al_{60}Cr_{40}N and Al_{70}Cr_{30}N coatings .......................................................................................... 94

Figure 7.4 Plan-view SEM images of the CrN and the AlCrN coated samples at low magnification (left) and high magnification (right). .......................................................................................... 95

Figure 7.5 Results of Rockwell C indent test on the sputtered AlCrN coatings: (a) CrN, Al_{50}Cr_{50}N, Al_{60}Cr_{40}N, and Al_{70}Cr_{30}N .................................................................................. 95

Figure 7.6 Plots of maximum breaking load and aluminum adhesion strength as function of Al/(Al+Cr) ratios for the CrN and AlCrN coated samples for the aluminum adhesion test .................................................................................. 96

Figure 7.7 Plan-view SEM images of the #1 AlCrN coating before (a) and after polishing (b) .......................................................................................................................... 97

Figure 7.8 Cross-sectional SEM images of the polished #1 AlCrN coating after the aluminum adhesion test. (a) secondary electron mode, and (b) backscattered electron mode. .................................................................................. 97
Figure 7.9  EDS mapping images of the soldering area of the polished #1 AlCrN sample after the aluminum adhesion test.................................................................98

Figure 7.10  Photographs of the polished #1 AlCrN coating on an H13 tool steel coupon: (a) as-received coupon and (b) coupon covered with tape.................................99

Figure 7.11  Photographs of the #1 AlCrN-coated H13 tool steel coupons from Supplier 1 after the aluminum adhesion test. The left halves of each coupon were polished using 6 µm diamond paste and the right halves left unpolished......................99

Figure 7.12  Breaking loads and aluminum adhesion strength of the #1 AlCrN-coated H13 tool steel coupons from Supplier 1 after the various treatments as shown in Figure 4.45.................................................................99

Figure 7.13  XPS concentration-depth profiles of aluminum, chromium, nitrogen and oxygen elements for the #1 AlCrN coatings from Supplier 1 as a function of sputter time for: (a) the unpolished side, (b) 6 µm diamond polished side, (c) the unpolished side plus thermal treatment at 700°C for 18 hour, and (d) polished side plus thermal treatment at 700°C for 18 hours.................................................................100

Figure 7.14  Light optical images of the surfaces of the samples after aluminum adhesion tests: (a) the 6 µm diamond polished side for the as-deposited sample, (b) the as-received sample, (c) the polished side plus thermal treatment at 700°C for 18 hour, and (d) the unpolished side plus thermal treatment at 700°C for 18 hours.................................................................102

Figure 7.15  SEM images of the polished side of the #1 AlCrN coating after thermally-treating at 700°C for 18 hours and aluminum adhesion tests: (a) plan-view, and (b-c) 45° tilt view and (d) the corresponding as-deposited side (45° tilt view)............102

Figure 7.16  Light optical micrographs (LOMs) and SEM images of the as-deposited #1 AlCrN coating after aluminum adhesion test: (a) LOM with focus slightly above the coating, (b) LOM with focus on the coating, (c-d) SEM images of the coating at 45° tilt. .................................................................................................103

Figure 7.17  SEM image (a) and its stereographic view of the bottom alloy from the AAT on the as-deposited #1 AlCrN coating.........................................................104

Figure 7.18  SEM images of the bare H13 tool steel coupon surface textured using femtosecond laser: (a-b) plan-view, and (c-d) 45° tilt view of the sample ...............105

Figure 7.19  SEM images of the surface-textured H13 tool steel coupon after cleaning with Naval Jelly for (a-b) 5 minutes and (c-d) 30 minutes. Images of (a) and (c) are plan views, and (b) and (d) are 45° tilt views.................................................................106

Figure 7.20  Photographs of the surface-textured H13 tool steel coupon after Naval Jelly cleaning for 5 minutes before and after aluminum adhesion test (AAT): (a) sample before AAT; (b) sample after AAT prior to separating mechanically; (c) sample tested by AAT plus mechanical test; (d) bottom view of the alloy; and (e) enlarged image of the alloy contact on the sample surface........................................107

Figure 7.21  Photographs of the surface-textured H13 tool steel coupon after Naval Jelly cleaning for 30 minutes before and after aluminum adhesion test (AAT): (a) sample before AAT; (b) sample after AAT prior to separating mechanically; (c) sample tested by AAT plus mechanical test; (d) bottom view of the alloy; and (e) enlarged image of the alloy contact on the sample surface...............107
Figure 7.22  SEM images of the surface-textured H13 tool steel coupon after aluminum adhesion test: with Naval Jelly cleaning for (a-b) 5 minutes and (c-d) 30 minutes. Images of (a) and (c) are plan views, and (b) and (d) are 45° tilt views.......................................................... 108

Figure 7.23  SEM image and EDS maps on the surface of surface-textured H13 tool steel coupon after aluminum adhesion test (sample used Naval Jelly cleaning for 30 minutes).......................................................... 108

Figure 7.24  SEM images of FIB milling process for the surface-textured H13 tool steel coupon after aluminum adhesion test: (a) top-view image (the rectangle with red dashed lines indicates the milling area, the milling direction is labeled as the red arrow), and (b-f) 52° tilt image of the continuous FIB milling process. ....... 109

Figure 7.25  SEM image and EDS maps of the surface-textured H13 tool steel coupon after aluminum adhesion test. EDS point scan at the yellow mark in the SEM image. ..... 110

Figure 7.26  SEM images of the AlCrN coating deposited onto: (a) the polished sample at 0° tilt, (b) the polished sample at 45° tilt, (c) the laser-textured sample at 0° tilt, and (d) the laser-textured sample at 45° tilt........................... 112

Figure 7.27  X-ray diffraction patterns for the polished (smooth) and laser-textured H13 tool steel samples with AlCrN coating.......................................................... 112

Figure 7.28  Cross-sectional SEM images and EDS mapping of the AlCrN coating on the polished H13 tool steel coupon .......................................................... 113

Figure 7.29  FIB milling of the AlCrN coated surface-textured H13 tool steel coupon. ............. 113

Figure 7.30  SEM images and EDS mapping of the AlCrN coated surface-textured H13 tool steel coupon after FIB sectioning. .......................................................... 114

Figure 7.31  Photographs of the AlCrN-coated H13 tool steel coupons for the aluminum adhesion test: the polished sample (top images) and the laser-textured sample (bottom images) both coated with AlCrN.......................................................... 115

Figure 7.32  SEM image and EDS mapping of the fracture area of the polished H13 tool steel coupon coated with AlCrN after the aluminum adhesion test ................. 115

Figure 7.33  SEM image and EDS mapping of the fracture area of the AlCrN coated surface-textured H13 tool steel coupon after aluminum adhesion test ................. 116

Figure 7.34  SEM images of the coupon surface (a-b) and the alloy bottom (c-d) for the laser-textured sample after the aluminum adhesion test. Image (b) was taken at 45° tilt. Image (d) was a stereo image with 7° tilt................................. 117

Figure 7.35  Schematic diagram of the alloy adhesion to the polished and femtosecond laser surface-textured H13 tool steel coupon coated with AlCrN for aluminum adhesion test.......................................................... 118

Figure 8.1  Schematic diagram of the casting product, the 4-Stroke gearcase: (a) 3D image, (b) cross-sectional image. The location of the AlCrN-coated loose insert is shown in red.......................................................... 120

Figure 8.2  Photographs of the #1 AlCrN coating coated loose die insert: before the casting trial (a-d) and after the casting trial from different views (e-h)................................. 121

Figure 8.3  The 3D model of the balance shaft housing casting............................................. 122

Figure 8.4  The 3D models of the moving (a) and fixed (b) halves of the balance shaft
housing die ........................................................................................................................................................................ 122

Figure 8.5 Photographs of the die after the casting stuck: (a) casting stuck in the die, and (b) bent core pin after the stuck casting had been extracted. ........................................ 123

Figure 8.6 Spray zone for the casting produced using a one second spray time. .................... 124
1.1 Motivation

High pressure aluminum die casting is a manufacturing process that is used to efficiently produce a number of complex-shape aluminum alloy products in a short time. During die casting, chemical reactions (mainly in the form of Al-Fe-Si based intermetallics) frequently occur between the aluminum alloy and the H13 steel dies [1-3]; this does not only degrades the dies and pins, but also causes severe sticking problems. To avoid detrimental soldering, a liquid lubricant is sprayed on the die surface prior to each shot for the purposes of cooling the dies and core pins, reducing the wear, and enabling the casting release. In practice, a large amount of liquid lubricant is used before each shot to prevent such soldering. A recent survey of a large die casting plant in Indiana revealed that a single casting plant annually purchased 29,000 gallons of concentrated die lubricant. Lube spray not only increases the cost of producing castings and adds time to the casting cycle, but also produces effluents that have environmental ramifications. The concentrated lubricant was diluted by water with the ratio of 1:70 prior to spray, and so more than two million gallons of water-based diluted die lubricant was produced. A huge amount of hot steam was generated for each shot due to the lube spray, increasing the difficulties of housekeeping and causing environment issues. Additionally, lube spray affects the casting quality as well. Thermal fatigue failure (also called heat checking) of the dies was mainly caused by the rapid cycles of alternatively heating by the die from molten liquid alloy injection and cooling the die with the lube spray. The thermal cracks formed on the die surfaces not only degrade the surface finish of the casting, but also shorten the die life by acceleration of soldering reactions of the cracks. In some cases, excess lube spray also accelerated the formation of defects such as gas porosity in the casting component degrading the product quality. Therefore, the concept of lube-free die casting has been of interest proposed for a long time. The primary goal of this study is to develop advanced coatings for die casting dies that are not adhered by the aluminum alloy with the long-term objective of circumventing the need to use liquid-based organic lubricants prior to each shot.

1.2 Hypothesis

If soldering of aluminum die castings is related to the reactivity between the liquid aluminum casting alloy and the composition and morphology of the external layer on the die surfaces, then minimizing the contact area and reducing the reactivity between the liquid alloy and the die surface will
minimize the tendency for soldering. Based on this hypothesis, five fundamental questions are raised in this study as follows:

1. Can a certain laboratory test be developed and used to evaluate aluminum adhesion to candidate coatings?
2. What is the effect of coating composition on the aluminum adhesion behavior?
3. How does the oxide layer on the coating surface affect the aluminum adhesion behavior?
4. What is the influence of surface topography on the aluminum adhesion behavior?
CHAPTER 2: LITERATURE REVIEW

In this literature review high pressure die casting, die casting failure modes, surface engineering for die surface protection, die coating methods, coating growth and defects, die coating failure modes, wettability and adhesion, and prior work on die coatings are described.

2.1 High Pressure Die Casting

High pressure die casting (HPDC) is a net-shape manufacturing process that has been widely employed in many fields (such as automotive, aerospace, consumer appliances and hand tools) due to its high productivity and low cost [4-6]. More than half of the light metal casting products in the world are produced by HPDC [5]. For HPDC of aluminum, cold-chamber die casting machines are always used. A typical process chain for a cold-chamber high pressure die casting cycle is shown in Figure 2.1, and consists of steps of lube spraying, die blowing out, die closing, melt dosing, die mold filling, melt solidification, die opening, and casting removal [5].

![Figure 2.1 The typical process chain for a high pressure die casting cycle [5]](image-url)
As shown in Figure 2.2, a certain amount of liquid aluminum alloy is generally ladled from a holding furnace at a desirable temperature and then poured into a shot sleeve, followed by a quick movement of the plunger pushing the liquid metal through the runner and gate into the die cavity [4]. Bonollo et al. [5] reported that the metal filling velocities were in the range of 30-60 m/s. Meanwhile, large intensification pressure (up to ~120 MPa) applied to the plunger helps minimize shrinkage and decrease the size of any gas holes.

Figure 2.2  Schematic illustration of high pressure die casting: (a) melt pouring and (b) cavity filled and casting produced [4]

Myers [7] documented the typical cycle times for aluminum HPDC as listed in Table 2.1. The total time for a cycle was 42 seconds during which time the alloy is in contact with the die for only 13 seconds whereas the time used for lubricant spraying and blowing off of the die (9.5+5.5=15 seconds) occupies almost 36 percent of the whole cycle. Hence, lube spraying significantly lowers the efficiency of the die casting process.

Table 2.1 – Typical times for aluminum high pressure die casting [7]

<table>
<thead>
<tr>
<th>Step</th>
<th>Time [second]</th>
<th>Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Cycle start (Die closed)</td>
</tr>
<tr>
<td>2</td>
<td>2.25</td>
<td>Pour metal</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>Make shot; Piston starts to stop</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>Dwell time (Metal solidification)</td>
</tr>
<tr>
<td>5</td>
<td>4.25</td>
<td>Die open; Signal to full ejection</td>
</tr>
<tr>
<td>6</td>
<td>5.5</td>
<td>Extract casting; Verify all parts are present</td>
</tr>
<tr>
<td>7</td>
<td>9.5</td>
<td>Spray time; Signal start to complete sweep</td>
</tr>
<tr>
<td>8</td>
<td>5.5</td>
<td>Blow off time</td>
</tr>
<tr>
<td>9</td>
<td>4.0</td>
<td>Die close; Signal to close until fully locked (Start of next cycle)</td>
</tr>
</tbody>
</table>
Figure 2.3 shows a typical lube spray at a die casting plant. The high pressure die casting process consisted of ~20 seconds lube spray for each cycle even longer than what Myers [7] documented in Table 2.1. A large amount of hot steam is also generated during the spraying procedure causing difficulties for die casting engineers in housekeeping and generates safety and environment concerns.

![Figure 2.3 Photograph of a typical lube spray for aluminum high pressure die casting](image)

### 2.2 Casting Alloys and Die Materials

Al-Si alloys comprise more than 90 percent of all aluminum castings [8]. The silicon content in these alloys varies from 4 to 22 percent. The silicon content is selected based on its effects on both fluidity and mechanical properties. The binary Al-Si phase diagram at the aluminum side is shown in Figure 2.4 [9], and the casting alloys can be subdivided into three types based on the silicon content: the hypoeutectic aluminum alloys with 4–9 percent silicon, the eutectic alloys containing 10-13 percent silicon, and the hypereutectic alloys (silicon over 14 percent). Hypoeutectic alloys are the most commonly used for commercial aluminum die casting. In this research project, hypoeutectic A380 alloy aluminum consisting of 7.5–9.5 percent silicon was chosen. The hypoeutectic alloys microstructures consist of α-Al dendrites as the primary phase and a eutectic mixture of Al + Si in the interdendritic regions [10]. Other elements in aluminum die casting alloys including Cu, Zn, Mg, Fe, Mn and Cr. Copper is used for achieving the highest strength levels in the as-cast condition, and the maximum solubility of copper in the solid aluminum is
slightly higher than 4 percent [8]. Zinc can dissolve in solid aluminum up to the concentration of 12 percent. The concentration of magnesium varies from 0.2 to 0.6 percent. Finally, iron, manganese and chromium are common impurities in the casting alloys and result in Al-Fe-Si constituent phases.

![Al-Si binary phase diagram](image)

Figure 2.4  Al-Si binary phase diagram (partial composition range) [9]

Due to the high metal injection velocities and the large thermal gradients (up to 1000°C/cm) characteristic of the die casting process, materials for the casting dies need to be carefully chosen [7]. The most widely used materials for die casting dies are the hot worked tool steels, such as H11 and H13. In this research project, H13 tool steel is used. The H13 tool steel is a medium-carbon chromium-molybdenum-vanadium alloy (composition shown later in Table 3.3), exhibiting high levels of hot strength, tempering resistance, creep strength and ductility, as well as low thermal expansion and high thermal conductivity [11]. In the past, many attempts have been made to develop new die materials having higher resistance to thermal fatigue, soldering, and washout [12]. These new die materials include but are not limited to some copper-base alloys, nickel-base alloys, titanium-base alloys, molybdenum-base alloys, tungsten-base alloys, yttrium-base alloys and niobium alloys. Zhu et al. [12] found that the core pins made
of the tungsten-base alloy Anviloy1150 showed better soldering resistance, washout resistance and thermal fatigue than those made of H13 tool steel.

2.3 Die Failure Modes

High-pressure aluminum die casting occurs in a severe thermo-chemical–mechanical environment because of the combination of high reactivity of the liquid aluminum alloy, high metal injection speeds, high holding pressures, and rapid thermal cycles of heating and cooling [5]. Die casting dies, core pins and inserts frequently degrade and fail. There are three main failure modes observed for the die casting die [4, 12-16]: soldering (or corrosion), erosion and heat checking.

Soldering is defined as the adhesion of the casting alloy to the die or core pin surfaces and the subsequent buildup of the aluminum alloy on the surface [12]. Soldering results in sticking during the ejection of the casting from the die. The mechanism of soldering involves both mechanical interlocking and chemical reactions [17, 18]. Mechanical interlocking is the adhesion of the alloy to the die surface defects through the presence of physical bonds at low temperatures. These surface defects are typically machining marks, cracks, pits and holes. At high temperatures chemical reactions occur between the die steel and the casting alloy with formation of a series of Al-Fe-Si based intermetallic phases that essentially join the alloy and dies together. These intermetallic phases show lower toughness and erosion resistance than the H13 die steel. The high hardesses and brittle nature of these intermetallics cause increased spallation tendencies and die degradation until failure [13, 18, 19]. As a result, soldering decreases the productivity and increases the cost of manufacturing parts [17, 20-22]. The mechanisms of formation and growth of the soldering layers have been studied for the past decades. Sometimes, corrosion is also mentioned along with soldering. But corrosion is considered to be the process of chemical dissolution of the steel into the melt [23]. Shankar et al. [24] found that the formation of intermetallic phases occurs by a diffusion-controlled reaction and that the growth of these intermetallics follow parabolic kinetics. The iron and the aluminum atoms diffused into each other resulting in the formation of a series of intermetallic phases at the interface. Holz [25] pointed out two conditions of high pressure die casting that promote die soldering: high filling velocity and hot spots on die surface areas (last locations to solidify). The HPDC experiments of Chen [4] indicated that hot spots were a key factor in die soldering rather than melt impingement. The soldering layers found on die cast aluminum samples are similar to ones found during dipping tests. The dipping test essentially consists of immersing of samples into an aluminum melt for certain periods. There have been a number of soldering studies using the dipping test [4]. Figure 2.5 shows a typical surface feature of a core pin after HPDC
covered with solder. Metallographic analysis revealed intermetallic formation at the interface between the adhered cast alloy and the tool steel [4].

Figure 2.5 Soldering sample in die casting: (a) a soldered core pin showing cast alloy build-up and (b) a cross section showing the presence of a soldering intermetallic layer. [4]

Erosion, also called washout, is considered to be the gradual physical removal of material from the die surface. It is caused by the physical impingement of the incoming liquid aluminum forced against the surface of the die. Corrosion is also mentioned in the literature as an erosive–corrosive failure mode [26]. During HPDC experiments, the areas of the die near the gate or those having complex shapes, such as ribs, cores, pins and corners tend to lose their dimensional tolerances for the parts being cast [12]. Zhu et al. [12] reported a typical washout appearance on a hard-H13 tool steel pin after fifty castings (see Figure 2.6).

Figure 2.6 Typical appearance of erosion on H13 tool steel pin surfaces [12].
Heat checking, also called thermal fatigue cracking, is the third most common die failure mode. Over 80 percent of dies fail via this failure mechanism [11, 27]. It is caused by alternately heating and cooling the die surface during the casting process. The large thermal gradients on the die surfaces alternatively generate high compressive stresses during heating upon injection of the melt, and a high tensile stress upon lube spraying, and can result in cracks on the die surfaces. Heat checking not only lowers the surface quality of the cast parts, but also accelerates soldering and erosion and ultimately causes die failure [15, 16, 28]. The density and depth of heat checking cracks increase linearly with the number of shots [11, 14-16].

2.4 Surface Engineering for Die Protection

Since the salt bath carburization process was developed in Japan in the 1960s for die casting die protection, surface engineering techniques consisting of surface treatments, coatings and duplex treatments have been applied to improve die performance and reduce die failures [1, 4, 13-15, 29]. Surfaces treatments include processes for adding residual stress, changing surface microstructure or thermally diffusing desirable elements into the die surface without the need of adding elements on the surface of the steel die. Hard coating techniques are defined as deposition of additional distinct films on the die surface with little effect on the intrinsic stress state and microstructure of the die subsurface.

The most common surface treatments for die casting dies are nitrocarburizing (carbonitriding) and nitriding. Carbonitriding is a thermochemical process that introduces interstitial carbon and nitrogen atoms into a ferrous matrix to form hexagonally close-packed \( \varepsilon \)-carbonitrides, \( \varepsilon \)-Fe\(_{2.3}\)(C,N) [30]. The die steel containing \( \varepsilon \)-carbonitrides is highly desirable in the HPDC industry due to its resistance to wear and fatigue due to presence of the \( \varepsilon \)-carbonitride phase. Based on the different processing temperatures, carbonitriding can be divided as austenitic carbonitriding or ferritic carbonitriding [7]. The temperatures for austenitic carbonitriding (675-775°C) exceeded the tempering temperatures of H11 and H13 tool steels, and therefore can cause core softening problems. Conversely, the ferritic carbonitriding process is carried out at a relatively low temperature (550-580°C) without the consequent issues of core softening. Dies having complex geometries utilize ferritic carbonitriding and show less distortion and deformation due to the lower process temperatures. Hence, ferritic carbonitriding is more common than austenitic carbonitriding for die casting dies.

The nitriding process is similar to carbonitriding surface treatments but only involves the interstitial diffusion of nitrogen atoms into the die surface. The nitriding process strongly depends on the presence of
nitride formers (aluminum, chromium, vanadium, molybdenum) in the die substrate to achieve improved wear capabilities. The processing temperature for nitriding is in the range of 500-550 °C.

Hard coatings have been successfully used as thin film physical barriers to protect dies for decades [29, 31-33]. The use of hard coatings can largely minimize soldering and erosion, resulting in a reduction of machine down-time, while significantly increasing die service life. Die coatings are mainly based on oxide, boride, carbide and nitride compounds. Most of the hard coatings are produced by thermo-reactive diffusion (TRD), chemical vapor deposition (CVD) and physical vapor deposition (PVD). The requirements for die coating materials are summarized as follows [34]: adequate adhesion to the substrate, good mechanical properties (hardness, ductility, and fatigue strength), good corrosion, oxidation and wear resistance, good thermal and impact resistance, and high thermal conductivity. However, no one coating satisfies all these requirements.

Industries utilize a combination of surface treatments and coatings to increase the hardness of die surfaces for better mechanical support of thin film coatings [35, 36].

2.5 Die Coating Methods

Potential coatings for die casting dies are produced by thermo-reactive diffusion (TRD), chemical vapor deposition (CVD) and physical vapor deposition (PVD). The descriptions of these practices are presented below.

2.5.1 Thermo-Reactive Diffusion (TRD)

Thermo-reactive diffusion (TRD) is defined as a thermochemical diffusion process that uses high potency carbide formers (V, Cr, Nb, B, Ta, W, Mo, and Ti) from a salt bath that diffuse into the steel substrate, while carbon, originally from the substrate, diffuses outwards and reacts with these carbide formers to form compound carbides (e.g. VC, CrC, and NbC) [15, 37, 38]. These TRD coatings exhibit dense microstructure are metallurgically-bonded to the die surface with a diffusion layer thickness of ~ 10 µm. However, all the TRD treated dies have to experience a post heat treatment since the temperatures for TRD processes are in the ranges of 850-1050°C, much higher than the ferritic-austenite transition temperature of the die steels.
2.5.2 Chemical Vapor Deposition (CVD)

The chemical vapor deposition (CVD) process is defined as the deposition of a material from its chemical vapor precursor that is decomposed by reduction or thermal decomposition onto a hot substrate. CVD is a reactive gas process that can produce a wide range of metal, ceramic and even polymer coatings. Since CVD is not a line-of-sight process, homogeneous coatings can be produced on any large and geometrically complex tool surface. Additionally, no moving or rotating of tools is needed during the process [39]. However, the substrate temperatures required for conventional CVD processes are in the range of 800-1200°C. Therefore, the substrates used for the CVD processes are limited to a narrower range of materials, such as cemented carbides (e.g. WC), but not tool steels. A disadvantage of the CVD process is the toxic nature of many of the chemical vapor precursors and by-products. Sometimes a post heat treatment is often required for the CVD-coated tools after processing which can cause distortions to the tool.

In recent years, plasma assisted chemical vapor deposition (PACVD) has been widely applied to produce hard coatings at much lower substrate temperatures (450-550°C) [29, 39-41]. In the PACVD process, substrates do not need to be kept at elevated temperatures for thermal reduction or decomposition of the precursors; instead, its success is based on the use of a plasma to dissociate and ionize the chemical vapor precursors. The much lower substrate temperatures used in the PACVD process allow for a wide range of substrates to be used, including tool steels. Different types of hard coatings can be produced by PACVD for aluminum die casting applications and include TiN, TiC, Ti(C,N), Ti(B,N) and (Ti,Al)(C,N).

2.5.3 Physical Vapor Deposition (PVD)

The physical vapor deposition (PVD) process is considered as the physical deposition of material either vaporized or sputtered from a solid source/target to produce a flux of ions or atoms which transfers in a vacuum chamber and condenses onto the substrate surface as a coating. PVD die coatings are often produced at substrate temperatures ranging from 150-500°C. Compared to TRD and CVD, these substrate temperatures usually do not affect the microstructures and properties of the tool steel used as the substrate. Therefore, the PVD-coated tools can be applied for die casting without the need of additional post thermal treatments [39]. Compressive residual stresses are often observed with PVD coatings, due to the intense energetic ion bombardment, and are desirable for inhibiting crack propagation [15]. However, PVD is a line-of-sight process, and so the necessity of moving or rotating the tools during the process, or adjusting
the target assembly to the tools because of the characteristic line-of-sight deposition for PVD, causes complications and expense to coat heavy and complex die molds [39].

Most common PVD techniques being used for die coatings are magnetron sputtering (MS) and cathodic arc evaporation (CAE). Table 2.2 shows the comparison of die coatings produced by MS and CAE. It is found that CAE typically has high ionization plasmas resulting in extremely dense coating microstructures. Due to the characteristic arcs generated on the cathode source (target), numerous macro-particles are transferred onto the CAE surfaces, resulting in relatively rough coatings. In the contrast, the MS coatings have relative smooth coating surfaces. It should be noted, that for most of the CAE coatings, substrates are usually etched by the metal arc plasma at high bias voltages (at -1000 V or above), which causes a thin metal ion implantation layer between the coating and the substrate significantly increasing the coating adhesion to the substrate.

Table 2.2 – Comparison of properties of hard coatings produced by conventional magnetron sputtering (MS) and cathodic arc evaporation (CAE)

<table>
<thead>
<tr>
<th>Type</th>
<th>Plasma Ionization</th>
<th>Surface</th>
<th>Growth Defects</th>
<th>Microstructure</th>
<th>Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>Low</td>
<td>Smooth</td>
<td>Pin-holes</td>
<td>Dense</td>
<td>Medium</td>
</tr>
<tr>
<td>CAE</td>
<td>High</td>
<td>Rough</td>
<td>Macro-particles &amp; Pin-holes</td>
<td>Extremely Dense</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Magnetron Sputtering (MS)

Magnetron sputtering (MS) is defined as a process by which a material is ejected from its solid state by energetic ion bombardment, and condenses onto the substrate surface as a coating. Magnetron sputtering is widely used for thin film deposition. Based on the types and arrangement of magnets located behind the sputter target, magnetron sputtering can occur in one of two modes: balanced and unbalanced. For the deposition of die coatings, magnetron sputtering shows evolution from balanced to unbalanced, and finally to close-field unbalanced systems.

Conventional magnetron sputtering is a balanced mode. It usually exhibits low deposition rates, low ionization efficiencies in the plasma, and high substrate heating effects. The plasma is confined by the magnetron field to the target vicinity, with a region of dense plasma extending about 60 mm in front of the sputtering target. During deposition, substrates have to be put inside this region for ion bombardment, which can strongly modify the structure and properties of the film. Otherwise, if substrates are positioned outside this region, it is difficult to produce fully dense, high quality coatings on large components.

To overcome these limitations, unbalanced magnetron sputtering was introduced in 1986 by Window and Savvides [42]. The main difference between balanced and unbalanced magnetrons is the
degree to which the plasma is confined. By strengthening the outer ring of magnets, some electrons in the plasma are no longer confined to the target region, but are able to follow the magnetic field lines and flow out towards the substrate, resulting in an increase in ion bombardment at the substrate with a consequent improvement in coating structure and quality.

However, it is still difficult to deposit uniform coatings on the complex components at acceptable rates from a single target in the unbalanced mode. Thus for commercial applications, multiple magnetron targets are used. Another important improvement was the introduction of closed-field unbalanced magnetron sputtering (CFUBMS) [43], in which the field lines are linked between the magnetrons. Therefore, the losses of secondary electrons to the chamber wall are low and the substrate lies in a high density plasma region [44]. Figure 2.7 shows the dual unbalanced magnetron configurations compared to the conventional and unbalanced magnetrons. It is found that the CFUBMS is the most common for die coating deposition.

Figure 2.7 A comparison of the magnetic configuration and plasma confinement in conventional, unbalanced and dual-magnetron closed-field systems [43]

Based on various voltage/current waves applied to the sputtering target, sputtering technologies can be also identified as direct current magnetron sputtering (DCMS), radio frequency magnetron sputtering (RF-MS), pulsed direct current magnetron sputtering (PDCMS), high power impulse magnetron sputtering (HiPIMS), and modulated pulsed power magnetron sputtering (MPPMS). DCMS is the most common
mode and has been widely used for many conductive materials, but is not suitable for electrically insulating material deposition, such as alumina, due to arcing problems.

Instead, RF-MS is usually used for the deposition of non-conducting coating. However, its deposition rate is very slow. In the past decade, PDCMS has been developed with goal of minimizing arcing events and stabilizing the reactive sputtering process [43, 45, 46]. It is usually pulsed in the mid-frequency range (10-200 kHz) [43]. There are two modes for PDCMS: unipolar pulsed sputtering, where the target voltage is pulsed between the normal operating voltage and ground; and bipolar pulsed sputtering, where the target voltage is actually reversed and becomes positive during the pulse-off period. Due to the much higher mobility of electrons in the plasma than ions, it is usually only necessary to reverse the target voltage to between 10-20 percent of the negative operating voltage to fully dissipate the charged regions and prevent arcing [46]. The mode with the target voltage not fully reversed is called as asymmetric bipolar pulsed DC. The asymmetric bipolar PDCMS is the most popular mode for the deposition of die coatings, since the process is stable with few arc discharges observed. It is noted that the deposition rate of PDCMS is comparable to DCMS, much higher than that of RF-MS.

During the last decade, the development of high power impulse magnetron sputtering (HiPIMS), also known as high-power pulsed magnetron sputtering (HPPMS), has shown considerable potential in improving the quality of sputtered films. By using pulsed, high peak target power for a short period of time a high degree of ionization of the sputtered species can be generated to achieve high plasma density, resulting in smooth and dense coatings with minimal amounts of macro-particles on the coating surface.

Unfortunately, early HiPIMS techniques showed a significantly decreased deposition rate as compared to traditional DC magnetron sputtering [47]: this is due to the low pulse-on cycles and the re-sputtering problems for the growth of films. Recently, an alternative HiPIMS deposition technique known as modulated pulsed power magnetron sputtering (MPPMS) has been developed [47]. This new sputtering technique is capable of producing a high ionization fraction of sputter target species resulting in extremely dense coating microstructures and smooth surfaces, while at the same time maintaining a high deposition rate. Figure 2.8 shows a comparison of duty cycle as a function of peak power density for DCMS, PDCMS, MPPMS and HiPIMS. Lin et al. [47-54] reported the successful deposition of dense nitride coatings (Cr$_2$N, CrN and CrN/AlN) using MPPMS for die casting applications. The improved mechanical properties, oxidation resistance, and tribological properties were observed for these MPPMS coatings when compared to the DCMS and PDCMS coatings deposited using similar conditions.
Cathodic Arc Evaporation

As mentioned in Table 2.2, one characteristic of cathodic arc coating is the surface volume of macro-particles on the coating surface, resulting in an increase in coating roughness and presumably degrading the coating performance in tribological applications. To reduce or eliminate the coating defects caused by macro-particles, macro-particle filters were introduced using magnetic coils [56]. Aksenov and co-workers introduced a classic 90° duct filter as shown in Figure 2.9.

Later, large-area filtered arc was developed by Gorokhovsky and co-workers to produce a smooth dense arc coating. The top view of their linear filtered arc system is shown in Figure 2.10 [57]. The system consists of two direct non-filtered arc sources (a, b) and two filtered sources (d, e). The purpose of the coils (f, g) is to provide the magnetic guiding fields which are necessary to establish the electrostatic potential distribution that steers plasma ions from the sources to the substrate platform.

Figure 2.11 shows the surface of 2 μm thick TiN coatings deposited by large-area filled arc of Gorokhovsky in comparison with a TiN coating deposited by conventional arc techniques without an electromagnetic filter [58]. A number of macro-particles (mainly α-Ti metal particles) ranging from sub-micron to 10 μm are observed on the conventional arc coating surface, resulting in rough surface morphology (Figure 2.11b). Conversely, a much smoother TiN coating with a surface nearly free of macro-particles is achieved using an electromagnetic filter.
Figure 2.9  Classic 90° duct filter developed by Aksenov and co-workers [59] consisting of: 1-cathodic arc source, 2-plasma duct, 3-insulator, 4-coils, 5-solenoid, 6-vacuum chamber, 7-insulators, and 8-substrate.

Figure 2.10  Top view of linear filtered arc system developed by Gorokhovsky [57]: two direct non-filtered arc sources (a and b), two filtered sources (d and e), and coils (f and g).
2.6 Structure Zone Diagram for PVD Coatings

It is well established that the mechanical, tribological, electrical, and optical properties of the physical vapor deposition (PVD) coatings are strongly affected by the coating microstructure [60-62]. However, the coating microstructure is, in turn, controlled by various deposition parameters, such as gas pressure, substrate temperature and bias voltage. The energy delivered to the growing film and the atom mobility on the surface are controlled by these coating deposition parameters [62]. Therefore, the general relationship between coating deposition parameters to the final coating microstructure is important to know.

The first structure zone model (SZM, also called classic MD model) was proposed by Movchan and Demchishin [63] in 1969 for thick evaporated coatings. They identified three structure zones as Zone 1, Zone 2 and Zone 3 for the evaporated coatings as a function of their homologous temperature \((T/T_m)\) (see Figure 2.12), where \(T\) is the substrate temperature and \(T_m\) is the melting temperature of the coating. In Zone 1 \((T/T_m < 0.3)\), the atom mobility is low resulting in continuous nucleation of grains. Coatings in Zone 1 exhibit fibrous-grain microstructures with numerous voids at the grain boundaries. Zone 2 coatings \((0.3 < T/T_m < 0.5)\) exhibit dense columnar structures due to the increase in atom mobility. At high substrate
temperatures (T/T<sub>m</sub> > 0.5), large grains are observed for Zone 3 coatings because of higher bulk diffusion and recrystallization.

![Structure Zone Diagram](image)

Figure 2.12 Structure Zone Diagram developed by Movchan and Demchishin (MD model) for the evaporation coatings at various substrate temperatures [63].

Later, Thornton [60] studied thick metal coatings of chromium, copper, aluminum and molybdenum deposited onto glass and metallic substrates using magnetron sputtering under various conditions of substrate temperature, argon pressure and plasma ion bombardment. The surface view and fracture cross sections of these thick metal coatings were characterized by SEM as shown in Figure 2.13 and Figure 2.14. Based on these coatings, the well known Structure Zone Diagram (SZD) of Thornton (see Figure 2.15) was developed for sputtered metal films as a function of argon pressure and T/T<sub>m</sub> ratio (where T is substrate temperature, T<sub>m</sub> is relative to the melting temperature of the film).

The Zone 1 films (deposited at low temperatures, T/T<sub>m</sub> < 0.2-0.3) have low density porous columnar structures due to low atom mobility. Because of the numerous voids/pores between the columnar grains and the rough surface, the films appear matte or even black as a result of trapped light. Films having Zone 1 microstructures often exhibit poor mechanical, optical and electrical properties. The Zone 1 films rarely exhibit significant residual stress values due to their porous structure.

Zone T is known as the transition zone located between Zone 1 and Zone 2. Zone T has T/T<sub>m</sub> ranges from 0.2-0.5 at low argon pressure. Maintaining a low substrate/melting temperature while increasing the argon pressure facilitates the formation of a Zone 1 structure. The Zone T films are smooth and dense due to the surface diffusion of the atoms to prevent pore formation. The Zone T microstructures consist of fibrous grains with reduced columnar structures, resulting in films with good mechanical properties of the films. The smooth surfaces also enhance the optical properties. However, film residual stress becomes significant with this increase in film density.

Zone 2 films are also obtained by means of increasing the substrate/melting temperature to T/T<sub>m</sub> of 0.2-0.5 but less influenced by argon pressure than Zone T. The surface diffusion of the atoms dominates overshadowing at Zone 2, resulting in recrystallized columnar grains and impenetrable grain boundaries.
The coatings exhibit high strength but low ductility. This structure is rarely used for optical applications due to the rough surfaces resulting from the columnar growth.

Zone 3 films are obtained at high substrate temperatures \((T/T_M > 0.5)\) and have extremely dense equiaxed or columnar grains, depending on stress distribution and structure. The surfaces of Zone 3 films are the smoothest among all the four zones due to the bulk diffusion of the atoms. The grain boundaries have a tendency to develop grooves, but most of the residual stresses are removed by the recrystallization. The Zone 3 films exhibit similar mechanical properties to the Zone 2 films. However, it should be noted that Zone 3 is rarely observed for most materials.

Figure 2.13  SEM fracture cross sections and surface views of chromium, copper and aluminum coatings (2A-2F, and 2G-2I) deposited at various substrate temperatures and argon pressures used to develop the Structure Zone Diagram of Thornton as seen in Figure 2.15 [60]
Figure 2.14 SEM fracture cross sections and surface views of aluminum, copper and molybdenum coatings (3A-3F) deposited at various substrate temperatures and argon pressures used to develop the Structure Zone Diagram of Thornton as seen in Figure 2.15 [60]

Figure 2.15 Structure Zone Diagram (SZD) developed by Thornton for metal films sputtered at various substrate temperatures and argon pressures [60]
Based on the SZD of Thornton, the film structures can be changed from one zone to another by adjusting argon pressure and $T/T_M$ ratio. For example, a Zone 1 film deposited at high argon pressure and low substrate temperatures can be improved to be a denser Zone T film by increasing the atom mobility on the surface by either decreasing the argon pressure or increasing $T/T_M$ or both. The structure zone diagram (SZD) is also ambitiously called Structure Zone Model (SZM), though it is not really a model but a simplistic representation of the expected coating microstructure trends as a function of deposition parameters [60-62, 64]. Although the structure zone diagram was developed from sputtered metal films, the trends also work for compound films [61].

It is a goal for most PVD coaters to produce dense coatings having Zone 2 and Zone 3 microstructures without increasing substrate temperature. Kelly and Arnell [65] reported that several metal coatings (aluminum, zirconium and tungsten) having dense columnar (Zone 2) and fully dense (Zone 3) microstructures can be deposited below the temperatures recommended by the SZD of Thornton by simply increasing the ion energy and ion flux ratio using CFUBMS with substrate bias. They found at using higher energy ion bombardment and higher ion-to-atom ratios had similar effects to the enhancement of the ad-atom mobility as increasing the substrate temperature.

In recent years, high power impulse magnetron sputtering (HiPIMS) and filtered cathodic arc evaporation are increasingly used and, therefore, it became desirable, to modify the structure zone diagram (SZD) of Thornton by including plasma-related deposition parameters. A new extended structure zone diagram was proposed by Anders for these energetic deposition methods as shown in Figure 2.16 [64]. The axes for SZD of Anders are comprised of the generalized homologous temperature, the normalized kinetic energy flux, and the net film thickness. The net film thickness can be negative because of ion etching.

![Figure 2.16](image.png)

**Figure 2.16** Structure Zone Diagram developed by Anders applicable to energetic deposition as a function of the generalized homologous temperature, the normalized kinetic energy flux, and the net film thickness [64].
2.7 Growth Defects in PVD Coatings

Growth defects in PVD coatings can cause local loss of coating adhesion, delamination, higher friction, voids, pitting corrosion and gas permeation [66], and a large density of these defects has a degrading effect on the PVD coatings’ mechanical properties, wear properties and corrosion resistance [67]. Since it is important to decrease coating the defect density, one must know and understand their origin.

Panjan and co-workers [66-70] investigated the growth defects in various hard PVD coatings prepared by arc evaporation and magnetron sputtering at various deposition conditions. The defects were found occasional and spatially localized, and their form, size and density depended on the substrate type, the pretreatment, and the deposition conditions. They analyzed the influence of inclusions in a steel substrate on coating defects and found that shallow craters and voids were observed on MnS inclusions, while the coating growth on SiO$_2$ inclusions was coherent [68]. PVD coating growth defects can be divided into four categories [66, 70]: (1) big, shallow craters with a size of 5-40 µm (macrodefects), (b) cone structures with a diameter of 1-10 µm (microdefects), (3) disk-like holes and (4) pin-holes extending through the whole coating.

In the form of either peaks or craters, growth defects on the coating surface can be identified as two major types [68]. The first types are nodular and flake defects as shown in Figure 2.17. These “peak” defects originate from different types of seeds, including, but not limited to, the substrate surface irregularities (e.g. asperities, scratches and pits), different particles remaining on the surface after pretreatments (e.g. dust and polishing residue) and fracture of the stressed coating generated during the coating process. The formation of nodular defects is mainly caused by shadowing effects during the deposition process initiated by asperities and the seed particles on the substrate surface because of the line-of-sight nature of the arc evaporation and magnetron sputtering processes [67, 71].

The second types of PVD coating defects are cavity growth defects including pin-holes, keyholes, craters, and flakes (see Figure 2.18) [68]. Keyhole and pin-holes (either close or open channels) are also caused by the shadowing effect, depending on the shape and size of the substrate irregularities as shown in Figure 2.18. The shadowing effect is known to cause weak bonding between the nodular and flake defects and the surrounding coating. Therefore, the “peak” defects (Figure 2.17c and Figure 2.17d) can easily be detached due to the internal or thermal stresses resulting in the formation of craters or flakes (Figure 2.18c and Figure 2.18d).
Figure 2.17 Types of nodular and flake growth defects in hard coatings prepared by physical vapor deposition (PVD) [68]

Figure 2.18 Types of cavity growth defects in hard coatings prepared by physical vapor deposition (PVD) [68]
2.8 Failure Modes of Die Coatings

Hard coatings have been used widely as a physical barrier to protect die casting dies, core pins and insets from soldering and erosion. Most of the PVD die coatings used for die protection have been considered as inert to liquid aluminum. Accordingly, the major failure modes for the PVD die coatings could be pit corrosion and subsequent soldering [36]. As discussed in Section 2.7, two major types of defects would exist for PVD coatings, either nodular growths defects or pin-holes. The defect density varies with the different sample preparation methods and depends on the various deposition parameters, and different coating techniques. Although great efforts have been made to decrease the defects, no perfect PVD coatings free of defects can be obtained. The pre-existing pin-holes defect for the PVD coatings may be more detrimental to the die coatings, since these pin-holes could be the first nucleation sites for pitting corrosion where aluminum penetrates through the coating and reacts with the steel substrate to form intermetallic compounds.

Jie et al. [21] suggested a sequence of sketched steps for the soldering process on the PVD-coated core pins. The process mainly consisted of five steps (see Figure 2.19). They are first local coating failure (I - II), second pit formation (III - V), third in-depth growth of a pit (VI - VIII), and fourth pit connection (IX - X), and finally formation of negative draft or undercut on a core pin (X). The actual negative draft or undercut is shown in Figure 2.20.

![Figure 2.19](image)

**Figure 2.19** Sketched steps for soldering process on coated core pins [21]
Wang [72] studied three types of PVD coatings used for extended die life, and found TiAlN, and CrN coatings exhibited better corrosion and erosion resistance to molten aluminum than TiN. The shorter service life for the TiN coating was caused by its lower oxidation temperature (500-600°C). Knotek et al. [73] found the PVD CrN coating performed better than the Ti-based coatings, e.g. TiN or Ti(C,N), in the practical die casting process with PVD-coated die casting cores. Therefore, oxidation resistance of the coating can be another failure mode for die coatings. Additionally, they also reported that aluminum soldering was clearly apparent, but due to casting shrinkage from solidification on the core. However, no mitigation practices were suggested for preventing such aluminum adhesion.

2.9 Wettability and Adhesion

Consider a flat, smooth and chemically homogenous solid surface in contact with a non-reactive liquid in the presence of a vapor phase. If the liquid does not completely wet the solid, an equilibrium contact angle \( \theta \) will be observed at the triple line of liquid-vapor-solid (if measured from two-dimensional view, it is a triple point) [74]. This measured \( \theta \) value is defined as the wetting angle of the liquid and obeys the classical Young’s equation [75] (see Equation 2.1)

\[
\cos \theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}
\] (2.1)

A contact angle lower than 90° means good wetting of the liquid on the solid, while over 90° indicates poor wetting. The work of adhesion (\( W_a \)) is defined as the free energy change per unit area after separating an interface into two surfaces, which is commonly used to assess the strength of the contact between two materials (see Equation 2.2).
Continuing Young’s equation (Young Model) for a flat solid surface, two more models were subsequently developed for the wetting conditions on rough and porous surfaces. They are known as the Wenzel Mode [76], and Cassie-Baxter Model [77]. The wetting conditions for the three modes are shown in Figure 2.21.

![Figure 2.21](Image)

The Wenzel Model [76] considers the case when the liquid droplet wets the rough solid, and the contact angle \( \theta_w \) can be defined as follows (where \( r \) is defined as the ratio of the total surface area to the projected area):

\[
\cos \theta_w = r \cos \theta
\]  

(2.3)

The Cassie-Baxter Model [77] shows the opposite condition when the liquid droplet only is supported by the rough tips on the solid surface, and the contact angle \( \theta_c \) is defined as:

\[
\cos \theta_c = \varphi(\cos \theta + 1) - 1
\]  

(2.4)

where \( \varphi \) is defined as the ratio of the liquid contact solid area to the projected area. In the case of hydrophobic surfaces (\( \theta > 90^\circ \)), the roughness increases the non-wetting properties such that the surface becomes super-hydrophobic with contact angels over 150°. Both models can exist for the liquid wetting rough surfaces, but the Wenzel state is often less desirable in practice, due to the higher adhesion to the substrate compared to the low adhesion for the Cassie state [79, 80]. Accordingly, over the past decades, a
number of studies have focused on the development of super-hydrophobic surfaces by reducing the liquid adhesion to the substrate and achieving non-wetting for the liquid [80].

Kam et al. [81] reported that the surface of Type 316L stainless steel can be textured to various micro-cone structures using femtosecond laser irradiation in air. They found the wetting behavior of water droplets on these laser textured surfaces can be changed from super-hydrophilic to hydrophobic along with contact angle change from $0^\circ$ to $113^\circ$ by tuning the processing conditions leading to the micro-cone feature changes (see Figure 2.22).

Figure 2.22 SEM micrographs of the laser textured Type 316L stainless steel surfaces and corresponding photographs of 3 μL water droplets on surfaces [81].

The contact angles of water or other liquids to various solid substrates can be easily measured at room or relatively low temperatures. However, when considering the wetting behavior of a liquid metal or its alloys at elevated temperatures (over 500°C), the conventional simple experimental apparatus cannot work because the oxygen in the air could cause oxidation. Instead, a sessile drop test is usually performed in a tube furnace either using flowing inert gas or maintaining a high vacuum. The sessile drop test consists of placing a small sample of solid alloy, e.g. A380 aluminum alloy, onto a test substrate and then increasing the system temperature until the alloy melts and reaches its equilibrium geometry on the solid substrate. The contact angle between the molten drop and the substrate can be measured as before, and then correlated to work of adhesion through the Young-Dupré equation [3, 74, 82]. The wetting behavior of certain liquid alloys onto other solids can be judged by the values of their contact angles, where $0\text{-}90^\circ$ means good wetting and $90\text{-}180^\circ$ indicates poor wetting.
2.10  Review of Past Work

Most prior work for die coatings prepared by physical vapor deposition (PVD) focused on soldering (or corrosion), erosion or heat checking. Only a few investigators studied the aluminum wetting and adhesion behavior of PVD coatings for die casting applications. Historically, there are two commonly-used approaches to assess the wetting behavior of liquid aluminum to different materials. The first is the sessile drop test, and the second is a relatively simple dipping test. In this Section, the sessile drop test, the dipping test and other tests, aluminum casting trials and die coating development work are reviewed.

2.10.1  Methods for Wettability/Adhesion Evaluation

Historically, sessile drop tests have been widely accepted by researchers as a means to study the wetting behavior of molten metals and alloys on solid substrates [3, 74, 82-84]. Dohotre et al. [85] summarized three types of interactions that could promote the high-temperature wettability in solid–liquid systems. They are (1) dissociation of surface oxides on the liquid, (2) chemical dissolution of solid in the liquid metal and interfacial adsorption of reactive solutes, and (3) formation of a wettable interfacial compound. At high temperatures, it is difficult for liquid metal to spread to an equilibrium shape when a solid reaction product on its surface (e.g. a surface oxide) prevents the spreading, resulting in a large value of the measured contact angle. It should be noted the sessile drop tests work well for more noble, non-oxide formers, e.g. copper, but are more difficult for aluminum and other metals that oxidize readily. Consequently the use of the sessile drop technique for aluminum and aluminum alloys results in wide variability in the results. An example is the wetting of sapphire by molten aluminum, which has been studied by many groups [14, 22, 86]. The published results, however, are quite mixed, with contact angles ranging from 83° to 126° at ~700°C. The large scatter in data is assumed to be caused by variations in the thickness of the oxide scales that exists on the molten aluminum surfaces rather than true variations in the wetting behavior. Shi et el. [2] calculated that the equilibrium oxygen partial pressure at 800°C has to be lower than $5 \times 10^{-39}$ Pa to avoid aluminum oxidation and such low oxygen partial pressures obviously cannot be achieved practically even under ultra-high vacuum conditions. At temperatures between 800°C and 1000°C, the native aluminum oxide layer is frequently disrupted due to the formation of a gaseous sub-oxide: $4\text{Al}(l)+\text{Al}_2\text{O}_3(s)=3\text{Al}_2\text{O}(g)$ [74, 87, 88]. Thus, elevated temperatures (over 800 °C) can result in less test errors, but such temperatures are not representative of the actual die casting processes where maximum die temperatures are around 550°C.
In efforts to obtain better intrinsic wetting data at these lower casting temperatures, a modified sessile drop technique has been developed [74, 84, 88, 89]. In essence, a small piece of aluminum is melted inside a ceramic tube under high vacuum or a reducing inert gas atmosphere, and then pushed through the tube so that the relatively fresh melt from the tube end drops onto the test substrate. The contact angle measured using this method is considered more reliable than that generated by a conventional sessile drop test. However, few data have been reported using this method for aluminum wetting on various hard coatings. The high cost of vacuum generation, the complex tube designs and process controls, coupled with long test times for the vacuum condition have limited the usefulness of this method. Finally, the results generated using this method may not be representative of the actual die casting applications because die casting is usually carried out under standard atmospheric conditions.

On the contrary to the complex sessile drop test setup, a relatively simple dipping test [24, 83, 90], also called immersion test, has been commonly used in die casting research to study aluminum adhesion and soldering behavior. For the dipping test, an uncoated or hard coating coated core pin is inserted into a container of molten aluminum alloy and then withdrawn and allowed to cool in air. This dipping test conducted under atmospheric conditions is obviously simple and direct, but is not quantitative and the results are often difficult to interpret because of the physical adhesion that occurs due to aluminum shrinkage around the pin.

Furthermore, Lin et al. [14, 16] developed an ease-of-release test with the goal of providing quantitative measurements of the aluminum adhesion behavior. Core pins with/without coatings were partially dipped into an aluminum alloy melt and then the aluminum was allowed to solidify. The load required to pull the core pin out of the solidified aluminum was measured in an effort to quantify the apparent bonding strength of the core pin to the aluminum matrix. However, the measured load may not reflect the intrinsic adhesion of aluminum to the pin surfaces, due to other factors such as aluminum shrinkage around the pin, and friction between the core pin and the aluminum matrix.

Recently, Terek et al. [91] developed an ejection test to measure the sticking tendency of a cast Al–Si alloy to uncoated and PVD coated H11 tool steel pins. Their test equipment, schematic diagram of the test, and main results are shown in Figure 2.23. Pins were positioned precisely in the special small die, protruding 20 mm up into the cavity. Then, via. gravity an aluminum melt was poured into the pin-die assembly with a graphite ladle. Letting the alloy solidify, after 120 seconds, the pin-casting assembly was removed from the die and the ejection force of pulling the pin out of the casting was measured. The bare, nitride and duplex treated (CrN and TiAlN coatings) H11 tool steel pins were examined using the ejection test. They found the ejection force was independent of the surface composition. However, the force of CrN and TiAlN coated samples increased with decrease in roughness. Also, a post polishing on the coatings enhanced adhesive wear and raised ejection force.
2.10.2 Development of Die Coatings

Considering the multiple factors affecting die failures, it is impossible to find a single coating that matches all the required properties to prevent such complex failures. One approach is to develop a coating system that has multiple layers, each layer to provide a specific function, e.g. adhesion to the substrate, accommodation of the thermal residual stresses, good tribological behavior, corrosion resistance and non-wettability with the molten aluminum [35]. Moore and co-workers [13, 14, 16, 24, 35, 92-94] developed and modeled an optimized die coating system comprised of multiple or graded layers. The schematic drawing of their proposed optimized coating architecture is shown in Figure 2.24. The total thickness of the coating architecture is 5-8 µm. The conceptual design of this optimized die coating architecture included four sections as listed as follows [14]:

(1) Modification of the H13 substrate: nitriding or ferritic nitro-carburizing to increase substrate hardness and provide increased mechanical support for the PVD hard coating.

(2) Adhesion layer: a thin layer of chromium or titanium (100-200 nm) deposited on the modified H13 tool steel surface to increase the adhesion of the coating to the substrate.

(3) Intermediate layers: the composition, microstructure and properties of these intermediate and graded multi-layers change continuously from the adhesion layer to the working layer to facilitate the accommodation of the thermal stresses produced by the process cycling.
(4) Working layer: the outer layer in direct contact with the molten aluminum and exposed to the harsh working conditions. Good wear resistance, oxidation resistance and chemical inertness (non-wettability) with aluminum are required for this working layer.

Salas et al. [35] investigated the tribological properties of a wide range of PVD hard coatings that are currently used and some with potential use for die casting, including CrC, CrN, ZrN, MoNx, MoZrN, TiAlN, TiN/TiC, TiBz/TiC, NiAl, NiAlN, MoSiC/SiC, TiBCN, and Cr3Si. They used scratch testing, wear testing, optical profilometry, microhardness, optical microscopy and X-ray diffraction, and found only three types of coatings had good wear and adhesion performance. They were TiAlN, TiN/TiCN, and CrN coatings.

Kearns [93] studied the wetting behavior of three types of aluminum alloy (A360, A380 and A390) on various PVD coatings using the sessile drop test. The tested samples were cooled down to room temperature and a special fixture was used to remove the solidified alloy droplet with the force recorded by a mechanical tester. The force (F) to remove these droplets was considered to be proportional to the soldering strength of the droplet. The volume (V) removed was equal to the fracture surface average depth times the fracture surface area. And the spreading percent (S) of the molten aluminum alloys on the selected materials was also measured. As a result, Kearns [93] defined a wetting index (T), which was the sum of the indices F, V and S. All the tested coatings were then ranked by their wetting index. The coatings with lower wetting indices ie, those with weaker interactions with molten aluminum were selected as having the greatest potential for die casting protection as the working layer. It was concluded that CrN, Al2O3 and TiBz/TiC coatings exhibited the lowest indices and were candidates for the working layer.
CHAPTER 3: EXPERIMENTAL PROCEDURES

This section describes the experimental parameters, equipment and experimental procedures used in this research project. Three main tests were performed in this study: dipping test, sessile drop test and aluminum adhesion test to evaluate aluminum alloy adhesion to various coated substrates. Additionally, some coatings were produced by magnetron sputtering on both polished and laser textured H13 tool steel coupons. Finally, the characterization techniques used in the study are described.

3.1 Dipping Test

The dipping test was considered a simple means of assessing the aluminum adhesion behavior of aluminum to the candidate materials. In this study, it was used for evaluating the aluminum adhesion to powder-painted steel rods, and uncoated steel pins (Table 3.1). The powders of interest were mixed with isopropyl alcohol and then painted onto the plain carbon steel rods, dried in air and then dipped into a molten aluminum bath containing commercial A356 aluminum alloy. The temperature of the molten aluminum bath was maintained in the range of 750 °C to 800 °C and the samples were dipped for ten seconds. Upon removal of the rods from the bath, the level of aluminum adhesion to each sample was estimated.

Table 3.1 – Powder materials used for the dipping test

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Graphite</td>
<td>C</td>
</tr>
<tr>
<td>D2</td>
<td>Boron carbide</td>
<td>B$_4$C</td>
</tr>
<tr>
<td>D3</td>
<td>Yttrium oxide</td>
<td>Y$_2$O$_3$</td>
</tr>
<tr>
<td>D4</td>
<td>Silicon carbide</td>
<td>SiC</td>
</tr>
<tr>
<td>D5</td>
<td>Chromium nitride</td>
<td>CrN</td>
</tr>
<tr>
<td>D6</td>
<td>Yttrium aluminum garnet</td>
<td>Y$_2$Al$<em>5$O$</em>{12}$</td>
</tr>
<tr>
<td>D7</td>
<td>Titanium diboride</td>
<td>TiB$_2$</td>
</tr>
<tr>
<td>D8</td>
<td>Zirconium oxide</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>D9</td>
<td>Chromium oxide</td>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td>D10</td>
<td>Titanium oxide</td>
<td>TiO$_2$</td>
</tr>
</tbody>
</table>

Uncoated steel pins were also assessed using the dipping test as a baseline for comparing on the tests for the powder-painted pins. Two uncoated pins made of plain carbon steel were chosen. Prior to the dipping process, these pins were ultrasonically cleaned using acetone, isopropyl alcohol, and dried by nitrogen gas. Different from the previous test using A356 aluminum alloy, the alloy was switched to
commercial A380 aluminum alloy maintained at 700°C. The dipping period varied from one to sixty minutes. The level of aluminum adhesion to the pins was visually assessed and then photographed after the pins were extracted from the bath. A concentrated KOH aqueous solution was used to dissolve the adhered alloy on the pin using ultrasonic vibrations for two hours. Finally, the pins were rinsed again using deionized water, acetone, and isopropyl alcohol, and dried by nitrogen gas for observation of any soldering or pits in comparison to their previous state.

3.2 Sessile Drop Test

The configuration of a tube furnace having a transparent quartz window was used for evaluating the wetting of molten aluminum alloy on uncoated and coated steel coupons. There are two experimental setups used in this thesis. One is the same as Zhong [94] and Kearns [93] previously described and used at Colorado School of Mines, and a schematic diagram of this setup is shown in Figure 3.1. The furnace can be heated to 1500°C. For the experiment conducted, uncoated Type 304 stainless steel coupons with the size of 25 mm × 38 mm × 2 mm were used as the substrate. A small cube of A380 aluminum alloy was placed on the coupon surface. Then, the coupon along with the alloy was pushed into the hot zone of the tube furnace and sealed off. An additional Type-K thermocouple as shown in the Figure 3.1 was inserted close to the test sample to track the temperature change during the experiments. The tube furnace was pumped to 80 mTorr using a roughing pump, and back filled with ultra high purity argon. This pumping and filling operation was repeated five times, and then the argon gas was set at a constant flow rate of 5 sccm for half an hour both before raising the furnace temperature and during the entire experiment. A Cannon digital camera was used to record the wetting profile of the alloy through the quartz window. The furnace temperatures were manually controlled to increase and maintain a certain values in the range of 550°C to 1200°C. When the temperature reached the set value, it was held for 15 minutes prior to any photographs being taken and, after 30 minutes, it was increased to a higher value.

![Figure 3.1 Schematic diagram of the sessile drop equipment at the Colorado School of Mines.](image)
The second sessile drop experiments performed in this study employed a high-vacuum tube furnace. The apparatus as shown in Figure 3.2 is located at THE ALUMINIUM RESEARCH CENTRE – REGAL, Canada, and the experiment was conducted by Dr. Robert Schulz and Sylvio Savoie. A turbo pump was used to achieve a high vacuum environment (10^{-5} Torr range) for the tube in order to effectively minimize the oxide effect during the sessile drop test. The sample holder is shown in Figure 3.2b. The space available for a sample is a slot 25 mm × 36 mm × 3 mm deep in the middle. The H13 tool steel coupon (25 mm × 38 mm × 2 mm) polished to 1 μm was used as the substrate. For this procedure, a pure aluminum wire was cleaned with sand paper to remove the oxide layer, then cleaned with acetone-methanol wipes and placed immediately onto a polished H13 tool steel coupon under vacuum to minimize re-oxidation. A digital camera was used to record the profile of the molten aluminum on the substrate during the heating process.

![Figure 3.2 Schematic diagrams and photographs of the sessile drop equipment with a higher vacuum capability: drawings of (a) the apparatus and (b) the sample holder, and the apparatus photographs (c-d).](image-url)

3.3 Liquid Adhesion Test

The liquid adhesion test (AAT) was designed to provide a quantitative assessment of the adhesion behavior of aluminum casting alloys to various materials and coatings. A schematic diagram of the AAT is shown in Figure 3.3. The test consists of the following steps: tube placement on coupon surface, liquid alloy pouring and impingement, alloy solidification, tube removal and tensile test.
Figure 3.3  Schematic of the aluminum adhesion test consisting of six steps: (1-2) tube placement on coupon surface, (3) liquid alloy pouring and impingement, (4) alloy solidification, (5) tube removal and (6) tensile test.

The methodology used with the AAT was based on two phenomena observed in our preliminary experiments. First, when the liquid aluminum alloy was gradually poured out from an alumina tube an oxidation product from the melt always stuck to the crucible’s inner wall and bottom (see Figure 3.4a), indicating that the liquid aluminum poured from the crucible left the majority of the oxide on the melt surface in the tube. Second, although new oxide scale forms immediately on the liquid during the pouring process, it is thin and easily ruptured upon contact with the coupon such that fresh liquid is expected to come into contact with the coupon surface. Figure 3.4 shows the alloy left behind in the alumina crucible after pouring the alloy; this remaining alloy did not stick strongly to the crucible and was easily removed as shown in Figure 3.4b.

Figure 3.4  Photographs of the small amount of A380 aluminum alloy and its oxide scales remained in the alumina crucible after the majority of the alloy was poured out during the aluminum adhesion test: (a) alloy left in the crucible, and (b) alloy removal from the crucible.
3.3.1 Equipment and Materials

The main items for the AAT include a furnace capable of heating above 700°C, a ceramic tube, a melting crucible, a pair of steel tongs, the aluminum alloy and the H13 tool steel test coupons (bare or coated with various thin films). A Carbolite furnace (Type 301) capable of 1200°C was used in this study. The alumina crucible used for melting the alloy was AD-998 grade purchased from CoorsTek Inc with the size of Φ28 mm × 40 mm as shown previously in Figure 3.4. Boron nitride (BN) tubes were used in this study because preliminary tests revealed that BN outperformed steel or graphite as a tube material given that BN is highly inert and non-sticking to liquid aluminum, is easily machined, and has good oxidation resistance in air. However, no commercial BN tubes had the desirable size for the AAT, so the tube were actually obtained from a BN rod (AX05 grade, Φ25 mm obtained from Saint-Gobain Boron Nitride Inc.) and then machined to a tube size of an outer diameter (OD) of 25 mm, an inner diameter (ID) of 13 mm and a height of 55 mm (Figure 3.5) and photograph of the BN tube.

The aluminum alloy used in this study was the standard die casting A380. The A380 aluminum alloy came from two different sources with slightly different compositions. The first alloy (Type I) was obtained from a secondary aluminum smelter. Its composition (Table 3.2) was measured using optical emission spectroscopy (OES) following the procedure described in ASTM standard E716-10 (Standard practices for sampling and sample preparation of aluminum and aluminum alloys for determination of chemical composition by spectrochemical analysis). The other A380 aluminum alloy (Type II) was

Figure 3.5 Boron nitride tube: (a) solid 3D drawing, (b) transparent 3D drawing, (c) 2D drawing, and (d) machined tube photograph

The aluminum alloy used in this study was the standard die casting A380. The A380 aluminum alloy came from two different sources with slightly different compositions. The first alloy (Type I) was obtained from a secondary aluminum smelter. Its composition (Table 3.2) was measured using optical emission spectroscopy (OES) following the procedure described in ASTM standard E716-10 (Standard practices for sampling and sample preparation of aluminum and aluminum alloys for determination of chemical composition by spectrochemical analysis). The other A380 aluminum alloy (Type II) was
supplied in the form of components die cast from a Midwestern die casting facility and the certified composition of the casting is also listed in Table 3.2. It should be noted that the Type I - A380 aluminum alloy was used for most of the aluminum adhesion tests, while the second Type II alloy was only used for the samples after femtosecond laser treatments to modify the surfaces.

Table 3.2 – Composition of the two A380 aluminum alloys used for the aluminum adhesion tests.

<table>
<thead>
<tr>
<th></th>
<th>wt %</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
<th>Zn</th>
<th>Ti</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Remainder</td>
<td>9.49</td>
<td>0.77</td>
<td>3.04</td>
<td>0.19</td>
<td>0.07</td>
<td>0.06</td>
<td>0.03</td>
<td>2.55</td>
<td>0.04</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type II</td>
<td>Remainder</td>
<td>7.67</td>
<td>0.73</td>
<td>3.44</td>
<td>0.43</td>
<td>0.01</td>
<td>0.05</td>
<td>0.04</td>
<td>2.15</td>
<td>0.15</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this study, a 311 mm × 146 mm × 120 mm piece of H13 tool steel in the annealed state was used as substrates for all of the aluminum adhesion tests was provided by Bohler-Uddeholm. The composition of the H13 tool steel is shown in Table 3.3 from the supplier.

Table 3.3 – Composition of H13 tool steel used for aluminum adhesion tests.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td>Remainder</td>
<td>0.39</td>
<td>1.0</td>
<td>0.44</td>
<td>5.3</td>
<td>1.3</td>
<td>0.9</td>
<td>0.01</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Upon receiving, the annealed H13 tool steel block was sent to an outside machine shop for cutting into small pieces 25 mm × 25 mm × 146 mm. Half of these machined rectangle pieces were sent to Century-Sun Metal Treating Inc. for the hardening thermal treatment. The thermal process included three heating stages of 649°C (1200°F) for thirty minutes, 843°C (1550°F) for thirty minutes, and 1027°C (1880°F) for forty minutes, one quenching stage at the condition of 200 kPa (2 bar) quenching pressure, and three subsequent tempering stages in the order of 571°C (1060°F) for four hours, 604°C (1120°F) for six hours, and 549°C (1020°F) for four hours. After the thermal treatment, the H13 tool steel specimen had a final hardness of 43-44 HRC.

Prior to coating or testing using the aluminum adhesion tests, both of the annealed and hardened steel bars were sliced using a high-speed saw (LECO, MSX250M2, Model No. 826-000-100) down to smaller coupon sizes of about 25 mm × 25 mm × 5 mm. Then, one side of these coupons was mechanically ground using a range of SiC papers from 240 grit to 1200 grit, followed by a final polishing procedure using LECO polishing cloths containing 1 µm diamond suspensions. The prepared mirror-polished coupons were finally rinsed in acetone and isopropyl alcohol, gently rubbed with cotton, dried by an electric fan and stored in plastic sample boxes prior to coating or AATs. It should be mentioned that most of the coupons that were used as substrates to support PVD coatings for initial test were in annealed condition given that the primary goal was to study the chemical effect of the coating on the sticking rather than the mechanical
properties of the substrate underneath. In contrast, those for the CrN and AlCrN coatings deposited at Colorado School of Mines were in the hardened state.

For the initial aluminum adhesion test, twelve different hard coatings plus one bare H13 tool steel coupon were evaluated as listed in Table 3.4. The twelve different hard coatings included ten from commercial coating companies and two coatings (metal chromium coating and TiN coating) prepared by the author and are considered laboratory coatings. The ten samples were prepared by six commercial coating companies (identified in this thesis as Supplier 1 through Supplier 6) using either cathodic arc evaporation (CAE) or magnetron sputtering (MS). Among them, three of the cathodic arc coatings (#6, #9, and #12) were given a post fine polishing step using 1μm diamond paste by the suppliers themselves. Two of the other cathodic arc coatings (#10 and #12) were prepared using a specialized, patented process that includes a filter designed to minimize deposition of macro particles. The laboratory coatings (also labeled as CSM in the Tables) were prepared using a laboratory-scale, closed-field unbalanced magnetron sputtering system (the chamber and deposition parameters are given in Section 3.4).

Table 3.4 – Information about the thirteen types of specimens used for the aluminum adhesion tests

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Supplier</th>
<th>Method &amp; Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlCrN</td>
<td>1</td>
<td>CAE</td>
</tr>
<tr>
<td>2</td>
<td>AlTiN</td>
<td>2</td>
<td>CAE</td>
</tr>
<tr>
<td>3</td>
<td>CrWN</td>
<td>2</td>
<td>Nitriding + CAE</td>
</tr>
<tr>
<td>4</td>
<td>AlTiN</td>
<td>3</td>
<td>CAE</td>
</tr>
<tr>
<td>5</td>
<td>TiAlN</td>
<td>3</td>
<td>CAE</td>
</tr>
<tr>
<td>6</td>
<td>CrN</td>
<td>4</td>
<td>CAE + Fine Polish</td>
</tr>
<tr>
<td>7</td>
<td>H13</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>Cr</td>
<td>CSM</td>
<td>MS</td>
</tr>
<tr>
<td>9</td>
<td>CrWN</td>
<td>4</td>
<td>CAE + Fine Polish</td>
</tr>
<tr>
<td>10</td>
<td>CrN</td>
<td>5</td>
<td>Filtered CAE</td>
</tr>
<tr>
<td>11</td>
<td>TiN</td>
<td>CSM</td>
<td>MS</td>
</tr>
<tr>
<td>12</td>
<td>AlCrN</td>
<td>5</td>
<td>Filtered CAE + Fine Polish</td>
</tr>
<tr>
<td>12a</td>
<td>AlCrN</td>
<td>5</td>
<td>Nitriding + Filtered CAE</td>
</tr>
<tr>
<td>12b</td>
<td>AlCrN</td>
<td>5</td>
<td>Filtered CAE</td>
</tr>
<tr>
<td>13</td>
<td>TiB₂</td>
<td>6</td>
<td>MS</td>
</tr>
</tbody>
</table>

CAE — Cathodic arc evaporation
MS — Magnetron sputtering

3.3.2 Test Procedures

A schematic of the AAT was shown in Figure 3.3 and involves following steps. First, a fresh piece of solid A380 alloy (14.5 ± 1.5 g) was placed into an alumina crucible and heated along with the BN tube
from room temperature to 700°C in about sixty minutes. An H13 test coupon (coated or uncoated) was then transferred into the hot zone of the furnace. Immediately, the hot BN tube was positioned on top of the coupon surface and the molten alloy poured from the alumina crucible into the tube. The furnace door was closed after pouring, and the coupon, tube and alloy was maintained at 700°C for 15 minutes. The furnace was then turned off and the furnace door opened to allow cooling. After the sample and furnace cooled to room temperature, the BN tube was gently removed from the solidified aluminum cylinder. If the alloy did not adhere to the coupon, the aluminum adhesion strength was recorded as zero; otherwise, the adhesion strength was measured using an Instron tensile machine (MTS A30-33).

A special pin mode fixture was developed in this study to test the adhesion force between the adhered solid aluminum alloy and the bare/coated H13 tool steel coupons. The fixture includes a special drill bushing, a test pin, a top fixture and a bottom fixture. The goal of the drill bushing is to make sure the small hole is drilled through the center of the solidified aluminum, and that the center line of hole is parallel to the plane of the H13 tool steel coupon. A photograph of the drill bushing is shown in Figure 3.6a. The use of the drill bushing involves the four main steps: (1) loosen the sample lock screw; (2) insert the sample and tighten the sample lock screw; (3) drill the sample through the bushing; (4) loosen the sample lock screw and take the sample out.

![Figure 3.6](image)

Figure 3.6 Drill bushing: (a) photographs with special labels, (b-e) steps for drill bushing use.

The drawings of the pin, top fixture and bottom fixture are shown in Figure 3.7. Based on this pin set of fixtures, the test sample can be hooked by the pin onto the top fixture and be locked in place by the bottom fixture shown in Figure 3.8.
Figure 3.7 Pin (top left), top fixture (top right) and bottom fixture (bottom middle): (a) solid 3D drawing, (b) transparent 3D drawing, and (c) the 2D drawing.

Figure 3.8 Schematic drawing (a) and photograph (b) of the novel set of pin fixtures.

Figure 3.9 shows typical photographs of the mechanical test: (a) at the beginning of the test, and (b) at the end of the test. It can be seen that the sample was hooked by the top fixture and the H13 coupon sits parallel to the bottom fixture. The load vs. time curves were recorded using the Instron tensile machine with a crosshead speed of 0.21 mm/min. After reaching the maximum sticking strength, the A380 aluminum alloy rod was separated from the H13 tool steel coupons. The maximum breaking loads were converted to
adhesion strengths based on the cross-sectional area of the A380 aluminum cylinder (determined by the ID of the BN tube).

![ Photographs of the A380 aluminum alloy adhered bare H13 tool steel coupon: (a) before and (b) after the mechanic test.]

Figure 3.9

The fracture surfaces of the broken of coupons and alloy parts were further characterized by optical microscopy, scanning electron microscope, EDAX energy-dispersive X-ray spectroscopy, and transmission electron microscopy, respectively (details of the characterization information will be listed in the following Section 3.6).

In order to measure the temperature change during the AAT test, a separate experiment was performed on an uncoated H13 tool steel coupon. A hole was drilled in an A380 aluminum alloy piece with a thermocouple of $0.5 \text{ mm}$ inserted. This thermocouple was designed to track the temperature change of the alloy during the heating process. Later, during the pouring period, this thermocouple was removed from the alloy and left to hang in the air of the furnace hot zone to track the furnace temperature. A second thermocouple ($0.5 \text{ mm}$) was spot welded to the center of a bare H13 tool steel coupon’s surface and used to record the temperature change at the aluminum alloy/H13 tool steel interface. The two thermocouples, along with the furnace control, were all calibrated to an accuracy of $\pm 2^\circ C$. The recorded temperature-time curves during the AAT are shown in Figure 3.10. When the furnace temperature (dotted black line) increases to $700^\circ C$, A380 alloy gradually converts to the liquid state (dash-dotted red line) at around $580^\circ C$. It should be noted that the surface of the uncoated H13 coupon has already reached about $325^\circ C$ after a short preheating period (~0.5 minute) prior to the melt contact as enlarged in Figure 3.10b. This temperature is similar to the die preheating temperature for the actual die casting process that typically ranges from $200^\circ C$.
Additionally, it should be noted from Figure 3.10c that the coupon temperature experienced a rapid increase to \(~550\)°C upon pouring and then gradually heated to almost 700° C before cooling.

![Temperature vs. time curves](image)

Figure 3.10 Temperature vs. time curves for the aluminum adhesion test on an uncoated H13 coupon: (a) entire test, (b) greater detail at the A380 pouring stage, and (c) greater detail at the 15 minute holding stage after pouring.

3.4 Coating Deposition

A four-cathode closed-field unbalanced magnetron sputtering (CFUBMS) configuration was used to prepare the Cr, Ti, TiN, CrN and AlCrN coatings at Colorado School of Mines. The size of the cathode targets was 292 mm × 102 mm × 6 mm. For Ti and TiN films, a single titanium target was used to sputter in the high purity argon environment with and without nitrogen gas, while for Cr and CrN films, a chromium target was used. The AlCrN coatings were deposited onto the polished H13 tool steel coupons by compound sputtering. The AlCr alloy targets with compositions of (at.\%): Al\textsubscript{50}Cr\textsubscript{50}, Al\textsubscript{60}Cr\textsubscript{40} and Al\textsubscript{70}Cr\textsubscript{30}, supplied by Plansee Inc., were used with the substrate coupons static facing the target similar to the single metal target sputtering.

The power supplies used in this study were pulsed direct current magnetron sputtering (PDCMS) and high power pulsed magnetron sputtering (MPPMS). The power supply for PDCMS is the Pinnacle Plus from Advanced Energy, Inc., and that of MPPMS is the SOLO/AXIS-180TM Pulsed DC Plasma Generator from Zpulser Inc. All the substrates were biased to -60 V using a special custom-made DC power supply that was modified by Zpulser Inc. Prior to the depositions, the base pressure for the chamber was pumped lower than 5×10\textsuperscript{-5} Torr. The substrate coupons were sputter etched using the PDCMS at an argon pressure.
The substrate etching parameter were: -620 V peak voltage, 100 kHz, 1 μs reverse voltage of 50 V, average power of ~110 W, and etch time of 45 minutes. After the substrate etched, the substrate coupons were rotated to the location facing the sputter target, and then the target was also sputter etched by argon bombardment for 10-15 minutes to remove any contamination on the target surface or coatings formed from previous depositions. Prior to any nitride coatings, another 5 minutes were added after purging the nitrogen gas with the substrate facing away from the target. The power supply used for etching the target was the same as that used for the deposition of the coating. Both the target etching and coating deposition was done at a constant pressure of 2 mTorr.

The deposition parameters for the Cr (#8) and TiN (#11) coatings for the initial aluminum adhesion test are listed into the Table 3.5. Two types of pulse files, 0227-750-6-12 (1k) and 1250-10-8 (1.5k), were used for the MPP sputtering. For the file of 0227-750-6-12 (1k), the length of the macro-pulse is 750 μs, and the micro-pulse on and off times are 6 μs and 12 μs, respectively. For the other file, the macro-pulse is 1250 μs, consisting of micro-pulses of 10 μs on and 8 μs off.

Table 3.5 – Deposition parameters for the #8 Cr and #11 TiN coatings using MPP

<table>
<thead>
<tr>
<th>#</th>
<th>Coating</th>
<th>Target</th>
<th>N₂%</th>
<th>Pulse File</th>
<th>Power [W]</th>
<th>Substrate-to-Target Distance [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Cr</td>
<td>Cr</td>
<td>0</td>
<td>0227-750-6-12 (1k)</td>
<td>1000</td>
<td>64</td>
</tr>
<tr>
<td>11</td>
<td>TiN</td>
<td>Ti</td>
<td>8</td>
<td>1250-10-8 (1.5k)</td>
<td>1500</td>
<td>64</td>
</tr>
</tbody>
</table>

The deposition parameters for the single/compound-sputtered CrN and AlCrN coatings for the aluminum adhesion tests are listed in Table 3.6. The file of 0227-750-6-12 (1k) was also used for the MPP system having the same macro- and micro-pulses. Also, a chromium adhesion layer and a CrN intermediate layer were used to improve coating adhesion.

Table 3.6 – Deposition parameters for the single/compound-sputtered CrN and AlCrN coatings using MPP

<table>
<thead>
<tr>
<th>#</th>
<th>Target</th>
<th>N₂%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC_1</td>
<td>Cr</td>
<td>50</td>
</tr>
<tr>
<td>MA50C50_1</td>
<td>Al50Cr50</td>
<td>50</td>
</tr>
<tr>
<td>MA60C40_1</td>
<td>Al60Cr30</td>
<td>50</td>
</tr>
<tr>
<td>MA70C30_0</td>
<td>Al70Cr30</td>
<td>25</td>
</tr>
<tr>
<td>MA70C30_1</td>
<td>Al70Cr30</td>
<td>35</td>
</tr>
<tr>
<td>MA70C30_2</td>
<td>Al70Cr30</td>
<td>50</td>
</tr>
</tbody>
</table>
3.5 Surface Texture Treatment Using Femtosecond Laser

The surfaces of the 1 μm polished H13 tool steel coupons were modified using a 10-kHz Yb:CaF$_2$ chirped pulse amplified femtosecond laser (producing 185 fs pulses at a central wavelength of 1040 nm) to create various surface textures. The laser was focused to a 10 μm spot (measured $1/e^2$ diameter of the central intensity) using a 1” focal length, 90 degree off-axis parabolic mirror. The coupon was then mounted on 3-axis specimen scanning stages (Aerotech Inc.) and translated with respect to the laser focus. The preliminary experiments suggested the optimal parameters to create a desirable 3D surface topography was limited to a 5 mm × 5 mm area with the power of 630 mW, a scanning speed of 20 mm/s, a distance between passes of 5 μm, and three repeated passes. Therefore, a total of nine adjacent patterns were produced on each coupon (see Figure 3.11) to match the ID of the BN tube for the aluminum adhesion test.

![Figure 3.11](image)

Due to the exposure of the coupon in air during the laser texturing process, oxide powders were observed on the treated coupon surface. Prior to deposition of the AlCrN coating onto the patterned surface, the coupons were cleaned using a commercial rust cleaner (Naval Jelly, a phosphoric acid) for periods ranging from five to thirty minutes, then cleaned with hot water, acetone, and alcohol, and dried using a pure nitrogen gas blow. The Al50Cr50 alloy was used as the sputter target and AlCrN coatings were deposited using the MPPMS power supply having similar parameters as the sample of #MA50C50_1 (see Table 3.6). The slight difference was using titanium as adhesion layer instead of the previous chromium adhesion layer and CrN intermediate layer, since titanium layer was easily distinguished from AlCrN layer using EDS mapping.

Additionally, it is noted that the cryopump used for the sputter chamber was replaced by a Veeco molecular turbopump was used during this Ti/AlCrN coating deposition. Therefore, the coating may have different properties (e.g. crystalline orientation) to the previous one due to the change pump.
3.6 Characterization Technologies

This section describes the various characterization techniques used in this study, including the X-ray diffraction, optical microscopy, scanning electron microscopy, focused ion beam, transmission electron microscopy, X-ray photoelectron spectrometry, nano-indentation, Calot-test, 3D optical profilometer, pin-on-disk test, and Rockwell C adhesion test.

3.6.1 X-ray Diffraction (XRD)

The crystalline and phases of the coatings were evaluated using a PANalytical X’Pert PRO X-ray diffraction (XRD) system operating in a conventional θ-2θ mode with Cu Kα (λ = 1.5406Å). In this mode, only the crystallographic orientation/texture parallel to the coating surface was measured. The scan range was from 20-150° and the scan time was about fifteen minutes. The PANalytical X’Pert High Score Plus was used to process the raw XRD data by stripping the Kα2 peaks and subtracting the background, and then the processed data were re-plotted using Origin 8 software.

To identify the phases in the thin surface oxide layers for the #1 AlCrN coatings before and after oxidation at 800°C, 900°C and 1000°C, glancing incident X-ray diffraction (GIXRD) was used with an incident angle of 2°. The GIXRD was conducted on a Phillips X-pert diffractometer using Cu Kα (45 kV and 40 mA) radiation. The scan range was set at 30-90° with the step size of 0.05° and the count time of 12 seconds.

The magnitude and type of residual stresses generated within the coating during deposition can be a key parameter for coatings deposited on die casting dies. For example, tensile residual stresses within the coating can promote cracking, or delamination at the interface between the coating and substrate. Alternatively, it is suggested in the literature that compressive residual stresses can have a beneficial impact on the fatigue stresses generated during the heating and cooling of the die (and coating) during each die casting cycle.

The residual stress in the coating can be measured by X-ray diffraction because the stress causes the lattice parameter of the coating to change (i.e. changing the distance between the atoms). Perry et al. [96] proposed an X-ray diffraction approach for the residual stress measurement, also known as the SSF and SSFX plots method. The angle of incidence (γ) of the X-rays was set at ~2°, and then different diffraction peaks were measured (similar to the GIXRD). Therefore, the measured lattice spacings (aχ) were plotted as a function of sin²χ (where χ = θ − γ), yielding a line of slope (k). Since the unstrained lattice parameter (a₀) can be estimated from the JCPDF standard database as 0.414 nm, the Poisson’s ratio...
(v) was considered as 0.25, and the Young’s modulus $E_{hkl} \equiv E_{\text{bulk}}$ measured by nanoindentation, the residual stress in the coating can be calculated using Equation 3.1 [96].

$$k = \left[ 1 + \frac{\nu_{hkl}}{E_{hkl}} \right] \sigma_\chi$$

(3.1)

Therefore, the GIXRD data measured by the same Phillips X-pert diffractometer at a glancing incidence angle of $2^\circ$ could be used for the SSF stress assessment. A typical example for the SSF approach for the residual stress calculation for the Al$_{60}$Cr$_{40}$N coating (MA60C40_1) was conducted. The scan for SSF was in the range of 30-150$^\circ$ with a step size of 0.05$^\circ$ and a count time of 12 seconds. With the help of using PANalytical X”Pert High Score Plus to fit the diffraction peaks, the SSF calculated data is shown in Table 3.7, with further plotting of the measured lattice parameter versus $\sin^2 \chi$ shown in Figure 3.12 (see page 47). The slope of the plot was calculated to be -0.01201, and the modulus $E$ of the coating was measured as 388 GPa, so the residual stress can be calculated as $-9.0$ GPa as compressive residual stress.

Table 3.7 – Data for the Al$_{60}$Cr$_{40}$N coating measured by X-ray diffraction method (MA60C40_1)

<table>
<thead>
<tr>
<th>Peak</th>
<th>20</th>
<th>$\chi$=0-\gamma</th>
<th>$\sin \chi$</th>
<th>$\sin^2 \chi$</th>
<th>$d_\chi$ (nm)</th>
<th>h</th>
<th>k</th>
<th>l</th>
<th>a$_\chi$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.335</td>
<td>18.6675</td>
<td>16.6675</td>
<td>0.2868</td>
<td>0.0823</td>
<td>0.2407</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>43.100</td>
<td>21.5500</td>
<td>19.5500</td>
<td>0.3346</td>
<td>0.1120</td>
<td>0.2097</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>63.300</td>
<td>31.6500</td>
<td>29.6500</td>
<td>0.4947</td>
<td>0.2447</td>
<td>0.1468</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>75.770</td>
<td>37.8850</td>
<td>35.8850</td>
<td>0.5862</td>
<td>0.3436</td>
<td>0.1254</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>79.970</td>
<td>39.9850</td>
<td>37.9850</td>
<td>0.6155</td>
<td>0.3788</td>
<td>0.1199</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>96.390</td>
<td>48.1950</td>
<td>46.1950</td>
<td>0.7217</td>
<td>0.5209</td>
<td>0.1033</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>109.000</td>
<td>54.5000</td>
<td>52.5000</td>
<td>0.7934</td>
<td>0.6294</td>
<td>0.0946</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>113.620</td>
<td>56.8100</td>
<td>54.8100</td>
<td>0.8172</td>
<td>0.6679</td>
<td>0.092</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>135.100</td>
<td>67.5500</td>
<td>65.5500</td>
<td>0.9103</td>
<td>0.8287</td>
<td>0.0833</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

3.6.2 Optical Microscopy (OM)

Both plan-view and cross-sectional of the coating surfaces of the polished aluminum adhered samples were examined using a PM-CUP Olympus optical microscope (OM). The Calo-tested samples (detailed in Section 3.6.8) were also characterized by OM.
3.6.3 Scanning Electron Microscopy (SEM)

The surface morphologies and thicknesses of all the coatings were characterized using an FEI Quanta 600i Environmental scanning electron microscope and a JEOL JSM-7000 field emission scanning electron microscope (SEM). Compositional analysis of the samples was measured using EDAX energy-dispersive X-ray spectrometers (EDS) attached to both SEMs. Backscatter electron (BSE) imaging and EDS mapping were utilized to distinguish and identify different phases within the microstructures. EDS point and line scans were also used to semi-quantify the phases in the microstructures.

To take cross-sectional views of the coatings, the coated-samples were cut using a high speed saw from the bottom of the substrate towards the coating side to thicknesses of 0.50–0.75 mm. The samples were then immersed into the liquid N\textsubscript{2} tank for 15 minutes. When the sample cooled down, a pair of pliers was used to fracture the sample into two parts through the cutting area, and then the fresh fractural surfaces and thickness of the coating were analyzed using the SEM.

The cross-section polisher was also used to prepare high-quality cross-sectional surfaces of the coatings. The coupons after mechanical testing were sectioned to a size of 3 mm × 5 mm using the high speed saw with adhered alloy on the surface. Colloidal silver was used to paint on the sample surface for more than ten times to obtain a thick protective layer on the sample. Then, the sample was dried and mounted in the polisher with the polishing parameters set as follows: argon flow rate of 3.5 sccm, acceleration voltage of 5 kV, time for 12 hours.

Figure 3.12 Plot of lattice parameters as a function of $\sin^2 \chi$ for the Al\textsubscript{60}Cr\textsubscript{40}N coating measured by X-ray diffraction (MA60C40_1).
3.6.4 Focused Ion Beam (FIB)

All the TEM samples in this study were prepared using a dual beam Helios Nanolab 600i focused ion beam (FIB) instrument. A 2-3 µm thick platinum coating was first deposited on the sample surface, and then a sample ~15 µm long × 3 µm wide × 8 µm deep was prepared, lifted out by welding to the Omniprobe tip and transferred to a copper grid. To minimize any sample bending cracking due to high residual stresses, only 3-5 µm wide windows were thinned to electron transparency (estimated as 50-150 nm thick) for the transmission electron microscopy and EDS characterization.

The FIB was also used to section the peaks of the laser textured samples to take cross-sectional SEM images and for EDS analysis. Similar to the TEM lift-out procedures, it included the steps of platinum layer deposition and gallium ion milling. The difference is to use EDS point, line and map scans on the sectioned surfaces instead of making a TEM foil. The FIB equipment also has an EDAX EDS detector similar to the JEOL JSM-7000 field-emission SEM.

3.6.5 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was used to analyze the microstructures, phases and compositions of the FIB-prepared TEM foils. Bright field (BF), dark field (DF), selected area diffraction pattern (SADP), microdiffraction pattern, convergent beam diffraction pattern images and EDS point measurements were taken using a Philips CM12 TEM (120 kV) and a Philips CM200 TEM (200 kV). To help identify the phases revealed by electron diffraction patterns, JEMS software was used to simulate the diffraction patterns.

EDS point, line and map scans were used to analyze the microstructures and compositions of the various interface regions using an FEI Talos TEM with spatial resolution of 0.12 nm. Besides BF and DF images, high angle angular dark field (HAADF) images were also taken using the Talos. The contrast in the HAADF images indicates Z-contrast.

3.6.6 X-ray Photoelectron Spectrometry (XPS)

The compositions of the polished and thermally-treated #1 AlCrN coatings on the H13 tool steel coupons were investigated using a PHI model 5800 X-ray Photoelectron Spectroscopy (XPS) system using an Al Kα x-ray source. An argon ion beam was used to gently remove the surface of the coating to generate depth-resolved information during the XPS characterization. The sputter rate at 5 kV was calibrated at
~2 nm per minute for a standard SiO$_2$ sample. It was presumed that the sputter rates for the AlCrN coating and the surface oxide layers were approximately the same as that of SiO$_2$; then, the depth of the AlCrN coating sputtered can be estimated, e.g. ~10 nm for five minutes of sputtering. Since the primary reason to use XPS was to determine the oxygen, nitrogen, and Al/(Al+Cr) ratio, only high-resolution spectra for carbon, aluminum, chromium, nitrogen, and oxygen were recorded. Carbon is a common surface contaminant when the samples are exposed to air, so the carbon concentration was excluded and only four other elements were normalized and studied.

3.6.7 Nanoindentation

The hardness (H) and Young’s modulus (E) of the coatings were measured using an MTS Nano Indentation XP (TestWorks®4, Version 4.06A) equipped with a diamond Berkovich tip. The indentation depths were supposed to be less than 10 percent of the total thickness of the coating to avoid any influence from the substrate [97]. In this study, typical indent depths were set at 100-300 nm, and a Poisson ratio of 0.25 was used as an estimated value for all the coatings. For each coating, sixteen random indents were made and at least ten points were used to measure the average H and E values. A fused silica standard sample was employed to calibrate the tip as it has known Young’s modulus of 72 ± 2 GPa.

3.6.8 Calo Test

Calo testing is a simple and inexpensive means for coating thickness measurements that has been well accepted and widely used in the hard coating industries. The Calo test was conducted at Tribologix Inc, Golden, CO, for the #1 AlCrN coating using a 20 mm-diameter WC ball, a low speed and 0.05 µm diamond paste as the slurry for five minutes. After the test, the sample was ultrasonically cleaned in acetone followed by alcohol, dried in flowing nitrogen gas, and examined by optical microscopy. Since the ball radius (r) is 20 mm, and the outer diameter ($d_1$) and inner diameter ($d_2$) can be measured due to the different colors or light reflections and the coating/layer thickness (t) can be calculated using a simple mathematical equation as Equation 3.2 along with the geometry drawing shown in Figure 3.13.

$$ t = \sqrt{r^2 - \frac{d_2^2}{4}} - \sqrt{r^2 - \frac{d_1^2}{4}} $$  \hspace{1cm} (3.2)
3.6.9 3D Optical Profilometer

The surface roughness ($R_a$ and $R_z$) of the coatings was measured using a 3D optical profilometer (WYKO profiler, A5500020 model). $R_a$ is the average roughness, the mean height calculated from the whole measured array. It is the arithmetic average of the absolute values of the heights within the area measured from the mean surface. $R_z$ is the average maximum height of the profile over the entire area. It is the arithmetic average of the greatest peak-to-valley distances. The surface roughness of the thirteen samples used for the initial aluminum adhesion test was characterized using the profilometer with area of $736 \times 480$ and the sampling of 3.32 µm. The filter of curvature & tilt was used. Figure 3.14 shows the typical 3D plot for the #1 AlCrN coating with $R_a$ ($17 \pm 3$ nm) and $R_z$ ($1.67 \pm 0.62$ µm) measured.

Figure 3.14 The 3D plot of the #1 AlCrN coating characterized by optical profilometry.
3.6.10 Pin-on-Disk Wear Test

The tribological properties of the coatings were examined using pin-on-disk testing in accordance with ASTM G-99 standard procedures. The test equipment was a custom-made apparatus at Tribologix.com. Tests on the #1 AlCrN coating from Supplier 1 were conducted using 6.35 mm (0.25 inch) WC and Si$_3$N$_4$ balls at an applied load of 1 N normal to the surface with 400 rpm and relative humidity of 40 percent for 10,000 cycles. Thus, each test took about 25 min. The diameters of the wear tracks were 10 mm for WC and 18 mm for Si$_3$N$_4$. The coefficient of friction was recorded as a function of number of cycles. The wear track profiles were measured with the optical profilometer. Wear rates were calculated based on the cross-sectional wear volume of the race track and the total distance abraded by the balls.

3.6.11 Rockwell C Adhesion Test

The Rockwell C indentation test is widely accepted by coating engineers and scientists as a destructive test for evaluating the coating adhesion to the substrate. The test was developed in Germany and is called the VDI 3198 indentation test [98]. This test method uses a standard Rockwell C hardness tester with maximum applied load of 150 kg to cause the coating/layers damage next to the edge of the indentation. Then, the damage area is visually evaluated using an optical microscope. Heinke et al. [99] defined the coating adhesion strength quality using HF index, from HF 1 to HF 6 based on the coating delamination and cracking network after the indentation test (as shown in Figure 3.15). The lower the HF value, the better adhesion the coating has. The coatings with HF 1-HF 4 are often considered as having “sufficient” adhesion to the substrate, while those with HF 5 and HF 6 are considered to poor adhesion.

![Figure 3.15](image)

Figure 3.15 Adhesion strength quality (HF 1-HF 6) based on the delamination and crack network after Rockwell C indentation test [99].
CHAPTER 4: DIPPING TEST

In an attempt to evaluate the potential of liquid aluminum alloys to wet and adhere to steel substrates, simple dipping tests were evaluated initially. This chapter describes the results from the immersion of steel pins in a liquid aluminum alloy bath. The effort reported in this section includes two studies: (1) uncoated steel pins, and (2) steel pins painted with various powder materials.

4.1 Uncoated Steel Pins

The uncoated steel pins were dipped into liquid A380 aluminum alloy held at 700°C. The immersion time ranged from one to sixty minutes. The photographs shown in Figure 4.1 display the conditions of the pins before and after the dipping test, as well as after being cleaned using a KOH solution. Aluminum was observed to have adhered to all the pins after extraction from the bath (Figure 4.1b and Figure 4.1e), independent of the dipping period. After the adhered alloy was dissolved in the KOH solution, it was found that no obvious soldering or pits had formed on the surface of the pin dipped for the shorter period (one minute dipping, see Figure 4.1c). However, soldering was observed on the surface of the pin dipped for 60 minutes (see the light gray color on the pin shown in Figure 4.1f). The fact that aluminum was observed to adhere to the surface of the pins independent of whether or not soldering or pit formation occurred suggests that the aluminum adhesion behavior is strongly affected by the physical shrinkage of the aluminum around the pin during solidification and cooling, independent of the soldering reaction.

4.2 Powder-Painted Steel Pins

To evaluate the impact of coatings on adhesion, a number of powder materials (listed in Table 3.1) were coated onto the surface of steel pins, and the coated pins were dipped in a bath of molten aluminum for ten seconds. The results are shown in Figure 4.2. After the coated pins were taken out of the bath, no aluminum alloy was observed to have adhered to any of these powder materials. One possibility is that all these powder materials are inert to and are not wetted by the liquid aluminum. However, it is more likely that the lack of aluminum adhering to the powder-coated pins was controlled by the fact that the powders were not strongly attached to the pins, and that any aluminum that did adhere to the powders fell off during extraction of the pins from the aluminum melt. This mechanism is discussed in more detail in the following section.
Figure 4.1 Photographs of the uncoated steel pins dipped in the A380 aluminum alloy for one minute: (a) before the test, (b) after the test and (c) after KOH cleaning; and sixty minutes: (d) before the test, (b) after the test and (f) after KOH cleaning.

Figure 4.2 Photographs of the two steel pins painted with powder materials before (a) and after (b) the dipping test.
4.3 Discussion and Summary

When uncoated steel pins were used for the dipping test, the aluminum alloy was observed to adhere around the pins, as shown in Figure 4.1. A schematic diagram (Figure 4.3) shows three possible conditions that can occur for the bare dipped pins: (I) no pits or chemical reactions occur, (II) pitting corrosion, and (III) chemical reaction with the formation of a continuous reaction layer (soldering). However, as noted above, aluminum was always observed to adhere to the uncoated pins, independent of dipping time or presence of any soldering, and so this observation suggests that the adherence occurs due to physical shrinkage of the aluminum around the pins during solidification and cooling, and not because of any chemical reaction between the aluminum and the steel.

![Figure 4.3 Schematic diagram of aluminum adhesion showing three possible types of behavior for uncoated steel pins: (I) no pits or chemical reactions, (II) pits, and (III) chemical reaction with formation of continuous reaction layer (soldering).](image)

On the other hand, when powder-coated pins were used in the dipping test, aluminum adhesion was never observed. Figure 4.4 shows a schematic diagram of a different mechanism for the powder-coated pins before and after dipping in the aluminum alloy bath. The powder materials painted on the pins will be either inert or reactive to the liquid aluminum. If inert, no interfacial layer would form between the alloy and the powder surface layer, as shown by Type I behavior in Figure 4.4, and upon extraction from the bath, the powder-coated pin would have no adhered aluminum. A second possibility is that the liquid aluminum does react with the powder, and in this case a reaction layer (blue color) would form between the alloy and powder (as shown by Type II behavior in Figure 4.4). The extent of the reaction and the thickness of the
reaction layer will largely depend on the test temperature, the dipping period and the coating material. However, if the powder is only loosely attached to the pin, when the pin is extracted from the aluminum bath, the surface powder is likely to fall off, along with any attached aluminum. Therefore, it is suggested here that, no matter which mode of behavior the powder experiences (I or II), after the pin is extracted from the bath, some of the loosely-packed powder will fall off, and so after extraction from the melt, no aluminum adhesion to the pin will be observed.

Figure 4.4  Schematic diagram of the two modes for a steel pin painted with powder materials before and after the dipping test: (I) powder material is inert to liquid aluminum; and (II) powder material is reactive with liquid aluminum.

Therefore, it was concluded that the simple dipping test is not a good method to evaluate for adhesion of aluminum either bare steel or coated steel substrates, and so it was discontinued.
CHAPTER 5: SESSILE DROP TEST

This Chapter describes the results of sessile drop testing. Sessile drop testing is typically used to investigate the wetting behavior of liquid phase materials onto flat solid substrates such that contact angles can be measured to quantify surface energies and wetting behavior of the liquid–solid interface. This test can be performed at ambient and elevated temperatures. High contact angles over 90° predict poor wetting of the liquid on the solid, while lower than 90° suggest good wetting. For the coatings used in die casting applications, contact angles over 90° are desirable in contact with the liquid aluminum. The sessile drop test was conducted in this study to measure the wetting behavior of A380 aluminum alloy onto 304 stainless steel substrates under flowing argon gas or high vacuum.

5.1 Argon Gas Atmosphere

Figure 5.1 shows the wetting behavior of a small cube made of A380 aluminum alloy on a Type 304 stainless steel substrate at temperatures up to 1200°C. Direct observations revealed no hemi-spherical shape of the molten alloy for the whole range of temperatures. The solid oxide scale on the surface of the alloy cube likely prevented the alloy from spreading and wetting the substrate. Since no equilibrium wetting conditions were achieved, no contact angles were measured from this study.

Figure 5.1 Sessile drop tests of a small A380 aluminum alloy cube on a Type 304 stainless steel coupon at various temperatures: (a) 550°C, (b) 750°C, (c) 800°C, (d) 950°C, (e) 1050°C and (f) 1200°C.
5.2 Vacuum Atmosphere

To effectively minimize the oxide effect, further tests were attempted using a turbo pumped vacuum chamber to achieve an intermediate vacuum environment (10\(^{-5}\) Torr range). These experiments were conducted at The Aluminium Research Centre – Regal, Canada. Solid pieces of aluminum were placed on “mirror-like” polished H13 tool steel coupons, transferred into a tube, and pumped to 10\(^{-5}\) Torr. Photographs of the typical wetting conditions are shown in Figure 5.2. The contact angle at 700°C was measured as 124.9°, indicating a non-wetting property of the liquid aluminum to the H13 tool steel. This value at 700°C does not seem realistic under high temperature die casting conditions and is thought to be incorrect due to the probable effect of the oxide layer on the aluminum alloy at the alloy-H13 tool steel interface. The profile of the liquid aluminum became nearly hemi-spherical only at temperatures higher at 750°C. Hence, 10\(^{-5}\) Torr vacuum level may only minimize the oxide layer effect, but is insufficient to prevent it and its effects on contact angle measurements at the die casting temperatures of 700°C or below.

![Figure 5.2 Sessile drop tests of a small piece of aluminum on polished H13 tool steel coupon at various temperatures: 460°C, 650°C, 700°C, 750°C, 800°C, and 850°C (measured contact angle is on the image right)](image)

5.3 Discussion and Summary

In this portion of the study, two different experimental procedures were attempted using either flowing argon gas or medium vacuum conditions. However, for both experimental conditions, no ideal (or equilibrium) hemi-spherical profiles of the alloy droplets were obtained due to the oxide scale on the aluminum alloy surface at temperatures of ~700°C or lower (die casting processing temperatures).

As is well known, a thin oxide layer is always present on aluminum exposed to air, and it grows thicker when the alloy is heated in an oxygen containing environment. The primary goal of the inert argon
gas and vacuum system was to reduce the partial pressure of the oxygen in the tube furnace, thereby generating thinner oxide scale. However, neither experiment worked well in either argon or under vacuum based on thermodynamic considerations, kinetics and practical view points. Ellingham diagrams plot the Gibbs free energy change (ΔG) for oxidation reaction of pure metal versus temperature. Since the ΔG of Al₂O₃ is much more negative than most of other oxides at 700°C, it is impossible to prevent the formation of the aluminum oxide using either hydrogen gas or carbon monoxide. Shi et al. [2] calculated that the equilibrium oxygen partial pressure at a higher temperature of 800°C has to be lower than 5×10⁻39 Pa to avoid aluminum oxidation. Thus, the low oxygen partial pressure to avoid aluminum oxidation cannot be achieved either under flowing inert argon gas or under vacuum. The rate of aluminum oxidation often increases as temperature increases, so only a small amount of oxygen in the system will enable the rapid growth of an aluminum oxide scale when the alloy is heated. Oxygen from the out-gassing of the tube furnace inner wall might also be abundant enough for severe alloy oxidation. Therefore, the previously-mentioned thin aluminum oxide layer covered the alloy (as shown in Figure 5.3) could most likely grow thicker due to high partial pressure of oxygen during the experiments at higher test temperatures, resulting in a nearly spherical shape or irregular shape depending on the thickness of the oxides. However, no matter which shape the liquid alloy exhibits, the thick oxide layer serves as a physical barrier between the alloy melt and the test coupon, thus the measured contact angle is not the equilibrium contact angle between the alloy and the substrate.

Researchers have preferred to use higher temperatures (over 1000°C) for the contact angle measurements of aluminum wetting on the various materials [74, 87, 88]. The reason is that at temperature ranges of 800-1000°C, the native aluminum oxide layer is reported to be frequently disrupted due to the formation of a gaseous sub-oxide: 4Al(l)+Al₂O₃(s)=3Al₂O(g). Thus, elevated temperatures, e.g. over 1000°C might result in more reliable wetting condition at the interface having less solid oxides and fewer test errors in contact angle measurements. However, such high temperatures are not representative of the HPDC in which most of the melted aluminum is actually held in the range of 600-700°C prior to casting, and therefore further consideration for the sessile drop testing was not pursued.

Figure 5.3 presents a schematic diagram showing the evolution of the oxide layer during the sessile drop test at temperatures of 550-700°C. When the solid alloy cube is heated from room temperature to liquid state: the oxide scale on the alloy surface grows thicker due to the residual oxygen in the test apparatus. It should be noted the thickness of oxide scale on the faceted liquid alloy surface is thicker than that on the hemi-spherical alloy, which in turn prevents its achieving equilibrium spreading and wetting conditions against the steel substrates. Most likely due to the oxide effect at the alloy/substrate interface, no correct contact angles can be measured.
Figure 5.3  Schematic diagram of the evolution of oxide scale on the aluminum alloy surface in the sessile drop equipment. Note: at elevated temperatures, either hemi-spherical alloy surface is obtained or faceted liquid alloy or depending on the thickness of oxide scale on liquid alloy surface.

In summary the sessile drop test is not a good means to predict the aluminum adhesion behavior at the die casting temperatures ($\leq 700^\circ$C) because of the oxide scale effect on the melt alloy surface independent of the conditions of either inert environment or vacuum.
CHAPTER 6: ALUMINUM ADHESION TEST – UNCOATED AND PVD-COATED H13

This chapter describes the results of the newly-developed aluminum adhesion test (AAT). It is a simple approach that could be used to effectively evaluate or predict molten aluminum’s adhesion to various materials. The ultimate goal of the AAT development was to better understand the interactions between various substrates and the molten aluminum alloys and more reliably predict the aluminum adhesion behavior of various coatings that are used in actual die casting operations, especially for the conditions of lube-free die casting. A variety of uncoated and PVD-coated H13 tool steel coupons were investigated using this new AAT approach and their aluminum adhesion strength was quantified and ranked using an ex-situ mechanical test.

6.1 Preliminary Results

Thirteen types of specimens were evaluated using AAT, including a bare H13 tool steel coupon (baseline) and twelve hard-coated H13 coupons. The breaking strengths of the solidified alloy to the different specimens were recorded using a mechanical tensile test after AAT and then ranked in order of increasing strength in Table 6.1 (see page 61) along with the information of coating method and treatment, coating composition and coating thickness (if coated). Due to the semi-quantitative nature and inaccuracy of EDS for light elements, only aluminum, chromium, titanium, and tungsten concentrations were quantified by EDS, while boron and nitrogen contents were uncertain as subscripted with an “x”.

From Table 6.1, it can be concluded that there were at least three coatings (#1 AlCrN, #2 AlTiN, and #3 CrWN) that appeared to have no alloy to coating adhesion strength (i.e. no obvious adhesion between the solidified alloy and the substrate). Two weakly adhering samples (#4 AlTiN and #12a labeled as *) broke after the AAT during handling. In addition, a fifth coating (#5 TiAlN) exhibited extremely low alloy to coating adhesion strength. Note that the maximum breaking strength (or aluminum adhesion strength) for #7 bare H13 tool steel coupon was not the highest, albeit it was considered as a baseline. The strongest strength of 2.54 MPa was obtained for the #13 TiB2 coating. Additionally, it should be noted that two commercially-used die coatings (#10 CrN and #12 CrAlN, both from Supplier 5), which are commonly used on die core pins and inserts under lubricated conditions, showed relatively strong adhesion behavior.

In the following sections, the individual AAT results, along with metallographic characterizations, are discussed in terms of possible reasons for the range in adhesion strengths.
Table 6.1 – 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

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Supplier</th>
<th>Method &amp; Treatment</th>
<th>Composition</th>
<th>Thickness [μm]</th>
<th>Breaking Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlCrN</td>
<td>1</td>
<td>CAE</td>
<td>Al$<em>{0.67}$Cr$</em>{0.33}$N$_x$</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>AlTiN</td>
<td>2</td>
<td>CAE</td>
<td>Al$<em>{0.68}$Ti$</em>{0.32}$N$_x$</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>CrWN</td>
<td>2</td>
<td>Nitriding + CAE</td>
<td>Cr$<em>{0.97}$W$</em>{0.03}$N$_x$</td>
<td>6.7</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>AlTiN</td>
<td>3</td>
<td>CAE</td>
<td>Al$<em>{0.62}$Ti$</em>{0.38}$N$_x$</td>
<td>3.3</td>
<td>0*</td>
</tr>
<tr>
<td>12a</td>
<td>AlCrN</td>
<td>5</td>
<td>Nitriding + CAE</td>
<td>—</td>
<td>—</td>
<td>0*</td>
</tr>
<tr>
<td>5</td>
<td>TiAlN</td>
<td>3</td>
<td>CAE</td>
<td>Ti$<em>{0.56}$Al$</em>{0.44}$N$_x$</td>
<td>1.8</td>
<td>0.01</td>
</tr>
<tr>
<td>12b</td>
<td>AlCrN</td>
<td>5</td>
<td>CAE</td>
<td>—</td>
<td>—</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>CrN</td>
<td>4</td>
<td>CAE + Fine Polish</td>
<td>CrN$_x$</td>
<td>4.4</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>H13</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>Cr</td>
<td>CSM</td>
<td>MS</td>
<td>Cr</td>
<td>2.2</td>
<td>0.12</td>
</tr>
<tr>
<td>9</td>
<td>CrWN</td>
<td>4</td>
<td>CAE + Fine Polish</td>
<td>Cr$<em>{0.95}$W$</em>{0.05}$N$_x$</td>
<td>4.2</td>
<td>0.26</td>
</tr>
<tr>
<td>10</td>
<td>CrN</td>
<td>5</td>
<td>Filtered CAE</td>
<td>CrN$_x$</td>
<td>5.0</td>
<td>0.78</td>
</tr>
<tr>
<td>11</td>
<td>TiN</td>
<td>CSM</td>
<td>MS</td>
<td>TiN$_x$</td>
<td>0.6</td>
<td>0.84</td>
</tr>
<tr>
<td>12</td>
<td>AlCrN</td>
<td>5</td>
<td>CAE + Fine Polish</td>
<td>Cr$<em>{0.54}$Al$</em>{0.46}$N$_x$</td>
<td>5.1</td>
<td>1.30</td>
</tr>
<tr>
<td>13</td>
<td>TiB$_2$</td>
<td>6</td>
<td>MS</td>
<td>TiB$_x$</td>
<td>1.5</td>
<td>2.54</td>
</tr>
</tbody>
</table>

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

6.2 Characterization of Uncoated H13 Tool Steel (#7, Baseline)

During the AAT, it was found that the solidified A380 aluminum alloy cylinders adhered to the bare H13 tool steel coupons. Photographs of the stuck bare H13 tool steel samples before and after mechanical testing are shown in Figure 6.1 along with the typical load vs. time curves. After testing, ie, the aluminum alloy/H13 tool steel joint separated (Figure 6.1b), a round fracture area with a grey-white color was observed, quite different from the adjacent areas that were brown due to the oxidation of the H13 tool steel in air. Two bare H13 samples were tested and the loads at fracture were 63.3 N and 81.6 N, converting to aluminum to substrate adhesion strengths of ~0.12 MPa and ~0.15 MPa.

One of these samples was cold mounted, sectioned, polished, and subsequently characterized using SEM and EDS. As observed in the photograph shown in Figure 6.2a, the interface between the A380 aluminum alloy and the bare H13 tool steel substrate contains no obvious gaps after the AAT. However, several voids can be seen in the A380 cylinder. Their size and shape indicate that they are likely gas porosity similar to the results Granath et al. reported [100]. Soldering reactions did occur between the A380 aluminum alloy and H13 tool steel as shown in Figure 6.2b-f. At higher magnifications, e.g. Figure 6.2c
Figure 6.1 Photographs of the bare H13 tool steel coupon with adhered A380 aluminum alloy (a) before and (b) after the mechanical test, and (c) the load as function of time curves.

Figure 6.2 Photograph of the cold mount sample (a) and (b)-(f) cross-sectional SEM backscattered electron images (BEIs) of the interface between the A380 aluminum alloy and a bare H13 tool steel coupon.

and Figure 6.2e-f, two reaction layers were observed and formed between the alloy and the H13 tool steel substrate. The compositions of the two layers (defined as the composite layer and the dense layer, respectively, and labeled in Figure 6.2c) were measured by EDS by averaging the data from at least five measurements. The dense reaction layer adjacent to the H13 tool steel substrate has an approximate
composition of (at.%) Al-20.1Fe-13.4Si-1.1Cr, while the second composite layer next to the A380 alloy is comprised of a mixture of α-Al (darker phase) and Al-Fe-Si-Cr intermetallics (brighter area). The brighter intermetallic in this composite layer has a composition of (at.%) Al-14.5Fe-10.9Si-2.8Cr. Nazari and Shabestari [90] reported similar soldering layers formed at the interface of H13 tool steel and A380 aluminum alloy at 680°C in their dipping tests. The morphologies and compositions of the reaction layers here after the AAT are consistent with the layers they reported. Han et al. [101] reported that the soldering formation was attributed to the diffusion of aluminum into the H13 tool steel substrate and dissolution of iron from the H13 tool steel substrate into the A380 aluminum melt, and the intermetallic reactions that occur accordingly. The big particles dispersed in the A380 aluminum alloy were also identified by EDS, and have a similar composition to the Al-Fe-Si-Cr intermetallic phase observed in the composite layer. These dispersed intermetallic particles could have originated either from the nearby reaction layer or from reaction of excess iron that diffused into the melt.

Additionally, as shown in Figure 6.2d-f, cracks were present between the H13 tool steel and the dense intermetallic layer at the sample edge, as well as within the dense intermetallic layer itself, but these cracks do not extend into the composite layer. These cracks are most likely caused by thermal stresses developed during the cooling process after solidification, due to the coefficient of thermal expansion (CTE) mismatch between the low CTE intermetallic layer and the H13 tool steel (~12.6×10^-6 °C^-1) [102]. Seifeddine and Svensson [103] mentioned the brittle nature of the intermetallics and therefore this likely contributes to the cracking behavior. The formation of both soldering and cracks found in this study suggests the presence of two actual problems in die castings. On the one hand, the formation of the composite intermetallic layer at the interface presumably leads to aluminum adhesion to the die (soldering). On the other hand, both the intrinsic brittle nature of the intermetallic and the CTE mismatch between the casting and the die steel lead to the intermetallic cracking and delaminating during cooling. Song et al. [21] reported that in the actual die casting process the delamination of the intermetallic layer enables fresh secondary contact of the alloy with the H13 tool steel surface, enhancing both corrosion and erosion of the die casting die. As noted in Table 6.1, the adhesion strength of the solidified alloy to a bare H13 tool steel coupon was significantly lower than some of the coated samples (#9-#12 coatings), presumably due to these pre-existing cracks found at the aluminum alloy/H13 tool steel interface as shown in Figure 6.2d-f and the brittle nature of the intermetallics in the dense reaction zone.

The EDS maps of the area (Figure 6.3) with intermetallic formation adjacent to the H13 tool steel inculcate that the composite layer contains α-Al (darker phase) and the Al-Fe-Si-Cr intermetallic (brighter area), and the dense layer next to the H13 tool steel substrate appeared to be chemically uniform. However, the interesting phenomenon observed was the continuous Si-rich layer at the interface between the alloy
and the composite layer; the reason for the silicon segregation at the interface is not clear at this time and warrants future investigation.

![Cross-sectional SEM backscattered electron images (BEIs) of the interface between the A380 aluminum alloy and a bare H13 tool steel coupon and the EDS mapping at the two interfaces between: (a) A380 aluminum alloy and the composite layer, and (b) dense layer and H13 tool steel substrate.]

To identify the exact nature of the intermetallic phases in the dense and composite layers, and to better understand why the cracks only initiate and propagate at the dense intermetallic layer close to the H13 tool steel substrate, transmission electron microscopy (TEM) was employed. A thin TEM foil was prepared by focused ion beam (FIB) across the dense layer/H13 tool steel interface from the location indicated by the red line labeled in the upper left inset of the backscattered electron (BSE) image in Figure 6.4 (see page 66). Bright-field TEM imaging shows that the Al-Fe-Si-Cr dense layer actually consists of a fine-grain layer (with thickness of about 1 µm) next to the H13 tool steel substrate and an thicker upper layer of coarser columnar grains. Using selected area diffraction, these phases were identified...
as shown in Figure 6.4. The thinner layer adjacent to H13 tool steel was identified as Al$_{13}$Fe$_4$ (C2/m), whose diffraction pattern down the [001] zone axis matches the pattern simulated using the JEMS software. The Al-Fe binary phase diagram, as shown in Figure 6.5 (see page 67) [104], confirms the possibility of the formation of Al$_{13}$Fe$_4$ intermetallic next to the H13 tool steel substrate. The coarse grains in the upper thicker layer were indexed as two separate phases, the Al$_8$Fe$_2$Si-type (P6$_3$/mmc) and Al$_{19}$Fe$_4$MnSi$_2$-type (Im-3), with their diffraction patterns also shown in Figure 6.4. Although no obvious difference in chemical composition was found by EDS analysis for the two types of grains due to the overlapping of the grains and the thick TEM foil, the dense layer actually being a mixture layer having both cubic and hexagonal Al-Fe-Si intermetallic phases was confirmed by randomly choosing grains and performing diffraction analysis.

TEM work was performed on the intermetallic(s) in the composite layer as well as the dispersed particles in the alloy and confirmed the intermetallics in both regions are the Al$_{19}$Fe$_4$MnSi$_2$-type (Im-3) phase (not shown here). Based on the previous SEM and TEM analyses, the phase distribution at the A380/H13 interface can be summarized using the schematic diagram shown in Figure 6.6b (see page 67). The soldering layer is comprised of four separate layers as follows:

1. Layer 1: a dense layer with a thickness of about 1 µm next to the H13 tool steel, having small grains of the Al$_{13}$Fe$_4$-type phase;
2. Layer 2: second thicker but less dense layer consisting of a mixture of the Al$_8$Fe$_2$Si (P6$_3$/mmc) and Al$_{19}$Fe$_4$MnSi$_2$ (Im-3) columnar grains and having the overall composition of (at.%) 65.4%Al-20.1%Fe-13.4%Si-1.1%Cr.
3. Layer 3: a composite layer with a mixture of Al$_{19}$Fe$_4$MnSi$_2$-type (Im-3) intermetallic grains and α-Al grains. The composition of the Al$_{19}$Fe$_4$MnSi$_2$-type intermetallic phase is (at.%) 71.8%Al-14.5%Fe-10.9%Si-2.8%Cr.
4. Layer 4: a continuous silicon segregation layer.

Note that the previously-observed crack area (highlighted in red in Figure 6.6a) contains a complex mixture of the phases Al$_{13}$Fe$_4$, Al$_8$Fe$_2$Si-type and Al$_{19}$Fe$_4$MnSi$_2$-type intermetallics. Cracks initiate and propagate in this complex area due to the brittle nature of these intermetallics and the CTE mismatch between the H13 tool steel and the intermetallic.
Figure 6.4 Cross-sectional SEM backscattered electron image (BSE) and bright-field TEM image of the interface between the A380 alloy and a bare H13 coupon and the corresponding electron diffraction images of the locations of a, b and c. (red rectangle area is the FIB lift-out area for the TEM foil)
Figure 6.5  Binary Al-Fe equilibrium phase diagram [104].

Figure 6.6  Backscattered electron (BSE) image of the crack zone at the interface between the A380 aluminum alloy and the bare H13 tool steel coupon and schematic diagram of the phase distribution at the interface.
6.3 Characterization of Cr-Coated H13 Tool Steel Coupon (#8, CSM)

The #8 elemental chromium coating showed similar aluminum adhesion strength to the bare H13 tool steel. After the AAT, one Cr-coated sample was cold mounted, sectioned, polished and characterized using optical microscopy and SEM on the as-deposited coating thickness. As shown in Figure 6.7a, the as-deposited chromium coating is about 2.2 µm thick and has a dense microstructure and a smooth coating surface. After the AAT with A380 aluminum alloy contact, it was found that the chromium coating was dissolved in the aluminum alloy, with no chromium layer left, and instead the solidified aluminum alloy was soldered to the H13 tool steel substrate. The dark layer adhered to the H13 tool steel substrate having the thickness ranging of 8-12 µm is considered as the reaction or diffusion zone formed by the chromium coating dissolving and reacting with the aluminum alloy as shown in Figure 6.7b.

![SEM image of fractured cross-section of the as-deposited chromium coating (a) and light optical microscopic image of the interface between the adhered A380 aluminum alloy and the reacted chromium coated H13 tool steel substrate (b).](image)

Thermodynamic analysis of the Al-Cr binary phase diagram indicates that liquid aluminum should react with chromium to form a number of Al-Cr intermetallic compounds as shown in Figure 6.8 (see page 69). Therefore, it is not surprising to find the chemical reaction or diffusion zone at the aluminum alloy/chromium coating interface as shown in Figure 6.7b.

The elemental distributions at the reaction/diffusion interface were revealed by SEM, EDS mapping and EDS line scanning with results shown in Figure 6.9 (see page 70). A chromium-deficient layer away from the H13 tool steel substrate is observed from the chromium map, confirming the chromium coating dissolution into the alloy and suggesting that chromium coatings are poor physical barriers to protect the H13 tool steel substrate. The EDS line scan (Figure 6.9c) shows a clear chromium-rich area at
certain distances away from the H13 tool steel substrate. The dense intermetallic layer formed adjacent to the H13 tool steel substrate is mainly Al-Fe-Si based intermetallics similar to what was found before for the bare H13 tool steel coupon (#7). One possible explanation for this layer is that after the coating reacted with the alloy and lost the barrier function, the alloy diffused through the chromium-rich reaction layer and further reacted with the H13 tool steel substrate to form Al-Fe-Si-Cr intermetallic layers at the new interface of alloy/H13.

Although no further TEM or XRD work was conducted to identify the phases at the alloy-coating interface, the conclusion is clear that chromium is not a good physical barrier to protect the H13 tool steel due to its high chemical affinity to aluminum.

### 6.4 Characterization of AlCrN-Coated H13 Tool Steel Coupon (#1, Supplier 1)

The #1 AlCrN coating from Supplier 1 was one of the best performers in the aluminum adhesion test, having a zero value for adhesion strength. After the AAT, the solidified A380 aluminum alloy was easily removed as shown in Figure 6.10c. There appears to be little change on the surface of the AlCrN-coated coupons in contact with molten A380 at 700°C for fifteen minutes, indicating the good thermal stability and oxidation resistance of this coating.
Figure 6.9  SEM image of the chromium-coated H13/A380 interface (a) along with the EDS maps (b) and line scan data (c). The red arrow in the SEM image indicates where the line scan was taken and the scan direction.

Figure 6.10  Photographs of the #1 AlCrN-coated H13 tool steel coupon provided by Supplier 1 for the aluminum adhesion test: (a) as-received state before the test, (b) and (c) after the test

The architecture of the #1 AlCrN coating was provided by Supplier 1 and has a titanium adhesion layer, followed by a TiN layer, an intermediate layer consisting of TiN/AlCrN multilayers, and the top AlCrN working layer. The cross-section of this AlCrN coating and its composition (see Figure 6.11) were characterized using SEM and EDS respectively after fracturing the sample in liquid nitrogen. The coating
shows the dense columnar growth structure (Zone T or Zone 2) [60]. However, due to the low resolution of the EDS mapping, the individual layers could not be distinguished.

The coating thickness and layer stack of the as-deposited #1 AlCrN coating was also evaluated using the Calo test. Various layers can be observed after this test using optical microscopy as shown in Figure 6.12. The TiN layer is gold and the AlCrN layer appears brown (see Figure 6.12b), matching the coating information given by Supplier 1. With the geometry of the Calo test ball known, it is possible to determine that the coating consists of a ~500 nm TiN bottom layer, a ~450 nm TiN/AlCrN intermediate multilayer, and a ~600 nm AlCrN top layer. However, the titanium adhesion layer could not be observed presumably because of poor contrast relative to the substrate. The total thickness of the #1 AlCrN coating was assessed to be ~1.5 µm using Equation (3.2), consistent with the SEM observation (Figure 6.11).

![Figure 6.11](image1.png)  
**Figure 6.11**  
SEM image of the fractured section of the #1 AlCrN coating and the EDS elemental maps.

![Figure 6.12](image2.png)  
**Figure 6.12**  
Optical microscope images of the pattern on the as-deposited #1 AlCrN coating after the Calo grinding test: (a) low magnification (5×) and (b) high magnification (50×).
The X-ray diffraction patterns shown in Figure 6.13 are from the #1 AlCrN coatings before and after the AAT. The as-deposited AlCrN coating has the cubic CrN crystal structure with no trace of the hexagonal AlN diffraction peaks. This result suggests the existence of aluminum is in solid solution in CrN. Both the AlCrN layer and the adhesion appear to TiN layer have strong [111] textures. No new phases or texture changes were detected with comparison of the patterns before and after the AAT, confirming the excellent oxidation resistance, thermal stability and lack of aluminum alloy adhesion to this AlCrN coating.

![X-ray diffraction patterns](image)

Figure 6.13 X-ray diffraction patterns of the bare H13 tool steel and the #1 AlCrN coating before and after the aluminum adhesion test (AAT).

To systematically study the oxidation resistance of the #1 AlCrN coating, the coated H13 tool steel coupons were annealed in air for one hour at 800°C, 900°C and 1000°C. After annealing, the changes in the coatings were studied by grazing incidence X-ray diffraction analysis with an incident angle of 2° with results shown in Figure 6.14. The as-deposited coating has the B1 (NaCl) structure exhibiting (111), (200), (220) and (311) diffraction peaks. Again, these peaks can be indexed as cubic CrN phase indicating that the coatings are solid solutions of aluminum atoms in CrN. No extra new peaks were detected after the coating was annealed at 800°C for 1 hour, indicating that the AlCrN coating is stable to at least 800°C. At 900°C and 1000°C, however, hexagonal AlN, hexagonal Cr$_2$N and rhombohedral Cr$_2$O$_3$ phases were observed, indicating that the AlCrN coating partially decomposes and oxidizes at these temperatures.
Figure 6.14 X-ray diffraction patterns of the as-deposited #1 AlCrN coatings supplied by Supplier 1 and the same coatings after annealing at different temperatures.

Figure 6.15 compares the surface morphologies of the AlCrN coatings from Supplier 1 before and after annealing at 800°C, 900°C and 1000°C. Both macro-particles and pin-holes are present on the as-deposited coating surface, which is characteristic of cathodic arc evaporated coatings. The surface morphology of the coating annealed at 800°C for one hour is similar to that of the as-deposited coating, confirming that the oxidation resistance of this type of coating is at least stable up to 800°C. However, after annealing at 900°C, some coarse grains (50-200 nm) appeared on the coating surface, which are likely \( \text{Cr}_2\text{O}_3 \). When the annealing temperature increases to 1000°C, these grains become larger and fully cover the coating surface as shown in Figure 6.15d.

Finally, the tribological properties of the #1 AlCrN coating from Supplier 1 were examined using the pin-on-disk method in accordance with ASTM G-99 procedures. As shown in Figure 6.16, the coefficient of friction (COF) is in the range of 0.4-0.5 against a tungsten carbide ball (WC), and the wear rate is \( 5.7 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1} \). When switching the ball to a softer material (i.e., silicon nitride (Si\(_3\)N\(_4\))), the COF jumps to ~1.0 and the wear rate increases \( 1.3 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1} \). The low wear rate suggests a good erosion resistance when using this coating for die protection.
Figure 6.15  SEM images of the plan-view of the #1 AlCrN coatings supplied by Supplier 1: (a) as-deposited, and after annealed at (b) 800°C , (c) 900°C  and (d) 1000°C.

Figure 6.16  Pin-on-disk results for the #1 AlCrN coatings supplied by Supplier 1 using WC and Si₃N₄ balls: (a) coefficient of friction as a function of number of cycles, and (b) wear rate.

6.5  Characterization of TiB₂-Coated H13 Tool Steel Coupon (#13, Supplier 6)

As summarized in Table 6.1, the #13 TiB₂ coating from Supplier 6 displayed the highest aluminum to coating adhesion strength (2.54 MPa) among the thirteen types of tested samples. The photograph shown in Figure 6.17 is a top-view image of the TiB₂ coated coupon after the AAT and mechanical test. Obviously,
the solidified A380 aluminum alloy has adhered to the TiB$_2$ coating at the circular, light-gray colored area in the center of the coupon.

Figure 6.17 Photograph of the #13 TiB$_2$-coated coupon after aluminum adhesion test

Figure 6.18 shows SEM cross-sectional views of the TiB$_2$ coating both as-deposited and after thermal heating at 700° C in air for fifteen minutes. The sample having a rough fracture surface shown in Figure 6.18a was prepared by fracturing in liquid nitrogen, while the other sample shown in Figure 6.18b was prepared using a JEOL cross-section polisher, showing a much smoother surface. The as-deposited coating has a cauliflower-like growth microstructure showing porous grain boundaries. The thermally-treated sample has a porous reaction product on the coating surface with thickness of 200-300 nm. X-ray diffraction was conducted to identify this layer as the TiO$_2$ rutile phase. The formation of the porous TiO$_2$ rutile oxide layer on the coating surface indicates the poor oxidation properties of the TiB$_2$ coating in air.

Figure 6.18 Cross-sectional SEM images of the TiB$_2$ coated H13 tool steel coupon: (a) as-deposited coating, and (b) area exposed to ambient atmosphere at 700° C.
Figure 6.19 displays cross-sections of the aluminum alloy-adhered coating area that was also prepared using the JEOL cross-section polisher. The alloy seemed well adhered to the coated H13 tool steel substrate. As mentioned previously in Figure 6.17, the A380 aluminum alloy adhered to the coating with the highest aluminum adhesion strength of 2.54 MPa. The ultimate tensile strength of the A380 aluminum alloy is about 320 MPa. Therefore, the measured adhesion strength is much lower than the tensile strength of the alloy. Numerous grey color particles and some cracks (black color) were observed in the alloy side close to the H13 tool steel substrate (Figure 6.19a). These grey particles were identified as an Al-Fe-Si intermetallic phase using EDS analysis, with a composition close to that of the cubic Al$_{19}$Fe$_2$MnSi$_2$-type intermetallic previously identified for the #7 bare H13 tool steel sample. Thus, one possible explanation for the low measured breaking strength is the presence of possible gas porosity in the alloy at the alloy/coating interface, and the unexpected high concentration of brittle intermetallic particles close to the interface. From Figure 6.19b-c, a number of lighter-colored particles around 50-150 nm in size were also observed distributed along the interface between the A380 aluminum alloy and TiB$_2$ coating. Below the particles, a continuous phase or maybe the A380 aluminum alloy was found and appeared to penetrate into a depth of about 100 nm between the TiB$_2$ grains from the coating/alloy interface (see Figure 6.19c). It is postulated that this phase worked like a glue to join the alloy and the coating together via mechanical interlocking which may be the reason for the highest adhesion strength measured for this coating.

![Figure 6.19](image.jpg)

**Figure 6.19** Cross-sectional SEM images of the interface between A380 aluminum alloy and TiB$_2$ coating at the sticking area of H13 tool steel coupon prepared by cross-section polisher: (a) low magnification image, (b) high magnification, and (c) enlarged image of the interface.

Because the resolution in the SEM was inadequate to identify the phase and composition of the particles and the continuous phase present at the interface, the FIB was used to prepare a thin foil for TEM examination. Figure 6.20 shows a low-magnification SEM image of this FIB lift-out foil along with a
bright-field TEM image of the A380 aluminum alloy-TiB$_2$ coating interface. The compositions of two particles labeled as Particle 1 and Particle 2 at the interface were determined by EDS in the CM12 TEM.

Figure 6.21 shows the EDS spectrum from Particle 2 in Figure 6.20. Clearly, this particle mainly contains magnesium, aluminum and oxygen, along with two other contamination peaks (carbon and copper). The carbon peak may have come from a build-up due to TEM chamber contamination, which is common for TEM-EDS operation. The strong copper peak is from the copper grid used to hold the FIB-prepared TEM sample.

![Image](image_url)

**Figure 6.20** SEM image of the sticking TiB$_2$ sample foil prepared by FIB (a), and bright-field TEM of the alloy-TiB$_2$ interface (b).

![Image](image_url)

**Figure 6.21** EDS spectrum from Particle 2 in Figure 6.20.
TEM microdiffraction patterns (Figure 6.22) from four different zone axes, namely, [011], [121], [112] and [031] of Particle 1 (upper right), and three different zone axes: [001], [013] and [112] from Particle 2 confirmed that both particles have the spinel structure (MgAl$_2$O$_4$, space group of Fd-3m). The identified spinel phase here matches the previous composition findings that the particles consist of magnesium, aluminum and oxygen. Therefore, the particles at the alloy-coating interface are spinel (MgAl$_2$O$_4$). The source of the magnesium is believed to be from the A380 aluminum alloy, but it is not clear whether the particles formed during the pouring process due to oxidation of the alloy in air, or if they came from reaction of the alloy with a thin oxide layer on the TiB$_2$ surface.

Another TEM sample was made using a different FIB-lift out method via thinning from the H13 tool steel substrate side to the alloy side. Most of the H13 tool steel substrate was milled away as shown in Figure 6.23a. The A380 aluminum alloy was observed to adhere well to the TiB$_2$ coating although there are a few voids or gaps at the alloy-coating interface. In addition, voids present at the grain boundaries of the TiB$_2$ coating, indicate that there are an intrinsic characteristic of these coatings.

As elemental EDS map of this same area is shown in Figure 6.24. The titanium and boron maps both reveal the porous microstructure of the TiB$_2$ coating. The composition of the dispersed MgAl$_2$O$_4$ spinel particles (sizes of 100-250 nm) at the alloy-coating interface were confirmed by the EDS maps of magnesium, aluminum and oxygen. The magnesium and oxygen maps also indicate that some fine MgO was possibly located at these porous grain boundaries of the coating.
The SEM, TEM and EDS data shown above confirmed alloy penetration of the aluminum alloy into the gaps between the grain boundaries of the TiB₂ coating. This nanometer-size mechanical interlocking probably resulted in the high adhesion strength in the AAT. The particles found at the aluminum alloy/ TiB₂ coating interface were identified as spinel (MgAl₂O₄), but its formation mechanism is unclear at this moment.
6.6 Characterization of CrN-Coated H13 Tool Steel Coupon (#10, Supplier 5)

The #10 CrN coating supplied by Supplier 5 is commonly used in commercial die casting operations under normal lubrication conditions. However, this coating has alloy to coating adhesion strength of 0.78 MPa. The interface between the adhered alloy and the CrN coating was characterized using SEM, TEM and EDS, with the primary goal of understanding the interaction of the alloy with the coating.

Figure 6.25 displays SEM cross-section images of the interface between the aluminum alloy and the CrN coating of the #10 sample. There appears to be no gaps between the alloy and the coating, suggesting good contact.

A FIB lift-out from the interface was prepared and examined by TEM (Figure 6.26). The bright-field TEM image in (a) indicates that there are no obvious gaps or voids at the interface. At higher magnification (b), a silicon particle containing twins was observed; this result was confirmed by the SADF in (c).

The region outlined by the yellow rectangle has been enlarged (and rotated) in the middle image showing the coating-alloy interface. The yellow circle was chosen for selected area diffraction (SAD) (image shown on the right) to identify the phase in contact with the coating. The SAD pattern matches the diffractions of the silicon phase (Fd-3m space group) at the zone axis of [101]. Note also that the silicon contains twins (straight lines in the image). Finally, a number of 20-100 nm particles can be observed at the alloy/coating interface.

Figure 6.27 shows the coating-aluminum alloy interface at higher magnification where the CrN coating was in contact with the silicon particle. A number of particles were observed at the interface. The microdiffraction pattern of these particle matches the spinel phase of MgAl₂O₄ (Fd-3m) down a <112> zone. In addition, there appears to be a thin black interfacial layer between the coating and the particles.
Figure 6.26 Bright-field TEM image (a and b) of the #10 CrN-coated sample provided by Supplier 5 at the interface of the solidified alloy and the coating along with the selected area electron diffraction pattern (SAED) from the twinned particle. The SAED (c) is taken from the area circled in the middle image down to zone axis of [101].

Figure 6.27 Bright-field TEM image (a) of the #10 CrN-coated sample at the interface of the solidified alloy and the coating. The microdiffraction pattern (b) was taken from one of the small particles at the interface and was indexed as a <112> zone from spinel.

The Talos TEM was again used to perform a composition analysis across this layer. A new FIB sample was prepared and characterized. The new sample was a little different from the first because the contact area at the alloy-coating interface is an α-Al grain, rather than a silicon grain. In addition, a large Al-Fe-Si based intermetallic particle was observed close to the coating. EDS dot maps (Figure 6.28) and elemental line scans (Figure 6.29) were taken at or across the alloy-coating interface. The presence of
numerous spinel particles at the alloy/coating interface and a thin black continuous layer consisting of magnesium and oxygen were confirmed. The formation mechanism of the spinel particles and the MgO layer is not clear at this point. However, the strong adhesion strength of 0.78 MPa appears to be due to the intimate contact of the layers of alloy/MgO/CrN.

Figure 6.28  Bright-field TEM image and elemental x-ray maps of the interface between the A380 aluminum alloy and the coating for the #10 CrN-coating after the aluminum adhesion test (scale bar: 200 nm).

Figure 6.29  Elemental line scans across the aluminum alloy/coating interface of the #10 CrN-coating.
6.7 Characterization of AlCrN-Coated H13 Tool Steel Coupon (#12, Supplier 5)

The #12 AlCrN coating supplied by Supplier 5 is also commonly used in commercial die casting operations under normal lubrication conditions. As seen from Table 6.1, this coating exhibited strong adhesion to the A380 aluminum alloy with a high alloy to coating adhesion strength of 1.30 MPa (larger than the #10 CrN coating). Figure 6.30 exhibits cross-sectional view of the interface between the alloy and the AlCrN coating characterized using SEM. Again, similar to CrN coating from the same Supplier 5 as described in previous section, Figure 6.25 shows no gap between the alloy and the coating, suggesting good contact between the molten alloy and the coating. No obvious reaction layer was observed at the interface. It should be noted that the numerous white particles observed in Figure 6.30b were AlCrN coating debris, not spinel particles. The debris was likely formed by grinding damage on the coating during sample preparation using conventional grinding and polishing procedures.

Figure 6.30 SEM images of the cross-section through the interface between the alloy and the AlCrN coating (Supplier 5) at a low magnification (a) and a high magnification (b).

Again, the FIB was used to make a TEM foil from the alloy-coating interface. The TEM bright-field image in Figure 6.31 suggests good contact between the AlCrN and the solidified aluminum alloy (mainly α-Al grains), although occasional gaps or voids were observed at the interface as shown in Figure 6.31a. Different from the previous section on the CrN coating (#10), also from Supplier 5, where a continuous MgO layer and numerous spinel (MgAl₂O₄) particles were observed at the interface, no reaction layer was observed at the interface between the aluminum alloy and the AlCrN coating.

Figure 6.32 shows the EDS maps from the adhered alloy-AlCrN coating interface. Good contact between the alloy and coating was observed. No Mg segregation or enrichment was observed.
Figure 6.31  Bright-field TEM images of the interface between the AlCrN coating from Supplier 5 and the adhered A380 aluminum alloy at a low magnification (a) and a high magnification (b).

Figure 6.32  Bright-field TEM image and elemental x-ray maps of the interface between the AlCrN-coated H13 steel from Supplier 5 and the A380 aluminum alloy after the AAT.
In an effort to quantitatively assess the elemental distribution across the interface, a line scan was taken as shown in Figure 6.33. It was found that the interface was a maximum of 50 nm wide, but had very little interdiffusion between the coating and the aluminum alloy. In addition, there was no indication of either Mg or Si segregation at the interface. This suggests that the alloy adheres to the coating directly without any obvious interfacial reaction products.

Figure 6.33 Elemental line scan across the interface shown in Figure 4.31 (left dark side is AlCrN coating, right light side is A380 aluminum alloy).

6.8 Summary

To overcome the drawbacks of the dipping test and the sessile drop test, the aluminum adhesion test (AAT) was developed to quantitatively measure the level of adhesion of aluminum A380 casting alloy to the thirteen types of samples. In summary, the coatings tested using the AAT can be split into four groups:

- The first group includes the coatings #1 AlCrN, #2 AlTiN and #3 CrWN, which had zero alloy to coating adhesion strength.
- The second group consists of reactive metals (e.g. #7 bare H13 tool steel and #8 chromium-coated H13 tool steel), which can dissolve in the aluminum alloy and form intermetallic phases.
- The third group includes coating such as the TiB₂ coating that exhibited the strongest aluminum adhesion. This coating has a porous structure with nano-meter size mechanical interlocking that caused its strong aluminum to coating adhesion.
- The fourth group includes most of the ceramic coatings having dense coating microstructures, which seem chemically inert to the aluminum alloy, but have a range of adhesion strengths.
CHAPTER 7: FACTORS AFFECTING ALUMINUM ADHESION

In this Chapter, the influence of coating composition, surface oxides, and roughness on aluminum adhesion are discussed in some detail.

7.1 Factors Affecting Aluminum Adhesion

As described above, a large number of uncoated and coated conditions were evaluated using aluminum adhesion test (AAT). The adhesion strengths of the solidified alloy to these different specimens were recorded and listed in order of increasing strength in Table 6.1. As noted, several samples exhibited zero aluminum adhesion strengths; among these, the AlCrN coating (#1) from Supplier 1 appeared to be the best candidate due to its excellent oxidation resistance and good tribological properties. However, it was shown that there is another AlCrN coating (#12) from Supplier 5 listed in Table 7.1 that exhibited higher aluminum adhesion strength (1.30 MPa) and an attempt was made to understand the factors controlling this difference in adhesion performance. The factors considered included: (a) coating composition, (b) surface oxide structure and composition, (c) surface roughness, (d) coating microstructure, (e) coating defects, (f) coating architecture and (g) overall thermal history.

Table 7.1 summaries the composition and architecture differences between the two AlCrN coatings where it can be seen that coating #1 had a higher Al/Cr ratio than coating #12. In addition, coating #1 utilized a stack of TiN/Ti adhesion layers whereas coating #12 used a CrN/Cr adhesion layer.

<table>
<thead>
<tr>
<th>#</th>
<th>Formula</th>
<th>Composition [at.%]</th>
<th>Ratio Al/(Al+Cr)</th>
<th>Adhesion</th>
<th>Coating Architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Al_{0.63}Cr_{0.37}N</td>
<td>47.1 27.1 21.4 4.4</td>
<td>0.63</td>
<td>No</td>
<td>AlCrN-TiN-Ti</td>
</tr>
<tr>
<td>#12</td>
<td>Al_{0.46}Cr_{0.54}N</td>
<td>33.7 39.1 22.8 4.4</td>
<td>0.46</td>
<td>Yes</td>
<td>AlCrN-CrN-Cr</td>
</tr>
</tbody>
</table>

The AlCrN coatings from different suppliers (#1 and #12) had different aluminum adhesion behaviors and, therefore, it was speculated that there must be some difference that led to the surprisingly different behaviors.

The first possible mechanism controlling aluminum adhesion is the chemical composition of the AlCrN coating. The possible chemical reactions between aluminum alloy and the coating might cause the different adhesion strengths. The ternary diagram for the Al-Cr-N system is used to predict or estimate if
CrN coating will react with aluminum (note that AlCrN can be considered the CrN phase containing aluminum atoms in substitution solid solution). However, no ternary phase diagram was found at 700°C, but only one at 1000°C as shown in Figure 7.1. The phase diagram at 1000°C indicates CrN can react with aluminum and might form a number of Al-Cr intermetallic compounds (e.g. Cr₄Al₉, and Cr₉.₅Al₁₆) and AlN, suggesting the possibility of reaction at the AlCrN coating/aluminum alloy interface. However, it should be noted that the PVD coatings were prepared at highly non-equilibrium conditions and the ternary phase diagram might fail to predict the actual reactions due to slower kinetics at the deposition and application temperatures and environments. Therefore, the effect of the composition of the Al-Cr-N coating on aluminum adhesion is unclear.

Figure 7.1  Ternary Al-Cr-N equilibrium phase diagram at 1000°C [106].
The second factor identified earlier that could control adhesion is the formation of an oxide layer on the coating. When any of the coatings are exposed to air, a thin oxide will form on the coating surface. Therefore, this oxide layer could play a greater role in determining the adhesion properties compared with the bulk composition of the coating. In fact, an initial hypothesis used to explain the lower aluminum adhesion tendency of the AlCrN coating #1 was that the higher Al/Cr ratio produced more inert and non-wetting Al-rich oxides on the coating surface compared with the AlCrN coating #12.

The third possible mechanism controlling adhesion is the roughness of the coating, given that it is well established that surface roughness can play a major role on wetting [84]. Researchers have shown that surfaces may exhibit hydrophobic or hydrophilic behavior simply by adjusting the surface roughness [107].

The surfaces of the tested samples were characterized by SEM both plan view and at a 45°-tilt view prior to conducting the AATs, in (see Figure 7.2 below), in an effort to show both the surface morphology and defects. A bare H13 sample (#7) was used as the baseline as it had the smoothest surface finish. The Cr-coated sample (#8) also exhibited a very smooth surface, comparable to the bare H13 tool steel coupon. Most of the coatings produced by cathodic arc (from #1 to #6) have numerous macro-particles on the coating surfaces and are considerably rougher than those coatings prepared by magnetron sputtering (#8 and #10). Post-polishing was used to remove the macro-particles and increase the smoothness of the arc coatings to some extent as shown for coatings #6, #9 and #12. It should also be noted that the filtered arc coatings [56, 57], e.g. the CrN coating #10 from Supplier 5, had a relatively smooth coating surface with few macro-particles but numerous small craters. A number of pin-holes are present on the surface of the smooth sputtered TiN coating (#11). The porous microstructure of the #13 TiB$_2$ coating has been shown previously in Figure 6.18a, and has occasional nodular defects on the coating surface as seen in Figure 7.2 (13a and 13b).

![Figure 7.2 SEM images of the thirteen coated samples (#1 - #13) tested using the aluminum adhesion test in (a) plan-view and (b) 45°-tilt view.](image-url)
Figure 7.2 Continued.
Figure 7.2 Continued.
Figure 7.2 Continued.
The surface roughnesses of the various samples tested were also quantitatively measured using a 3D profilometer, with $R_a$ and $R_z$ values listed in Table 7.2. As defined previously in Section 3.4.9, $R_a$ is the arithmetic average of the absolute values of the heights within the area measured from the mean surface, and $R_z$ is the average maximum height of the profile over the entire area. Therefore, $R_a$ is equal to the smoothness of the coating surface under the ideal conditions of no macro-particles or pin-holes, and $R_z$ is equal to the distance of the highest peak of the macro-particles to the deepest valley of the pin-holes. Neither $R_a$ nor $R_z$ reflect the actual surface conditions of the tested samples, especially for the defect distribution on the sample surfaces (macro-particles and pin-holes). For example, the #1 AlCrN coating exhibited more surface macro-particles than the #12 AlCrN coating (see SEM images in Figure 7.2), and higher roughness values were expected for this coating. However, the $R_a$ for the #1 coating was $17 \pm 3$ nm, whereas it was $45 \pm 4$ nm for the #2 coating, and their $R_z$ values were close as $1.67 \pm 0.62$ µm and $1.76 \pm 0.39$ µm as listed in Table 7.2. Therefore, it appears problematic to compare the roughness of the coating using either $R_a$ or $R_z$. Finally, no clear relationship can be found between the measured $R_a$ and $R_z$ values and the various aluminum adhesion strengths measured using the AAT.

Table 7.2 – Surface roughness of the samples tested by aluminum adhesion test

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Supplier</th>
<th>$R_a$ [nm]</th>
<th>$R_z$ [µm]</th>
<th>Breaking Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlCrN</td>
<td>S1</td>
<td>$17 \pm 3$</td>
<td>$1.67 \pm 0.62$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>AlTiN</td>
<td>S2</td>
<td>$18 \pm 2$</td>
<td>$1.79 \pm 0.66$</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>CrWN</td>
<td>S2</td>
<td>$246 \pm 64$</td>
<td>$4.02 \pm 0.44$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>AlTiN</td>
<td>S3</td>
<td>$32 \pm 9$</td>
<td>$3.66 \pm 0.91$</td>
<td>0*</td>
</tr>
<tr>
<td>5</td>
<td>TiAlN</td>
<td>S3</td>
<td>$24 \pm 8$</td>
<td>$0.76 \pm 0.25$</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>CrN</td>
<td>S4</td>
<td>$69 \pm 5$</td>
<td>$1.77 \pm 0.26$</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>H13</td>
<td>—</td>
<td>$13 \pm 3$</td>
<td>$0.16 \pm 0.03$</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>Cr</td>
<td>CSM</td>
<td>$14 \pm 2$</td>
<td>$0.17 \pm 0.03$</td>
<td>0.12</td>
</tr>
<tr>
<td>9</td>
<td>CrWN</td>
<td>S4</td>
<td>$65 \pm 17$</td>
<td>$2.07 \pm 0.40$</td>
<td>0.26</td>
</tr>
<tr>
<td>10</td>
<td>CrN</td>
<td>S5</td>
<td>$41 \pm 17$</td>
<td>$0.98 \pm 0.33$</td>
<td>0.78</td>
</tr>
<tr>
<td>11</td>
<td>TiN</td>
<td>CSM</td>
<td>$11 \pm 2$</td>
<td>$0.27 \pm 0.09$</td>
<td>0.84</td>
</tr>
<tr>
<td>12</td>
<td>AlCrN</td>
<td>S5</td>
<td>$45 \pm 4$</td>
<td>$1.76 \pm 0.39$</td>
<td>1.30</td>
</tr>
<tr>
<td>13</td>
<td>TiB$_2$</td>
<td>S6</td>
<td>$24 \pm 4$</td>
<td>$1.57 \pm 0.20$</td>
<td>2.54</td>
</tr>
</tbody>
</table>

*— Sample breaking apart during the drilling process

Panjan et al. [66, 69] studied the coating topography of PVD hard coatings and growth defects. The defect sizes and shapes were characterized by SEM and the defect distributions were characterized using a 3D stylus profilometer. An area over 10 mm × 10 mm was scanned and the surface density and height
distribution of all the micrometer-sized defects on the surface were estimated as average number of peaks per mm$^2$ over a certain height, e.g., 200 peaks higher than 0.5 µm, and 20 peaks higher than 2 µm. However, the profilometer used in this study does not have such function, and so the relationship between the defect distribution (average number of peaks per mm$^2$ over a certain height) and the aluminum adhesion strength has not been found.

In summary, both bare and Cr-coated H13 tool steel are highly reactive to liquid aluminum with the formation of intermetallic compounds at the alloy coating interface. The porous #13 TiB$_2$ coating was also highly reactive. Excluding these reactive samples, it seems that the rougher the coating surface is, the lower the adhesion strength, suggesting that coating surface roughness might affect the aluminum adhesion. However, as noted above, the most likely controlling factors are expected to include coating composition, surface oxide layer and coating surface roughness. The following sections will address each of these factors in more detail and discuss their effect on the aluminum adhesion strength.

7.2 Effect of Composition of AlCrN Coatings on Aluminum Adhesion

It was suggested in previous sections that the difference in the aluminum content of the AlCrN coatings may play a role in determining the A380 alloy adhesion behavior (#1 AlCrN coating vs. #12 AlCrN coating). The primary goal of this portion of the project was to prepare AlCrN coatings with various Al/(Al+Cr) ratios and study the effect on the adhesion of aluminum to these AlCrN coatings. The AlCrN coatings were prepared by sputtered using AlCr alloy targets. In an effort to evaluate the effects of coating composition, three AlCr alloy targets with Al/Cr ratios of (at.%) 50/50, 60/40 and 70/30 and 0/100 were used. Thus, one CrN coating and three AlCrN coatings with Al/(Al+Cr) ratios of 0.5, 0.6 and 0.7 (labeled as Al$_{50}$Cr$_{50}$N, Al$_{60}$Cr$_{40}$N and Al$_{70}$Cr$_{30}$N) were deposited onto polished H13 tool steel coupons as summarized in Table 7.3. MPPMS was used in this study because of its highly ionized plasma that can make dense coatings [47, 50-52, 54]. The coating thicknesses, compositions and residual stress were measured using SEM, EDS and X-ray diffraction SSF method (see Section 3.6.1), respectively. Both the CrN and AlCrN coatings showed large compressive residual stresses, and the residual stresses increased with aluminum content in the coatings.
Table 7.3 – Deposition conditions and properties of AlCrN coatings prepared by compound sputtering using the MPP power supply on various AlCr alloy targets

<table>
<thead>
<tr>
<th>#</th>
<th>Label</th>
<th>Target</th>
<th>Thickness [µm]</th>
<th>Chemical Formula</th>
<th>Residual Stress [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC_1</td>
<td>CrN</td>
<td>Cr</td>
<td>1.6</td>
<td>CrN</td>
<td>-3.6</td>
</tr>
<tr>
<td>MA50C50_1</td>
<td>Al_{50}Cr_{50}N</td>
<td>Al-50Cr</td>
<td>2.4</td>
<td>Al_{0.51}Cr_{0.49}N</td>
<td>-6.8</td>
</tr>
<tr>
<td>MA60C40_1</td>
<td>Al_{60}Cr_{40}N</td>
<td>Al-40Cr</td>
<td>2.1</td>
<td>Al_{0.56}Cr_{0.44}N</td>
<td>-9.0</td>
</tr>
<tr>
<td>MA70C30_2</td>
<td>Al_{70}Cr_{30}N</td>
<td>Al-30Cr</td>
<td>2.3</td>
<td>Al_{0.68}Cr_{0.32}N</td>
<td>-9.4</td>
</tr>
</tbody>
</table>

The morphologies of the four coated samples were characterized using SEM. The cross-sectional images are shown in Figure 7.3 and confirmed the dense microstructure of these coatings, and with coating thicknesses ranging from 1.6 to 2.4 µm.

![Cross-sectional SEM images of compound-sputtered CrN, Al_{50}Cr_{50}N, Al_{60}Cr_{40}N and Al_{70}Cr_{30}N coatings.](image)

The plan-view SEM images at low magnification (see Figure 7.4) showed that the H13 substrates were fully coated, although occasional scratches and coating debris were present. Images at high magnification confirmed the extremely dense microstructure consisting of small grains for these coatings.
Figure 7.4 Plan-view SEM images of the CrN and the AlCrN coated samples at low magnification (left) and high magnification (right).

Rockwell C hardness measurements were used to evaluate the coatings’ adhesion to the substrate and the results are shown in Figure 7.5. The CrN and Al$_{70}$Cr$_{30}$N coatings exhibited the best adhesion to the H13 tool steel substrates with an HF1 index. The Al$_{50}$Cr$_{50}$N and Al$_{60}$Cr$_{40}$N coatings showed lower adhesion, but still acceptable index of HF 2 and HF 3 (see Figure 3.15 for reference), respectively. The circular cracks are consistent with a highly compressive residual stress in the coatings [108] as indicated in Table 7.3.

Figure 7.5 Results of Rockwell C indent test on the sputtered AlCrN coatings: (a) CrN, Al$_{50}$Cr$_{50}$N, Al$_{60}$Cr$_{40}$N, and Al$_{70}$Cr$_{30}$N.
Aluminum adhesion tests were conducted on these four samples, and the results of the maximum breaking load (aluminum adhesion strength) as function of Al/(Al+Cr) ratios are shown in Figure 7.6. All four samples exhibited strong alloy adhesion with strength in the range of 1.41-6.51 MPa. This result clearly suggests that the composition of the AlCrN coatings (or Al/(Al+Cr) ratio) is not a controlling factor affecting the aluminum adhesion.

Figure 7.6 Plots of maximum breaking load and aluminum adhesion strength as function of Al/(Al+Cr) ratios for the CrN and AlCrN coated samples for the aluminum adhesion test.

7.3 Effect of Surface Roughness and Oxides of #1 AlCrN Coating on Aluminum Adhesion

In this Section, the results of a series of tests performed to determine the influence of surface roughness and surface oxides on the aluminum adhesion of the #1 AlCrN coating is described. Several #1AlCrN-coated H13 coupons were subjected to different treatments including post-polishing and thermal treatments and subsequently evaluated using the AAT.

First, post-polishing PVD coatings with diamond suspensions is challenging given that the size of the diamond in the polishing paste is comparable or larger to the thickness of the coatings (PVD coatings are often only several μm thick). In this study, the first attempt was carried out on the #1 AlCrN-coated coupon by grinding initially with 1200 grit SiC paper and polished using the diamond pastes in the order of 6 μm and 1 μm. The surface of the coating prior to polishing has a number of micrometer-sized macro-particles and pin-holes (Figure 7.7a). After polishing (Figure 7.7b), the majority of the
macro-particles were removed by the polishing operation, and only pin-holes were left on the polished surface along with some polishing marks or scratches.

Figure 7.7 Plan-view SEM images of the #1 AlCrN coating before (a) and after polishing (b).

The polished coating was reevaluated using the AAT and found to have aluminum alloy adhered to the polished surface (Note: the un-polished sample had zero aluminum adhesion strength and no adhered A380 aluminum alloy). To understand why the alloy adhered to the polished coating, the whole sample (before mechanical testing) was cold mounted, sectioned through its center-line and polished down to 1 μm for SEM examination. A cross-section view (Figure 7.8) of the interface between the adhered alloy and the polished coating indicates that the adhered aluminum alloy penetrated the polished AlCrN coating through a fractured location (width of ~25μm) and reacted with the H13 substrate with the formation of Al-Fe-Si intermetallic compounds. The fractured coating might come from the prior polishing damage.

Figure 7.8 Cross-sectional SEM images of the polished #1 AlCrN coating after the aluminum adhesion test. (a) secondary electron mode, and (b) backscattered electron mode.
The EDS elemental mapping (Figure 7.9) of the intermetallic compounds indicated that they are enriched in aluminum, iron, silicon and chromium, similar to the previous soldering layers found on the bare H13 tool steel sample. The titanium and chromium maps indicate the discontinuous nature of the AlCrN coating at the soldering area. The titanium signal came from the TiN/Ti layers and chromium from the AlCrN layer. Therefore, the aluminum adhesion to the polished sample is attributed to the soldering formation through the fractured coating or pin-holes.

![Figure 7.9 EDS mapping images of the soldering area of the polished #1 AlCrN sample after the aluminum adhesion test.](image)

It was concluded that polishing using 1200-grit initially was too coarse, resulting in a fractured coating or enlarged size pin-holes. Subsequently, a more gentle polishing technique was used with only 1\(\mu\)m diamond paste (designated as fine polishing), but this failed to remove the largest macro-particles on the coating surface, as confirmed by SEM observations. The goal of polishing was to smooth the surface of coating and leave a minimal number of macro-particles and little damage to the thin coating. Finally, an intermediate polishing approach using 6 \(\mu\)m diamond paste was employed. Using this more optimized polishing procedure, three more #1 AlCrN coated H13 tool steel coupons were polished for five minutes. However, only half of the coupons were polished. This arrangement was accomplished by covering half of the surface using tape (see Figure 3.11). After polishing, the tape was removed, and all the coupons were ultrasonic cleaned successively with soap water, acetone and alcohol, and dried with nitrogen gas. Of these three polished coupons, two were placed in the Carbolite furnace at 700°C air for 1 hour and 18 hours, respectively. The use of relatively longer thermal treatment time (18 hours) was selected in order to increase the thickness of the oxide layer formed on the #1 AlCrN coating surfaces.

Subsequently, these three coupons were evaluated using the AAT using the same test conditions as documented previously. The aluminum alloy adhered to all three samples, as shown in Figure 7.11. However, the aluminum appeared to adhere only to the polished sides of the coupons, but not to the unpolished sides. Adhesion strength is shown in Figure 7.12.
Figure 7.10  Photographs of the polished #1 AlCrN coating on an H13 tool steel coupon: (a) as-received coupon and (b) coupon covered with tape.

Figure 7.11  Photographs of the #1 AlCrN-coated H13 tool steel coupons from Supplier 1 after the aluminum adhesion test. The left halves of each coupon were polished using 6 μm diamond paste and the right halves left unpolished.

Figure 7.12  Breaking loads and aluminum adhesion strength of the #1 AlCrN-coated H13 tool steel coupons from Supplier 1 after the various treatments as shown in Figure 4.45.
XPS analysis was conducted initially to show the surface chemistry of these polished/unpolished coupons prior to the AATs. The data are shown in Figure 7.13 in reference to the polished/unpolished sides of the as-deposited coupon and the 18-hour 700°C treated coupon. The #1 AlCrN coating has an AlCrN working layer and, for simplicity, the concentrations of aluminum, chromium, nitrogen and oxygen elements are normalized. Al-Cr-O-N oxy-nitrides were present on the coating surfaces for the unpolished and polished sides of the as-deposited coupons. The depth of the inner diffusion of oxygen from the air, and the outward diffusion of metals (aluminum and chromium) from the bulk coating, were both less than 2 nm (corresponding to one minute sputter). However, for the thermally-treated sample, the diffusion of oxygen to the bulk coating was observed to a depth greater than 10 nm (corresponding to five minutes of sputtering). Meanwhile, a drop in the nitrogen concentration as a function of depth was also observed as expected. It should be noted the surfaces of the thermally-treated samples were almost covered completely with oxides with traces of nitrogen or nitrides.

![Figure 7.13](image)

**Figure 7.13** XPS concentration-depth profiles of aluminum, chromium, nitrogen and oxygen elements for the #1 AlCrN coatings from Supplier 1 as a function of sputter time for: (a) the unpolished side, (b) 6 µm diamond polished side, (c) the unpolished side plus thermal treatment at 700°C for 18 hour, and (d) polished side plus thermal treatment at 700°C for 18 hours.
The Al/(Al+Cr) ratios at the surfaces of the #1 AlCrN coatings (i.e., with no argon sputtering) are summarized in Table 7.4 as a function of their alloy adhesion conditions. The coatings with no alloy adhesion corresponded to an Al/(Al+Cr) ratio over 85 percent, while the coating with a lower ratio of 79 percent exhibited strong alloy adhesion. The higher the aluminum contents in the oxy-nitride/oxide surface layer, the lower or weaker the alloy adhesion. Likewise, the thicker the surface oxide layers with higher aluminum contents, the lower is the aluminum adhesion strength. Therefore, the nature of the surface oxide layer (Al-concentration and thickness) seems to influence the aluminum adhesion significantly.

Table 7.4 – The Al/(Al+Cr) ratios on coating surface and thickness of oxygen-rich layers for various treated the #1 AlCrN coating coated-coupons along with their aluminum adhesion conditions

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Al/(Al+Cr) Ratio on Surface [%]</th>
<th>Thickness of Oxygen-rich Surface Layer [nm]</th>
<th>Aluminum Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpolished</td>
<td>84.9</td>
<td>&lt; 2</td>
<td>No</td>
</tr>
<tr>
<td>Polished</td>
<td>78.6</td>
<td>&lt; 2</td>
<td>Yes</td>
</tr>
<tr>
<td>Unpolished + 700°C 18 h</td>
<td>92.0</td>
<td>&gt; 10</td>
<td>No</td>
</tr>
<tr>
<td>Polished + 700°C 18 h</td>
<td>88.2</td>
<td>&gt; 10</td>
<td>No</td>
</tr>
</tbody>
</table>

Optical microscope images of the sample surfaces in the as-deposited and thermally-treated for 18 hours conditions after AATs are shown in Figure 7.14. As can be seen, in Figure 7.14a, the polished side of the as-deposited coupon was fully covered with a thick layer of the aluminum alloy, while the unpolished side of the same coupon had no visual alloy adhesion at the magnification used (Figure 7.14b). The black dots in the optical images are coating defects and are either peaks (macro-particles) or valleys (pin-holes), but cannot be easily distinguished due to the poor lateral and depth resolution of the optical microscope at the magnifications used. Optical images containing similar black features/defects were reported in cathodic arc coatings by Panjan et al [69]. In comparison to Figure 7.14a, only a small amount of alloy adhered to the surface of the polished and thermally-treated coating; this alloy appears as the bright phase in Figure 7.14c and corresponds to a near-zero aluminum adhesion strength. No visible differences were observed between the unpolished sides of the coupons with and without the thermal treatments.

For the thermally-treated sample at 700°C for 18 hours tested by the AAT, the aluminum alloy was found to occasionally adhere to the smooth area on the coating surface, consistent with the weak aluminum adhesion strength. However, the more interesting findings included some agglomerations formed on sample surface as shown in Figure 7.15. The EDS analysis indicated that these surface agglomerations were enriched in titanium and oxygen indicating that they are probably are titanium oxides. The source of the oxide agglomerations are believed to be the oxidation product of the TiN or Ti layer underneath the AlCrN coating, due to oxygen from the air reacting with the Ti and TiN in the regions of pinholes. The onset of severe oxidation was reported at 300°C for Ti [109], 500°C for TiN [110] and 900°C for AlCrN [92, 111].
Figure 7.14  Light optical images of the surfaces of the samples after aluminum adhesion tests: (a) the 6 µm diamond polished side for the as-deposited sample, (b) the as-received sample, (c) the polished side plus thermal treatment at 700°C for 18 hour, and (d) the unpolished side plus thermal treatment at 700°C for 18 hour.

Figure 7.15  SEM images of the polished side of the #1 AlCrN coating after thermally-treating at 700°C for 18 hours and aluminum adhesion tests: (a) plan-view, and (b-c) 45° tilt view and (d) the corresponding as-deposited side (45° tilt view).
The oxidation data suggest that both Ti and TiN coatings are readily oxidized at 700°C, while the AlCrN coating is not. This situation is consistent with recent reports that the TiO$_2$ rutile phase is the only stable oxidation product of Ti and TiN coatings at temperatures above 500°C [109, 110]. An XRD scan was conducted on this sample and was found to contain weak diffraction peaks from the rutile phase as expected confirming that the surface agglomerations were indeed rutile TiO$_2$ structure. These agglomerations increased the coating roughness, and appear to be consistent with suggestion that both surface oxides and surface roughness (Figure 7.12) are important for decreasing the soldering of the liquid aluminum although it remains unclear which is more important.

In Figure 7.16 it is clear that the unpolished surface of the as-received #1 AlCrN-coated coupon after AAT contains a number of small bright pillars that appear to have adhered to the coating defects. SEM images (Figure 7.16c and d) confirmed that these pillars were attached to the peaks of the large macro-particles. The composition of the pillars was determined by EDS to be mostly aluminum.

Figure 7.16 Light optical micrographs (LOMs) and SEM images of the as-deposited #1 AlCrN coating after aluminum adhesion test: (a) LOM with focus slightly above the coating, (b) LOM with focus on the coating, (c-d) SEM images of the coating at 45° tilt.

Figure 7.17 shows an SEM plan view and the stereographic SEM images of the bottom of the A380 aluminum alloy cylinder after the AAT of the as-deposited #1 AlCrN coating sample. The alloy pillars observed on the alloy surface were at approximately the same distribution as those observed in Figure 7.16a.
on the #1 AlCrN coating-coated coupon side. The 3D morphology of these pillars can be observed from the SEM stereographic image (red glass on left eye and green glass on right eye).

Based on the above results, it seems that surface oxide layer thickness, Al/(Al+Cr) ratio, and coating roughness all influence the aluminum adhesion. However, from the more detailed characterization of #1 AlCrN coating on the coupon surface and alloy bottom, it appears that coating roughness might dominate the aluminum adhesion behavior. A possible model to explain this behavior is as follows: At the beginning of the AAT when the alloy is poured and makes contact with the coated substrate, the alloy may only touch the highest peaks of the macro-particles (assuming there is a sufficient density of them on the surface, and not spread out due to the air that becomes in between them. After the alloy solidifies and is pulled away from the substrate, the only locations that sticking appears to have occurred is at the macro-particles as evidenced by the pillar tails that are left behind (Figure 7.16). This situation results in coatings that appear to have no apparent aluminum adhesion.

7.4 Effect of Surface Roughness Using Femtosecond-Laser Texturing on Aluminum Adhesion

In previous Sections it was concluded that roughness affects the aluminum adhesion, and that polishing was not an ideal way to smoothen or roughen a coating having μm thickness. Therefore, a femtosecond laser was used to produce a more controlled surface roughness on the H13 tool steel substrate prior to the AAT. Since the AlCrN coatings mentioned in Section 4.5 appear to provide a barrier preventing
chemical reaction between the A380 aluminum alloy and the H13 tool steel, the textured H13 tool steel was then coated prior to the AAT.

7.4.1 Laser-Textured Bare H13 Tool Steel Coupon

Prior to laser texturing, the surface of the H13 tool steel was polished smooth as shown in photographs 7a and 7b in Figure 4.40. After exposure to the femtosecond laser pulses, a conical surface pattern was produced as shown in Figure 7.18. As is evident, the conical pillars produced have peak-to-peak distances of 20-25 \( \mu \text{m} \) and are covered with a porous coating which appears to be an oxide generated by the heat produced from laser pulses and the reaction of the hot steel with the surrounding air.

![SEM images of the bare H13 tool steel coupon surface textured using femtosecond laser: (a-b) plan-view, and (c-d) 45° tilt view of the sample.](image)

To remove this porous oxide, the textured surfaces were cleaned using Naval Jelly, a commercial rust cleaner containing phosphoric acid for 5 or 30 minutes. As seen in the SEM images in Figure 7.19, only conical features were visual after the cleaning procedures with no evidence of the previously identified porous oxide.
Figure 7.19  SEM images of the surface-textured H13 tool steel coupon after cleaning with Naval Jelly for (a-b) 5 minutes and (c-d) 30 minutes. Images of (a) and (c) are plan views, and (b) and (d) are 45° tilt views.

Figure 7.20 shows the photographs of the laser-textured and uncoated H13 tool steel sample cleaned for 5 minutes before and after AAT. It should be noted that the as-prepared laser-textured area appears black due to the lower light reflection characteristic of the conical surface structure as shown in Figure 7.20a. The aluminum adhesion strength was measured to be only ~ 0.06 MPa (7.6 lbs) and consistent with a small amount of aluminum adhering to the upper surfaces of the peaks as will be shown below.

Figure 7.21 shows photographs of another laser-textured H13 tool steel sample that was cleaned for 30 minutes before and after the AAT. The aluminum adhesion strength was measured by to be ~ 0.05 MPa (5.9 lbs), and the other results were similar to that for the sample cleaned for 5 minutes.

SEM images (Figure 7.22) of the surfaces of the laser-textured H13 tool steel samples after AAT contain numerous μm size pillars adhered to the surfaces. The pillars seemed to adhere to and react with the conical peaks produced by the texturing. This indicates that the molten alloy apparently did not penetrate into the valleys between the conical structures as speculated above.

The EDS mapping was conducted on the 30-minute cleaned sample after the AAT. The pillars mainly contained Al and Si as shown in Figure 7.23, suggesting it was from the A380 aluminum alloy.
Figure 7.20 Photographs of the surface-textured H13 tool steel coupon after Naval Jelly cleaning for 5 minutes before and after aluminum adhesion test (AAT): (a) sample before AAT; (b) sample after AAT prior to separating mechanically; (c) sample tested by AAT plus mechanical test; (d) bottom view of the alloy; and (e) enlarged image of the alloy contact on the sample surface.

Figure 7.21 Photographs of the surface-textured H13 tool steel coupon after Naval Jelly cleaning for 30 minutes before and after aluminum adhesion test (AAT): (a) sample before AAT; (b) sample after AAT prior to separating mechanically; (c) sample tested by AAT plus mechanical test; (d) bottom view of the alloy; and (e) enlarged image of the alloy contact on the sample surface.
Figure 7.22  SEM images of the surface-textured H13 tool steel coupon after aluminum adhesion test: with Naval Jelly cleaning for (a-b) 5 minutes and (c-d) 30 minutes. Images of (a) and (c) are plan views, and (b) and (d) are 45° tilt views.

Figure 7.23  SEM image and EDS maps on the surface of surface-textured H13 tool steel coupon after aluminum adhesion test (sample used Naval Jelly cleaning for 30 minutes).
The FIB was used to mill and polish a surface pillar with adhered Al to better assess how the alloy interacted with the conical H13 microstructures and determine whether any chemical reactions occurred at their interfaces. SEM images of the FIB milling process (Figure 7.24) though a single adhered pillar were recorded and listed in the order of b to e at the tilt view as SEM images. For Figure 7.24e, the adhered pillar appears as a dark zone, where the contact conical microstructures were brighter zone.

Figure 7.24 SEM images of FIB milling process for the surface-textured H13 tool steel coupon after aluminum adhesion test: (a) top-view image (the rectangle with red dashed lines indicates the milling area, the milling direction is labeled as the red arrow), and (b-f) 52° tilt image of the continuous FIB milling process.
EDS maps (Figure 7.25) were taken of the FIB milled surface and it is clear that the conical surfaces were covered with a thin phosphorous layer, indicating residual Naval Jelly on the sample after cleaning. Thus, while Naval Jelly appears to be an efficient way to remove the oxides, it appears to leave residual contamination that is difficult to remove using water and alcohol. The effect of residual phosphorous on the aluminum adhesion is unclear at this point and suggests that a better cleaning process should be used to remove the oxides in future work. Even so, the pillars did contain some reaction product (soldering) between the alloy and the H13, that consisted of Al, Fe, Si and Cr. An EDS point scan taken from the yellow point in Figure 7.25a indicated that the intermetallic had a composition of (at.%) Al-21.7Fe-9.4Si-2.6Cr. This result is comparable to the overall composition of the dense layer (Al-20.1Fe-13.4Si-1.1Cr) consisting of Al$_8$Fe$_2$Si-type and Al$_{19}$Fe$_4$MnSi$_2$-type intermetallic phases for the bare H13 tool steel sample (see Section 4.3.2).

Figure 7.25 SEM image and EDS maps of the surface-textured H13 tool steel coupon after aluminum adhesion test. EDS point scan at the yellow mark in the SEM image.
While the H13 tool steel coupons were successfully surface-textured to produce the conical structures using femtosecond laser pulses, these coupons still showed aluminum adhesion due to the soldering reaction between the alloy and the H13 peaks. Therefore, it appears that creating a patterned surface does not preclude chemical reactions or aluminum adhesion although it does result in lower adhesion strengths due to the lower contact area.

7.4.2 Polished and Laser-Textured H13 Tool Steel Coupons with AlCrN Coating

In an effort to clarify this roughness effect and reduce the reaction/adhesion of the Al, an Al$_{50}$Cr$_{50}$N coating was selected to coat the textured surface. This AlCrN coating was deposited using modulated pulsed magnetron sputtering onto both a polished and a laser-textured H13 tool steel coupon. Different from the previous section describing the deposition of AlCrN coatings having CrN/Cr adhesion layers, the AlCrN coating described in this section was deposited using a Ti adhesion layer. This Ti layer is easily observed using EDS mapping in the SEM.

The surface morphologies of the two coated samples were characterized by SEM with the samples oriented (a) orthogonal to the beam and (b) 45° to the beam (see Figure 7.26). The coating deposited onto the surface polished H13 tool steel coupon was smooth as expected although there was some coating debris on the surface probably due to arcing events during deposition. On the contrary, the coating placed on the laser-textured coupon maintained the same 3D conical morphology as the H13 tool steel substrate, having numerous nearly-ordered peaks and valleys with a peak-to-peak distance of 20-25 µm.

Figure 7.27 shows the X-ray diffraction patterns of the two coated samples. Both coatings showed the face-centered cubic CrN-type crystal structure. However, it appeared that the coating on the polished sample exhibited a (111) texture, while that on the laser-textured substrate appeared more random.

Figure 7.28 shows the SEM cross-sectional images and the corresponding EDS mapping for the coating on the polished substrate. It should be noted the cross-sectional surface was prepared by FIB milling using gallium ion. The chemical composition and the thickness of the coating layers were revealed as ~0.3 µm for titanium layer and ~5.4 µm for AlCrN as shown in the SEM image in Figure 7.28.

For the coated conical microstructures sample, the FIB was also used to section one cone. As shown in Figure 7.29, the cone microstructure was firstly protected using a platinum layer with the help of gallium ion beam. Then, milling the cone from the front to the back and finally the cross-section surface was obtained as shown in the last image (Step 5) in Figure 7.29. The interfaces between the platinum layer, coating, and the H13 tool steel substrate can be seen.
Figure 7.26  SEM images of the AlCrN coating deposited onto: (a) the polished sample at 0° tilt, (b) the polished sample at 45° tilt, (c) the laser-textured sample at 0° tilt, and (d) the laser-textured sample at 45° tilt.

Figure 7.27  X-ray diffraction patterns for the polished (smooth) and laser-textured H13 tool steel samples with AlCrN coating.
Figure 7.28  Cross-sectional SEM images and EDS mapping of the AlCrN coating on the polished H13 tool steel coupon.

Figure 7.29  FIB milling of the AlCrN coated surface-textured H13 tool steel coupon.
Figure 7.30 shows the SEM images of the FIB-sectioned cone and the EDS maps. First, it should be noted that the peaks of the cones were effectively coated and that the AlCrN coating even reached into the valleys. Not surprisingly, the coating thickness decreased from the peak area to the valley area. Finally, both the AlCrN layer and the titanium adhesion layer were observed.

Figure 7.31 shows the photographs of the two AlCrN-coated samples before and after AAT. The polished sample had high adhesion strength of 4.73 MPa, while the laser-textured sample had almost zero adhesion strength. After the alloy separated from the polished sample, both coating delamination and alloy adherence were observed. On the other hand, for the laser-textured sample coated with AlCrN, no obvious evidence of the alloy adhering to the coating was observed at low magnifications. This result clearly suggests that surface roughness greatly reduces aluminum adhesion during the AATs.

Figure 7.32 shows the SEM image and the EDS mapping on the fracture surface of the polished coupon at the alloy contact area. As can be seen, the coating delaminated and broke with strong signals from the H13 tool steel substrate (EDS iron signal) and the titanium adhesion layer. The area with strongest aluminum and silicon signals was regarded as the Type 2 area, where the fractured aluminum alloy adhered to the AlCrN coating.
Figure 7.31 Photographs of the AlCrN-coated H13 tool steel coupons for the aluminum adhesion test: the polished sample (top images) and the laser-textured sample (bottom images) both coated with AlCrN.

Figure 7.32 SEM image and EDS mapping of the fracture area of the polished H13 tool steel coupon coated with AlCrN after the aluminum adhesion test
Figure 7.33 shows the SEM image and the EDS mapping on the laser-textured AlCrN coated sample after the AAT. Note that the EDS signal was not uniform across the sample surface due to the 3D topography of the laser-textured sample surface, as shown in the signal map, where blue area indicated poor signal collection corresponding to the valleys of the conical microstructures. The SEM image indicated that some alloy pillar adhered to the peaks of the cones, which consisted of mainly aluminum.

Figure 7.34 shows the SEM images of the coupon surface and the alloy bottom for the laser-textured sample after the AAT. With the comparison of Figure 7.34a and Figure 7.34c, it appeared that the alloy contacted the laser-textured surface at the pillar peaks as expected. These pillars were broken after AAT as shown in Figure 7.34, probably due to the thermal stresses generated when the solidified alloy cooled. Note that the bottom of the alloy was relatively flat compared to the rough conical microstructures of the coated H13 tool steel surface; this observation is consistent with the fact that the liquid aluminum alloy only contacts the upper extremities of the patterned surface as speculated previously.
7.4.3 Discussion and Summary

From these current observations, it can be concluded that aluminum adhered to the laser-textured bare H13 tool steel coupons but with weak adhesion strength of 0.05-0.06 MPa, caused by the chemical reaction of the liquid Al with the peaks in the H13 coupons which result in the formation of brittle intermetallic phases locally. However, the aluminum adhesion to the AlCrN coating on the polished substrate and the laser-textured substrate were different, with adhesion strengths of 4.73 MPa for the polished sample and of essentially zero for the laser-textured and coated sample. A schematic diagram of the alloy adhesion to the polished and femtosecond laser-textured H13 tool steel coupon coated with AlCrN using aluminum adhesion test is shown in Figure 7.35.
Figure 7.35  Schematic diagram of the alloy adhesion to the polished and femtosecond laser surface-textured H13 tool steel coupon coated with AlCrN for aluminum adhesion test.

For the smooth sample (e.g. polished H13 tool steel coupon coated with AlCrN), when the liquid A380 aluminum alloy is poured and contacts the sample surface, the alloy can break its thin oxide scale and spread out on the coating surface with the area confined by the inner diameter of the BN tube. The thin disrupted oxide layer might be dissolved into the alloy with the increase of holding time, and the fresh alloy interacts with the coating. Since no additional oxygen exists at the alloy/coating interface, no interfacial oxide layer grows at the alloy/coating interface for the holding temperatures of fifteen minutes. After the alloy cools, it strongly adheres to the AlCrN coating. Thus, upon measuring the adhesion strength, the fracture occurs on the adhered alloy side or the coating side or both. It depends on the ductility of the coating and its adhesion to the substrate.

For the laser-textured sample coated with AlCrN, however, when the liquid A380 aluminum alloy is poured and touches the sample surface, the numerous sharp peaks penetrate the thin oxide scale of the aluminum, with local wetting between the coated peaks and the fresh alloy at these locations. However, due to a combination of trapped air and surface tension, the liquid does not penetrate in the valleys of the texture surface and the resulting adhesion strength is very low accordingly. Specifically, although the alloy appears
to adhere to the coating at the numerous pillar tips, the total contact area is relatively small and the resulting adhesion strength is low.

Therefore, it can be concluded that the success of achieving near-zero aluminum adhesion is based on two conditions. First, the substrate should be more or less inert in liquid aluminum and this appears to be possible using AlCrN coatings. Second, surface roughness also plays a role in controlling adhesion. When the AlCrN surface is rough (either from the deposition of macro-particles, or via laser-texturing), the aluminum only contacts the high points of the surface, thereby minimizing adhesion.
CHAPTER 8: DIE CASTING IN-PLANT TRIALS

Die casting in-plant trials were used to assess the validity of the laboratory test, the aluminum adhesion test (AAT), and whether it can be used to predict the adhesion behavior of die coatings for lubricant free commercial die casting applications. Two trials were conducted at Mercury Casting’s facility in Fond-Du-Lac, WI and both trials used the #1 AlCrN coating from Supplier 1, as it had been identified as the best candidate by the AAT. The first trial was utilized a small die insert, while the second coating an entire die.

8.1 First Trial

In the first plant trial, only a single cavity was coated and tested. The objective of the trial was to test the durability of the coating in a commercial die casting environment, and to make sure that the coating did not introduce any problems to the die casting operation. The trial was performed in December, 2015. The casting produced during the trial is a gearcase (Figure 8.1), and this casting is produced using two loose die inserts that are ejected from the die casting die with the aluminum casting, which are then extracted from the casting on the bench adjacent to the die casting machine. Mercury typically uses about four separate inserts, which are used in rotation in the casting cycle. For this trial, only one of the loose inserts was coated (Figure 8.1).

Figure 8.1 Schematic diagram of the casting product, the 4-Stroke gearcase: (a) 3D image, (b) cross-sectional image. The location of the AlCrN-coated loose insert is shown in red
The loose insert was made of H13 tool steel with a hardness of 46-48 RC. For normal operation, prior to every shot to prevent the aluminum from sticking to the die steel, the main die cavity is sprayed with a water-diluted liquid lubricant with a dilution ratio of approximately 100:1, while the uncoated loose pieces are simply dipped in the undiluted lubricant. For the lube-free trial, the dies and the uncoated insert were sprayed as normal. However, the AlCrN-coated insert was sprayed with the same lubrication only for the first five shots – after that the coated insert was run without lubricant to assess the soldering behavior of this coating. The aluminum alloy used in the in-plant trial was A362 aluminum alloy with the composition shown in Table 8.1.

Table 8.1 – Composition of the A362 aluminum alloy used for the in-plant trials [wt.%]

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Ni</th>
<th>Zn</th>
<th>Ti</th>
<th>Sr</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reminder</td>
<td>10.5-11.5</td>
<td>0.25</td>
<td>0.2</td>
<td>0.25-0.35</td>
<td>0.5-0.7</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.05-0.07</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.2 shows eight views of the insert coated with #1 AlCrN coating before and after the trial. For the plant trial, the first five shots were produced with lubricant sprayed onto the coated insert, but for the next twenty shots, no lubricant was applied to the coated insert, and no evidence of sticking or soldering was observed. On the following day, another twenty shots were produced without lubricating the coated insert, and again no evidence of soldering or sticking was observed. Over the two-day trial, a total of forty shots were produced without any lubricant applied to the AlCrN coated insert. The Mercury plant-floor personnel suggested that they would expect sticking or soldering to occur after about three shots for an uncoated and un-lubricated insert.

Figure 8.2 Photographs of the #1 AlCrN coating coated loose die insert: before the casting trial (a-d) and after the casting trial from different views (e-h).
8.2 Second Trial

For the second plant trial, performed in May 2016, an entire die was also coated with the #1 AlCrN coating from Supplier 1. The casting used for the trial was a balance shaft housing (see Figure 8.3). It is produced in a single-cavity die using a 700 ton die casting machine. The balance shaft housing weights about ~0.8 kg (1.75 pounds) and is 165 mm (6.5 inches) tall.

Figure 8.3 The 3D model of the balance shaft housing casting.

The 3D models of the moving and fixed halves of the die are shown in Figure 8.4. The entire die was coated the #1 AlCrN coating, including the shot block, cavity, vent block and cores of the moving side, and the cavity and vent block of the fixed side.

Figure 8.4 The 3D models of the moving (a) and fixed (b) halves of the balance shaft housing die
Prior to the trial, Mercury Castings had experience producing this casting in a previous die, where 90,000 shots had been produced. Experience with the old die indicated that twelve seconds spraying was necessary to avoid sticking and soldering of the casting to the uncoated die.

On the first day of the trial, seventy castings were produced using a two seconds spray time, and no evidence of sticking was observed. This accomplishment is an 83 percent reduction in spray compared with that used with the older die. The Mercury personnel then reduced the spray time to one second (a 92 percent reduction in spray), and again little-to-no sticking was observed. The Mercury personnel then attempted to produce a casting with no spray, and the first casting stuck and bent on ejection (Figure 8.5a). Once the stuck casting was extracted, it was found that one of the core pins had been bent (Figure 8.5b), and so the die was disassembled and all the core pins replaced with new AlCrN coated core pins. The die was then re-assembled and re-installed on the machine overnight.

![Figure 8.5](image)

Figure 8.5 Photographs of the die after the casting stuck: (a) casting stuck in the die, and (b) bent core pin after the stuck casting had been extracted.

On the second day of the trial, another 96 castings were produced using the one second spray. Again, little-to-no evidence of sticking was observed. Analysis of the one second spray showed that only the gate area of the casting was actually being sprayed (see Figure 8.6), with the upper portion of the cavity essentially operating in an un-lubricated condition.

Therefore, it can be concluded that #1 AlCrN coating was successful in decreasing the amount of lubricant spraying during actual die casting operation, without any obvious aluminum adhesion problem (92 percent reduction in lube spray). However, the condition of running without any lubricant spray was not achieved in this trial, but it certainly suggests the potential of achieving lube-free operation in the future.
Figure 8.6 Spray zone for the casting produced using a one second spray time.
CHAPTER 9: SUMMARY AND CONCLUSIONS

The objective of this study was to identify PVD coatings that are not wetted by liquid aluminum, so they can be applied to die casting dies, to eliminate the need for the application of an organic lubricant before each shot. A second focus of the work was to identify a laboratory test that could be used to evaluate a number of coating materials in order to determine which coatings are best suited for commercial die casting applications. In the following the overall results are summarized and conclusions are made accordingly.

Dipping Test (Chapter 4):
1. Uncoated steel pins, immersed in liquid aluminum for one minute, had aluminum adhered to their surfaces, but no interfacial reactions, so adhesion presumably occurred due to physical shrinkage of the aluminum around the pin during solidification and cooling.
2. Uncoated steel pins, immersed in liquid aluminum for 60 minutes, did have an interfacial reaction between the liquid aluminum and the steel pin.
3. Pins painted with various powders exhibited no aluminum adhesion after 10 seconds of immersion, but this was attributed to the powder not strongly sticking to the pins rather than the lack of a reaction between the powders and the liquid aluminum.
4. It was concluded that the dipping test is not effective for evaluating aluminum adhesion behavior.

Sessile Drop Test (Chapter 5):
1. Sessile drop tests were determined to be difficult for the highly reactive liquid aluminum alloy resulting due the tenacious oxide that was always present on the Al surface, which kept the melted aluminum samples from achieving a spherical cap shape below 750 °C.
2. The oxide scale on the aluminum surface supported the aluminum during the tests thereby preventing the liquid from achieving intimate contact with the steel substrates.

Liquid Adhesion Test (Chapter 6 & Chapter 7):
1. A new adhesion test (AT) was developed in which liquid A380 aluminum alloy was poured into a BN tube held on the surface of either coated or uncoated H13 tool steel substrates and the assembly was held at 700 °C for 15 minutes before slowly cooling to room temperature. After cooling, if the aluminum adhered to the substrate, the adhesion strength was measured by tensile testing to obtain a
semi-quantitative measurement of the load required to break the solidified aluminum away from the substrate.

2. Among the thirteen different specimen types examined, three, AlCrN (#1), AlTiN (#2) and CrWN (#3) exhibited zero adhesion strength. The remainder exhibited adhesion strengths up to 2.54 MPa.

3. Of these, AlCrN was considered the most promising for die casting applications as it had the best high temperature oxidation resistance (stable up to 800 °C), high hardness, and a relatively low wear rate. It should be noted that more than 15 AlCrN coated samples from Supplier #1 were tested and always exhibited non-sticking behavior in the as-deposited condition.

4. The soldering of A380 to bare H13 consisted of four distinct layers as follows:
   i. A dense layer (~1 µm thickness) adjacent to the H13 tool steel consisting of small grains of the Al_{13}Fe_{4} phase.
   ii. A second, thicker dense layer (~23 µm) containing a mixture of Al_{8}Fe_{2}Si and Al_{19}Fe_{4}MnSi_{2} columnar grains.
   iii. A third layer (~90 µm thickness) that was a mixture of Al_{19}Fe_{4}MnSi_{2} and α-Al.
   iv. A fourth thin but continuous layer that was Si-rich.

5. The low adhesion strength to the bare H13 was correlated with the brittle nature of these reaction zones.

6. For the other coatings that performed poorly in the adhesion test, there were a variety of reasons for their poor performance ranging from reaction zones to poor oxidation resistance (e.g., TiAlN) and these were categorized accordingly.

7. The zero adhesion strengths for the AlCrN coatings was examined in some detail and it was shown that (a) the coating needs to be chemically inert in the presence of liquid Al, (b) this inertness is affected by the presence of the oxides on the coating surface, and (c) that surface roughness plays an important role in the adhesion behavior where some roughness is desirable.

Die Casting In-Plant Trials (Chapter 8):

- The best AlCrN coating performed extremely well in the in-plant die casting trials at Mercury Marine. While lube-free casting was not achieved, a reduction in lubrication by 92% was deemed possible with this coating.
CHAPTER 10: FUTURE WORK

Future work should be focused on two aspects: (1) improving the adhesion test and (2) improving the coating design for casting trials with no lubrication spray.

10.1 Improving the Adhesion Test

The adhesion test (AT) in this study was carried out by hand, so significant test deviations or errors might have occurred. To better control the test conditions and normalize the operations, it is highly desirable to design a robot to operate the alloy pouring process. Although the AAT appeared to predict the die casting behavior effectively, both pressure of the alloy and casting speed effects need to be examined in future studies. In addition, better control of the environment as well as the substrate temperature is needed to better simulate the casting process.

10.2 Coating Design for Lube-Free Die Casting

Because roughness was shown to be a key factor affecting the aluminum adhesion behavior, it is important to better control the surface roughness such that its effects can be understood in greater detail and so that surface roughness can be engineered into the die surface architecture. The ideal coating for lube free die casting might involve doping with some elements, such as vanadium, gold, and silver as self-lubricating agent that help casting release and also enhance its tribological properties.
REFERENCES


[75] T. Young. An essay on the cohesion of fluids, Philosophical Transactions of the Royal Society of London 95 (1805) 65-87.


COPYRIGHT PERMISSIONS

This Appendix includes expressed, written permission from the copyright holders granting permission for republication of the material contained in Chapter 6 and Chapter 8. Written consent for republication from all Co-authors is also included.
This Agreement between Bo Wang ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number 3938560205117
License date Aug 29, 2016
Licensed Content Publisher Elsevier
Licensed Content Publication Journal of Materials Processing Technology
Licensed Content Title Method to evaluate the adhesion behavior of aluminum-based alloys on various materials and coatings for lube-free die casting
Licensed Content Author Bo Wang, Gerald R. Bourne, Andras L. Korenyi-Both, Alex K. Monroe, Stephen P. Midson, Michael J. Kaufman
Licensed Content Date November 2016
Licensed Content Volume Number 237
Licensed Content Issue Number n/a
Licensed Content Pages 8
Start Page 386
End Page 393
Type of Use reuse in a thesis/dissertation
Intended publisher of new work other
Portion full article
Format both print and electronic
Are you the author of this Elsevier article? Yes
Will you be translating? No
Order reference number
Title of your thesis/dissertation 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
Expected completion date Aug 2016
Estimated size (number of pages) 136
Elsevier VAT number GB 494 6272 12
Requestor Location GOLDEN, CO 80401 United States Attn: Bo Wang
Total 0.00 USD
I hereby permit Bo Wang to reproduce the following works as part of his thesis:


Steve Midson
Of course you have my permission to use our work in your thesis.

Alex