Determination of Interactions Between Molten Aluminum and Selected Die Coatings for Aluminum Die Casting

By
Kurt Raymond Kearns

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 Master of Science (Metallurgical and Materials Engineering).

Golden, Colorado

Date 6-30-02

Signed: ______________
Kurt Kearns

Approved: ______________
Dr. John J. Moore
Thesis Advisor

Approved: ______________
Dr. Brajendra Mishra
Thesis Co-Advisor

Golden, Colorado

Date 6/25/02

____
Dr. John J. Moore
Professor and Head,
Department of
Metallurgical and
Materials Engineering

Abstract

Aluminum die-casting provides parts used in the manufacture of lightweight technical machinery and has become a very large and important industry in the modern manufacturing environment. In order for the die casting process to continue to grow and become more efficient and profitable it is necessary to continue to improve the materials used within the industry. The energy consumption as well as the capital investments involved in the process have a major influence upon the final cost of each casting, which has a major effect upon the cost of the final products the castings are used to produce. These costs, coupled with the possible savings in energy, are the main reasons this research has been conducted.

The major consideration for this research is the interface between the molten aluminum and surface used to give the aluminum its solidified shape. Improving the durability of the materials that the molten aluminum comes into contact with, will make the die casting dies last longer and reduce the amount of time the dies are not in operation due to repair and or replacement of the die components. By improving the number of castings that a die can produce before needing maintenance, it is possible to improve the efficiency of the overall operation.

The goal of this research is to improve the die casting dies by using surface treatments and or coatings to act as a barrier between the molten aluminum and the die material. The main category of coatings that have been investigated for this research are physical vapor deposition (PVD) coatings, which offer many new and exciting opportunities due to the ability to control the coating process very precisely. Industrial companies as well as the university laboratory applied selected coatings to H13 tool steel, which is the most common material used for die casting dies in the aluminum die casting industry. The coatings were tested using an experiment that holds aluminum alloys in contact with the coatings and surface treatments, for an extended period of time, at a temperature above its melting temperature.

By comparing the interactions of the aluminum with the various coatings and surface treatments a set of trends have been observed which give insight as to which coatings offer the greatest potential. The amount of energy between the aluminum alloys

and the various coatings and surface treatments was inferred by the amount of spreading of the liquid aluminum, the strength of the bond between the solidified droplet and surface, and the amount of material the aluminum absorbed while liquid.

The goal was to find which coatings and surface treatments were the least reacting, and the best barrier to molten aluminum alloys. It was found that the coatings each reacted differently with the different alloys. There is likely an ideal coating or surface treatment for a each aluminum alloy. An index was developed in order to determine the coating, which was the best candidate for more than one alloy. This coating was identified and will be used as the working layer film for a thin film coating system.

Table of Contents

List of Figures

List of Tables

Acknowledgements

I would like to thank my advisors, Dr. John J. Moore, and Dr. Brajendra Mishra, for their support, guidance, and patience during the course of this project. I would like to thank my committee members and all of the professors in the Metallurgical and Materials Engineering department for their instruction and encouragement. I would also like to thank the advisory board from the North American Die Casting Association for their insight and guidance throughout the project, especially Peter Ried.

I would like to thank all of the members and students of the Advanced Coatings and Surface Engineering Laboratory for their friendship and support of this research. In particular I would like to thank Stacy Carrera, Chris Muratory, Asher Woolverton, Jianliang Lin, and Guglielmo Gottolli, whom were great colleagues and office mates. As well I would like to thank Alice Jenson for her help and patience as the ACSEL administrator.

I would also like to thank Dr. John Steele, Ed Walton, Benny Sarrussi, Scott Pawelka, and Steve Donnelson for their help and guidance in developing and building the thermal fatigue dunk tester. The project became very complex and time consuming and without their help it would have never been done in such a professional manner.

I would like to thank my family and my friends for their love and support, without which I may not have been able to do any of this work. I especially want to thank Glen Hyatt, Chad Foxworthy, and Jim Olson, for listening to me talk at length about things that they may or may not have understood. Finally I would like to thank god for his love, blessings, and guidance.

I dedicate this thesis to my mother and my brother; I love you both very much.

1. Introduction

The productivity of aluminum die casting dies has been improved through material selection and development. This research is oriented toward improving the dies through the improvement of the materials at the interface between the aluminum and the die surface. Through the application of surface treatments and coatings it is possible to prolong the life of die casting dies, which are commonly made of H13 tool steel.

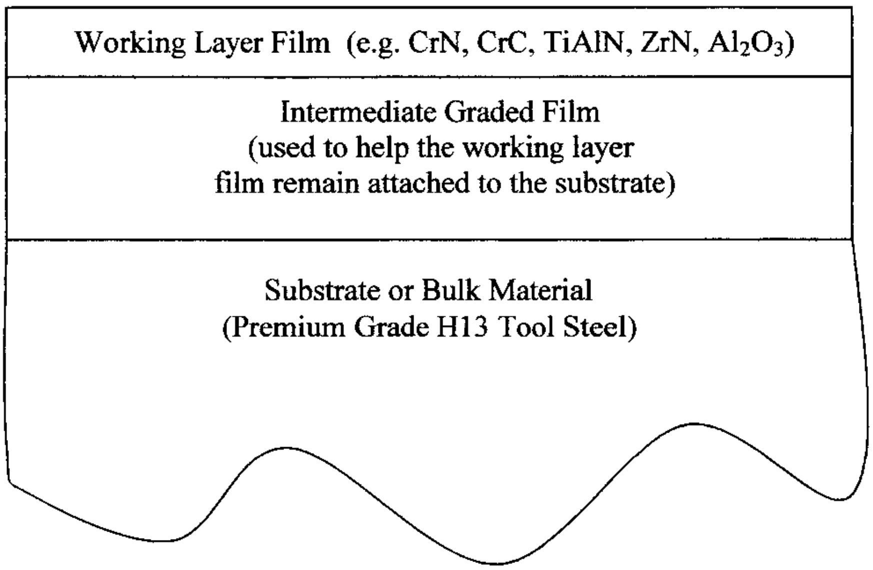

Figure 1: Schematic of the thin film coating system that is being developed for the improvement of the productivity of aluminum die casting dies.

Surface treatments and coatings offer the possibility of increasing the life of the dies and decreasing down time, as well as improving the surface finish of the cast products. The main modes of failure for the dies are soldering of aluminum to the die surface, heat checking or cracking, and washout of the die materials. It is desirable to emulate these problems in the laboratory, but it is not possible to accurately reproduce the actual conditions that occur within the die casting dies. The pressures that exist at the die surface, when aluminum is injected into the dies at high speed, are hard to produce in a laboratory setting. For this reason multiple experiments are necessary in order to converge upon the surface treatments or coatings that offer the best characteristics when in contact with molten aluminum, followed by plant trials of the new coatings

The sessile drop experiment was used to determine which of the coatings offer the best barrier to wetting and the highest interfacial energy with molten aluminum. The coatings were all applied to the same fully characterized H13 tool steel. The coatings included industrial coatings as well as some that were produced at the Colorado School of Mines ACSEL laboratory. Four aluminum cast alloys that are commonly used in industry were selected; viz. 360, 380, 383, and 390 aluminum alloys. The coatings were tested with the different alloys in order to determine the best coating and or surface treatments that handle each of the aluminum alloys the best.

The aluminum was cut to a cube shape and then melted in contact with each of the coatings in an oxygen-depleted atmosphere. The aluminum was held in contact for an extended period of time at a high temperature. The initial contact angle that the aluminum made with the coatings was recorded and used in a comparative manner to determine the respective interfacial energies with the aluminum alloys. The aluminum was allowed to cool in the furnace and then the solidified droplet was removed from the surface using an instron mechanical tester to measure the amount of force required to remove it, which is related to the soldering strength of the two materials. The fracture surface was then investigated for the amount of material that was removed with the aluminum, which is related to how far the aluminum was able to penetrate the coating and the H13 tool steel.

To test the coatings further a dunk tester was designed and built. The dunk tester manipulates a sample through thermal cycling, which is similar to a typical aluminum die casting shot cycle. The manipulator moves a coated sample in a molten bath of aluminum and then cools the sample in a high pressure spray chamber, repeating this for a period of time or set number of cycles. The molten aluminum is a high temperature corrosive environment and tests the coatings ability to act as a barrier to the aluminum; at the same time the sample expands and contracts due to thermal forces, which cause the coatings to cycle through high levels of compressive and tensile stresses. The coatings that are capable of withstanding both the thermal and the corrosive forces will likely perform best in a die casting die.

The dunk tester, which is a thermal fatigue film durability tester, was designed to be very flexible and consistent. It was decided to modify an industrial robot to perform the tasks. The computer control used for an industrial robot is more dependable than a traditional desktop computer. At the same time it was desirable to control the robot with a point and click program, rather than having to manually write a new program every time a change in the experiment is desired. A desktop computer with a windows based operating system interfaces with the robotic controller to allow the operator to write multiple programs easily and quickly in a manner that is consistent so that the samples can be easily compared with one another.

A frame was designed and built to secure the robot and allow for the use of multiple stations. One of the stations is a crucible furnace with molten aluminum that the coatings are rotated in. One of the stations is a high pressure spray chamber, which is used to remove any aluminum that remained on surfaces such as core pins after a casting is removed and to cool the sample. The thermal cycling of the coating substrate system is a main mode of failure for thin films due to the thermal coefficient of expansion mismatch between the materials. Testing the coatings in a laboratory setting makes the evaluation less expensive and more quickly achieved than testing the coatings in an industrial setting.

2. Background

2.1 Aluminum Die Casting

Aluminum die-casting is used to produce parts that are lightweight, strong, have complex shapes, and are inexpensive. The parts produced in this process can be large, such as engine blocks, transmission housings, or quite small with tight tolerances such as a part that is 12 in. (305 mm) with a 0.0015 in. (0.04 mm) tolerance (Bauer 1960). These parts are often used within complex machines and are a factor in the final cost of the machines.

The process is continually being made more efficient and profitable through the selection and use of materials in the die casting dies. The type and grade of steel used for the die is important, because it is the material that is coming into contact with the aluminum and also provides the structural support for the die casting die. Salt bath nitriding is a surface treatment that has shown an improvement in the service life of die casting dies as a result of improved wear resistance, heat resistance, hardness, corrosion resistance, and safety against fracture (Schmauser 1985). Through the use of better materials at the interface between the die casting dies and the aluminum alloys it is possible to increase the useful life of the dies and therefore the profitability of the process.

Making aluminum die cast parts is done by injecting molten aluminum into a cavity that has a shape that is opposite the shape the aluminum is desired to have. The aluminum is then rapidly cooled giving the solidified aluminum the shape of the die cavity. Normally the die-casting die is designed to produce more than one part in one cycle and there are many areas within the dies that are under a higher stress than other areas within the die, due to complex shapes and the flow characteristics of aluminum as it is injected into the die. Once the aluminum is within the die cavity it is rapidly cooled until the aluminum becomes solid; at which time the aluminum parts are removed and cooled further.

Die casting dies are expected to last an extended period of time; typically a campaign will contain more than 100,000 shots with 2,500 shots per day. The die casting dies are subjected to severe conditions including flow velocities of 40 meters per second and die temperature gradients of 1000 Celsius per centimeter (Venkatesan 1995). While these conditions are necessary for high production rates they also highly limit the types of materials that can be used in the die casting dies. H13 tool steel is the primary material that is used and it is prone to failure in three main ways, which are erosion, corrosion, and thermal fatigue (Aharonov 1999).

The first mode of failure is erosion also known as washout. This mode of failure is when the die material is removed from the surfaces within the die cavity. Washout is caused by the physical impingement of the incoming aluminum forced against the surfaces of the die, as the alloy is injected into the die. The dies tend to have complex shapes such as ribs, cores, pins, and corners, which causes the dies to lose the necessary tolerances for the parts being produced. The dies then have to be repaired, which is time consuming and is very expensive.

The second mode of failure is soldering of aluminum to the die surface, which is followed by corrosion. This mode of failure is caused by a physical bond between the die surface and the aluminum and is followed by chemical interactions and cavitation of the die casting surface. The adherence of the aluminum causes defects in the parts produced and the die casting operation must be shut down in order to repair the die.

The third and main mode of failure for die casting dies is thermal fatigue or heat checking. This is caused by the thermal gradients that are induced in the dies when the die goes through the heating and cooling cycle for producing each part. The large thermal gradients cause the die surface to go through a high compressive stress during heating and a tensile stress upon cooling. This situation leads to cracks, which lower surface quality of the parts and ultimately cause the die to fail.

The promise of increased productivity, die life, and ultimately the increased profitability of the die casting process have induced much research in the areas of coatings and surface treatments. Coatings are increasingly being used to reduce die failures. There is still little information on why certain coatings succeed and others do not (Balasubramaniam 1997). The coatings being investigated include physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), and thermal spray. Surface treatments include carburizing, nitriding, cold working, as well as some others that are not mentioned. The use of coatings is continuing to grow, as well as the knowledge gained from trial and error, slowly the science is being developed which will help to develop a coating system and architecture that will be capable of substantially increasing the life of aluminum die casting dies.

2.2 Wettability

Wettability is a term used to describe whether or not the atoms within a liquid and a solid have an affinity for each other. The atoms within the solid and within the liquid that are in contact with each other are either attracted to each other or repelled from each other. If the atoms in the liquid are attracted to the atoms in the solid the liquid will wet the solid, and a film (or reaction layer) will form on the surface of the solid. If the atoms are repelled from each other, the liquid will form a droplet on the surface of the solid. The droplet will have an area of contact with the solid and will form an angle of contact with the solid. This contact angle can be used to determine the wettability and the interfacial energy between the solid and liquid (Devereux, 1983).

2.2.1 Surface Tension

For a liquid, the higher the surface tension the greater the attractive forces are between the molecules within the liquid. Intermolecular forces change at the interface where a liquid is in contact with a solid (Devereux 1983). The forces can go up or down depending on how much attraction or repulsion that exist between the molecules at the interface when the solid and the liquid come into contact. This change can cause the liquid to spread out (attraction) on the solid lowering the surface energy, or the liquid may have a higher surface energy if it creates a shape allowing the least amount of surface in contact with the solid as is possible (repulsion).

The atoms within a liquid experience forces between the other atoms in the liquid and also with the atoms in the solid. There are also interactions between atoms in the gas that is surrounding the solid-liquid interface. The intermolecular forces that the atoms within the liquid experience, when atoms of the same kind surround them, is much different from the atoms that are at the surface of the liquid. The atoms that are at the surface have only molecules to the sides and below them: this causes an inward attractive force on the atoms. In order for more surface area to be made energy must be added to the system. The liquid will have the smallest possible surface area in order to be at the lowest possible energy, and is why liquid droplets will have a spherical shape. The spherical shape is the lowest possible area for a given volume, and thus has the lowest surface energy for a given amount of material.

The physico-chemical properties of a solid can directly affect the ability of a liquid to "wet" the surface of the solid. If the solid is not wettable with a liquid it is said to be hydrophobic. This phenomenon is of great importance for separation techniques used in the minerals processing field, for flotation (Wills 1997). The process of flotation depends upon the difference in surface activities of the different solid particles that are to be separated and the interfacial energy that exists with air bubbles. The better the adhesion of the bubble to the surface of the particle compared to the other materials in the slurry, the easier it will be to separate the different materials. The force required to break the interface of the particle-air interface is called the work of adhesion, and is very similar to the surface tension or interfacial energy. Much of the research done with wettability was done for the minerals industry and a considerable amount of knowledge, which can be applied to other fields, has been gained.

2.2.2 The Young Equation and The Work of Adhesion

The Young equation is a force balance in which surface tensions are considered force vectors that are in equilibrium with each other. The normal model of this system is one where the solid is immersed in a liquid and an air bubble is attached to the solid, an example can be seen in Figure 2.1.1. The angle that the bubble makes with the solid is an indication of the amount of energy that exists between each of the phases. The contact angle (θ) relates the surface tensions of the different phases (solid, liquid, and gas) by the Young Equation.

$$\gamma_{\mathrm{lg}} \cos\theta = \gamma_{sg} - \gamma_{sl}$$

The angle is always measured from the solid through the liquid to the gas, as can be seen in Figure 2.1. The Young equation is a force balance between the three vectors. This force balance is used to find the amount of wetting that will occur between the solid and air, or similarly with the liquid and solid of interest. The wettability of a surface by a liquid is of great interest for many different systems since it is an indication of the amount of surface energy that exists between the solid and the liquid.

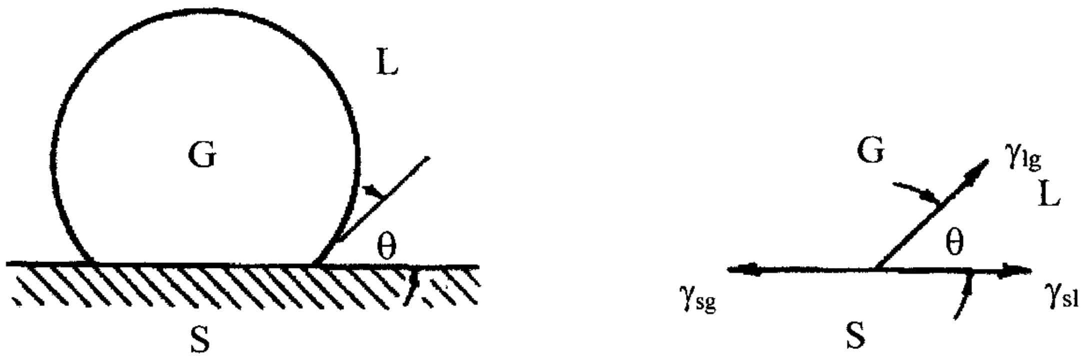

Figure 2.1: Three phase contact showing vectors, surface tensions, and contact angle (Devereux 1983)

When a liquid comes into contact with a solid, the interface between the two materials experiences a change in the interfacial free energy associated with it, which is also the work gained, and is given by the equation;

$$-W_{ad} = \gamma_{sl} - (\gamma_{sg} + \gamma_{lg})$$

when combined with the Young equation it becomes the familiar Young-Dupre equation: (Shimbo 1989)

$$\cos\theta = \frac{W_{ad}}{\gamma_{lg}} - 1$$

where $$W_{ad} = \gamma_{lg}(1 + \cos\theta)$$

Many of the values for the liquid gas surface tensions have been studied and are listed in tables, which makes it possible to calculate the work of adhesion for many different liquid solid systems: once the contact angle has been measured.

2.2.3 Sessile Drop Experiment

A sessile drop experiment allows one to measure the contact angle that a liquid makes with a solid in a relatively simple manner and it can be used for both reactive and chemically inert systems. These experiments can be done at a wide variety of temperatures and also with a wide variety of systems, varying the solid, liquid, and gaseous atmospheres. Using this type of experiment, it is possible to determine the surface energy of a liquid and gas γ_{lg} and the angle that forms is an indication of the surface energy between the liquid and the solid γ_{ls}; because of the Young equation.

$$\gamma_{sl} = \gamma_{sg} + \gamma_{\mathrm{lg}} \cos\theta$$

where the experimental setup is with a liquid in contact with a solid and it is surrounded with a gas, as can be seen in figure 2.2.

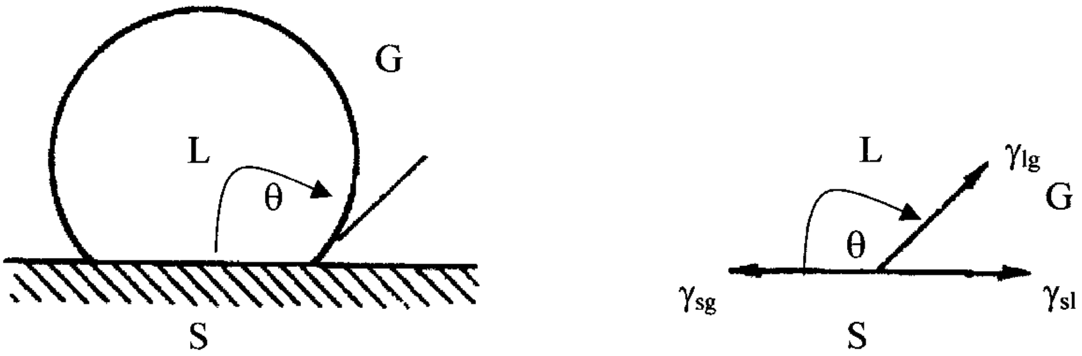

Figure 2.2: Three phase contact showing vectors, surface tensions, and contact angle

Under ideal conditions, the best way to do a sessile drop experiment is to place a liquid droplet in contact with a horizontal flat substrate and allow the liquid and solid to come to a state of equilibrium, and is the best time to make a contact angle measurement. The state of equilibrium can occur with time for a system that is chemically inert, without impurities, the right size droplet is used, and the substrate is smooth. In this type of situation the liquid will spread out onto the solid increasing the solid liquid interface until the advance of the liquid is no longer energetically favorable (Eustathopoulos 1999).

The interface between the three phases is not at equilibrium in reactive systems, and so the analysis done with the Young equation can only be considered accurate for a given moment in time. The interfacial energies of the three phases will change with a chemical interaction that will occur between most systems. Along with this change in interfacial energies will be a change in the contact angle between the phases. The chemical interactions of the phases will cause an exchange of atoms in many cases, and a reaction layer will form at the interfaces of the three phases.

The interaction layer will become larger (spread) as time progresses. The diffusion of atoms from one phase into another is a time dependent process, and will be dependent upon the type of interactions that occur between the elements. The rate of diffusion will decrease from a gas to a liquid to a solid; which is the system in which the wetting of a solid by a liquid in a gaseous atmosphere is being considered. The rate of diffusion will depend upon the system and conditions (temperature, pressure etc), and will always be dependent on the slowest reaction or the slowest diffusion of atoms to feed a reaction, and is known as the rate limiting factor.

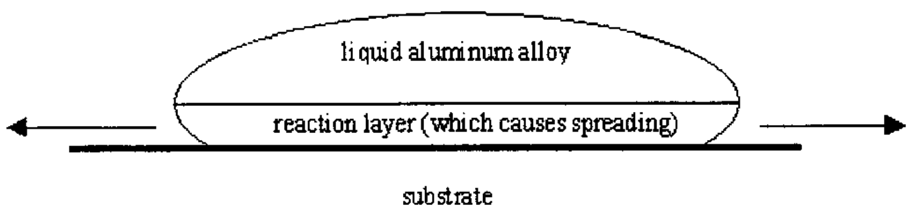

Figure 2.3: Sessile drop showing an exaggerated reaction layer and the spreading action caused by the changing free energy.

2.3 Thermodynamic Considerations

A lowering of the overall energy of the system drives chemical reactions; the study of the energy associated with the reactions is called thermodynamics. Which of the reactions that are likely to occur can be determined through thermodynamics. It is not possible to determine how quickly a reaction will occur by thermodynamics but it is possible to determine under what conditions the reaction can occur. At high temperatures, which this research is centered around, chemical reactions occur more readily. The higher reaction rate is due to the higher mobility of atoms at high temperatures, and the intrinsic relationship between temperature and entropy.

In order to determine if a reaction, such as aA + bB = cC + dD, is likely to occur the second law of thermodynamics must be invoked. The conditions under which most high temperature oxidation occurs has a constant pressure and temperature, and so the equation can be written as:

$$G' = H' - TS'$$

Where H′ is the enthalpy of the system (the heat within the system), and S′ is the entropy of the system (the randomness of the system).

When:	$\Delta G' < 0$	a spontaneous reaction is expected
	$\Delta G' = 0$	the system is at equilibrium
	$\Delta G' > 0$	the reaction is thermodynamically impossible

The equation for $\Delta G'$, the change in energy for the reaction aA + bB = cC + dD, is:

$$\Delta G' = \Delta G^{\theta} + RT\ln\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) \qquad \text{Van't Hoff isotherm}$$

Where ΔG^{θ} is the free energy change when all of the species are present in their standard states, and a is the thermodynamic activity (which describes the deviation from the standard state for a given species).

$$a_i = \frac{p_i}{p_i^{\theta}}$$

p_i is the partial pressure of a gaseous species, and p_i^{θ} is the partial pressure of the quantity corresponding to it's standard state.

Expressing the activity in this form requires the approximation that the species (solid, liquid, gas) will behave in an ideal manner at relatively low pressures (atmospheric) and higher temperatures. The standard free energy change for the system is expressed as:

$$\Delta G^{\theta} = c\Delta G_C^{\theta} + d\Delta G_D^{\theta} - a\Delta G_A^{\theta} - b\Delta G_B^{\theta}$$

Where ΔG_i^{θ} is the standard free energy of formation for a given species.

The reaction of a pure metal and pure diatomic oxygen to form the metal oxide has a standard free energy that can be obtained from the Ellingham diagram, which can be seen in Figure 2.3.1. For a pure solid the activity coefficient is equal to 1 and the activity of the gasses can be approximated by their partial pressures: and liquids and solids by their mole fractions. The equation for free energy:

$$\Delta G' = \Delta G^{\theta} + RT\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right)$$ which reduces to

$$\Delta G^{\theta} = RT \ln p_{O_2}$$

When the system is considered to be at equilibrium then $\Delta G'$ is equal to 0. The standard free energy of a system can be used to predict what reaction products and the conditions under which the products are stable. When the partial pressure of the oxygen along with the temperature of the system is known one can determine whether a metal will favor its pure form or whether it will react with other elements to lower its energy state. For most metals the most stable form is not pure and it wants to react with the oxygen, and it will be found in nature as an oxide. Using this diagram it is possible to determine the conditions that are necessary for the reaction to move in the opposite direction for example equilibrium partial pressure of oxygen for the reaction:

$$2M + O_2 = 2MO$$

and $$\Delta G^{\theta} = RT \ln p_{O_2}$$

and $$a_M = 1 = a_{MO}$$

For example, the temperature is chosen, a vertical line is drawn through the line representing the reaction of interest, from the '0' on the left side, and the partial pressure of the oxygen that is necessary for the reaction to want to occur is known for that given temperature. So for titanium at 400°C a partial pressure of oxygen below 10^{-38} atmospheres is necessary for the titanium to remain in its pure form. Any pressure above this amount will cause the titanium to react with oxygen to form TiO_2. Knowing how to use the thermodynamics, it is possible to predict the reaction direction and possibly control the reaction itself.

2.4 Kinetic Considerations

There are three kinetic laws that govern the oxidation rates of many of the common metals and alloys. These laws are linear, parabolic, and logarithmic. The rate laws are a measurement of weight gain as a function of time. Weight gain measurements must be interpreted carefully. The oxides do not always form continuous adherent scales, some oxides continually spall off of the surface of the metal and some vaporize or form a liquid phase.

The parabolic rate law of oxidation is proportional to the square of the film thickness.

$$x^2 = k_p t$$

Where x is the thickness of the film, t is time, and k_p is the parabolic rate constant. Assuming the film is adherent and compact and that the migration of ions through the oxide layer is the rate controlling step in the oxidation process, then Fick's first law can be used. Which is

$$\frac{dx}{dt} = CD\left(\frac{\Delta c}{x}\right)$$

Where D is ionic diffusivity, C is a constant, and Δc is the constant concentration difference across the oxide thickness. Then $k_p = CD\Delta c$ and is proportional to the diffusivity of the rate controlling species for an electronically conducting oxide surface. The weight gain of a sample can be substituted for x if the values for k_p and C are changed then a plot of W^2 as a function of time, t, will be linear if the parabolic rate law is obeyed. The parabolic rate law is the standard for the analysis of high temperature oxidation kinetics where the diffusion of ions through relatively thick films is the rate controlling step in the reaction.

2.5 High Temperature Reactions

High temperature corrosion is a form of deterioration to which most metals, subjected to the correct atmosphere, are vulnerable. Many technical applications depend upon the stability of engineered alloys and pure metals. The degradation of the material will lead to an eventual need to replace the piece or part. The cost involved in the degradation of these metals can be of great importance to any company that is dependent upon these materials. There is therefore a large amount of interest in the control of the mechanisms by which the oxidation process is occurring.

In order for any chemical interaction to occur there are three things that are necessary. First there must be elements in contact with each other and second there must be a driving force for the reaction, in order for it to occur spontaneously. In order for the reaction to continue, there must be a supply of fresh elements that feed the reaction and this is the third and probably the most important mechanism for the degradation process.

For the control of any process that occurs on a spontaneous basis thermodynamics, which is the study of the driving force for the process, must be considered. For many types of reactions there is a lowering of energy that causes heat to be released (Devereux 1983). For the other reactions energy is required, heat must be given, and the overall energy of the system is increased. The increase in energy will make the system unstable and it will want to go back to a lower energy state. A reaction will spontaneously occur, which will make the elements go back to the original state.

For any type of chemical reaction to continue the mobility of the atoms that feed the reaction and, or the mobility of the product from the reaction, can be the most important factor in controlling the speed of the process. For this reason kinetics is also an important tool in understanding the oxidation process. The movement of atoms and molecules is the only way for reactions to continue.

The reaction product can grow in two main ways. The first way is when the film forms a continuous layer of oxidation product that is relatively stable and adheres well to the metal. The metal is protected from further oxidation by the reaction product and the oxidation process becomes slower. The other way is when the oxidation product does not adhere well to the base material. The oxidation process will proceed at a higher rate when it does not have the oxidation product as a barrier between the oxidizing environment and the material being oxidized. This type of deterioration causes a loss of mass or structural integrity of a piece or part and is therefore the less desirable of the two main types of high temperature corrosion.

The prediction of which alloys and thin films will corrode compared to which will not corrode in a specific environment is very difficult. New alloys and thin films are used in conditions that have not been investigated and there is no way of knowing how well they will perform. The interaction of specific compounds with the atmosphere surrounding the piece or part is unpredictable. For this reason many tests must be done before any new material can be put into a specific application. Without running tests it is difficult to know how well it will perform. For many systems it is possible to simulate the conditions that the metal will be subjected to.

2.5.1 Oxidation Reactions:

High temperature corrosion is a form of deterioration that most metals, subjected the right conditions, will undergo. There must be a lowering of energy for the system in order for the elements to react. The reactions will continue if there is a supply of fresh elements that can come into contact with each other. Knowing which of the steps is the slowest step for the particular reaction can control the rates at which the reactions occur. Preventing the reaction from occurring is not always possible but controlling the speed at which the reaction occurs is often good enough for the time the material is in service.

There are many reactions that occur spontaneously, the only reaction that will be described here will involve oxygen and a pure metal. Other reactions will be mentioned in later sections but will resemble the following reactions. The first and most simple is when diatomic oxygen gas interacts with a pure metal:

$M + O_2 \rightarrow MO_{2}$. or more generally:

$xM + 1/2\ (yO_2) \rightarrow M_xO_y$.

The oxygen required for the reaction can be supplied in other ways than as pure oxygen gas. For instance the oxygen can be supplied by water or it can be supplied by carbon dioxide which take the form of the following reactions:

$$xM + yH_2O \rightarrow M_xO_y + yH_2$$

and $$xM + yCO_2 \rightarrow M_xO_y + yCO.$$

As long as oxygen is attracted more to the metal than it is to itself, the hydrogen, or the carbon, it will dissociate and form a new compound with the metal.

This process cannot happen in one step most of the time. The oxidation process happens in multiple steps. First, oxygen will adsorb to the surface of the metal either by itself or within a compound, which will then dissociate to form atomic oxygen. Next a chemical reaction will occur between the metal and the oxygen. The product from the reaction will form a continuous surface layer, which could adhere well to the surface, or it may have defects, or low adhesion to the surface, and fall away. If it forms a layer that adheres well to the surface the product will become a barrier to the continuation of the process. If the product from the reaction does not adhere well to the surface the reaction will continue with no barrier to the oxidation process will be present.

2.6 Physical Vapor Deposition

Physical vapor deposition is a process used to produce coatings that offer a wide variety of uses and applications. The interface between the material and the phase it is in contact with is of great importance in the performance of the material. The coatings are applied to bulk materials so that one can obtain properties that are not present in the bulk material alone. The bulk material is often selected for structural reasons and coatings offer the opportunity to change the appearance, thermal, electrical, magnetic, mechanical, or chemical properties of the surface (Smith 1995).

The use of coatings to protect a bulk material is not new but PVD is a relatively new method used to produce coatings. PVD coatings can be applied in a very precise manner due to the way in which the coatings are applied. The process is done in a high vacuum using very pure materials for the source of the coatings. By controlling the contaminants, as well as having the ability to control the amount of energy that is put into the system, it is possible to produce coatings that have very good adherence to the bulk material and properties that are desirable for specific applications (Vossen 1978).

Many coatings are being investigated for use in the aluminum die casting industry. The ability to increase the useful life of a component that is within the die casting die allows for the die casting die to run longer without maintenance, making the process more profitable. The parts that are being coated presently are small and of relatively simple geometries (Chellapilla 1997). As the coatings are improved and the ability to coat more of the surfaces that come into contact with molten aluminum is increased, the time the dies can stay in operation and the efficiency of the process will continue to improve.

2.6.1 Application of Coatings

Controlling film deposition process parameters influence the properties of the thin film coating system; namely the adherence, performance and appearance of the coating. There are many different techniques that are used to coat a material. Each of the processes has advantages and disadvantages.

The main considerations are:

- Generation of the plasma
- Ion bombardment energy
  (process, bias, power, substrate-target distance, etc.)
- Pressure

The heat and energy of the incoming particles along with the surface conditions will affect the growth and the final structure of the film. These energy controlling parameters change for the different coating processes, and there is an optimal set of process parameters for each coating substrate combination (Maissel 1983).

The interface that exists between the bulk material and the coating is of great importance. The ways in which the atoms stick to the surface determine whether the coating will adhere. There is a sticking coefficient that is used to quantify the probability of an atom or an element to attach to the surface. Incoming particles do many different things as they collide with the surface of the growing film. Some of the things they will do include adhering to the surface, bouncing back, or penetrating the surface of the film or substrate. Each of these possibilities has a different effect upon the residual stress within the coating and the final microstructure of the coating.

If the energy of the incoming particles is at the right level the particles will adhere to the bulk material and a very even coating across the surface of the bulk material will occur. The atoms will not adhere to the substrate most of the time due to a distribution of energies for the incoming particles. This distribution will have a range in which most of the atoms have a similar energy and a small percentage of the atoms will have much higher or much lower energies than the majority of the incoming particles (Smith 1995). The particles with low energy will simply bounce off the surface; some of them will collide with incoming particles and lower their energy. The high energy particles will also bounce off of the surface on occasion but these particles will impart more energy to the surface and could change the properties or temperature of the growing film. It is also possible for the incoming particles to penetrate the surface of the material. The penetration of the atoms could have beneficial or detrimental effects. These atoms will change the arrangements of the atoms within the lattice and change the amount of residual stress within a few atom diameters from the final location where the atoms come to rest. Often this penetration is useful for adhesion and a general grading of the interface between the film and the bulk material will occur. A graded structure is used to decrease the overall energy that exists at the interface between the two materials, which is often caused by the lattice mismatch for the crystal systems.

Each of the materials will have a nano crystal structure or an amorphous type of structure, which is when there is a lack of periodicity for the atoms. As the temperature changes, the film and the bulk material should expand or contract about the same amount. The mismatch is thermal expansion of the two materials is a very common problem in film deposition. The deposition process occurs at an elevated temperature of about 250° C, when the system cools if the coefficients of thermal expansion are not the same the film will not remain attached to the bulk material (Maissel 1983).

The type and amount of defects that exist within the lattice is also of great importance to the amount of energy that exists within the coating system. Vacancies within the lattice system are sometimes desirable, if they cause the desired level of residual stress within the lattice they can improve certain properties. Most of the time defects are not desirable in a coating system. Many times a defect is the location where the thin film is most vulnerable to failure.

The stress that is incorporated in a film during deposition can be controlled in a number of ways. Some of these include limiting the thickness of the film, using energetic particle bombardment during deposition to maintain a zero stress condition. Periodically alternating the bombardment conditions, to form layers with alternately tensile and compressive stresses that will offset each other. By deliberately generating a dense columnar morphology stress cannot be transmitted through the bulk of the material. Periodically adding alloying or reacting materials (reactive sputtering) or the mixing of layers within the film can also reduce the stress level.

The deposition process can be designed for each system of coating and bulk material combinations. The stress induced during the deposition can vary widely and some of the uses for the material may require a specific type and amount of stress. This stress must always be within a range in order for the film to remain attached.

2.6.2 Residual Stress

Stress retained within a thin film is of great importance in the performance and stability of the coating. The adherence of the film is the most important of the properties that a film possesses. The stresses are generally either tensile or compressive in nature. If the stresses are too high in either of the cases the film will not adhere well to the substrate. A good film will generally have a compressive residual stress.

The surface of any material has a higher energy associated with it than the inner bulk of the material. This higher energy is due to the lack of surrounding atoms to bond with. There is also a mismatch for the number of bonds between a film and the bulk material which causes a residual high energy state. The system will try and find a way to lower the energy and at high temperatures the diffusion of atoms becomes likely, especially if there are large numbers of grain boundaries, and properties of the film will change. The interface between the two materials will be the main influencing factor as to how well the film adheres to the bulk material, and the microstructure of the film along with the type and amount of defects will be the main factors in the overall performance of a coating.

The stress or energy of a thin film is intrinsic in the properties of the coating; through proper control of the deposition parameters it is possible to create a thin film with acceptable performance parameters. The deposition is controlled by three main factors, which are substrate surface condition, reactivity of the arriving material, and energy input (Smith 1995). The energy input can have a profound effect upon the properties of the film through both the composition and structure of the film. Substrate temperature during deposition and the thermal coefficient of expansion mismatch between the film and the substrate can cause the residual stress in the film to exceed the yield strength of the material the film is comprised of, and the film will fail.

2.6.3 Film Free Surface

The properties of the free surface are often what one is attempting to change or enhance when coating a bulk material. The properties could be oxidation resistance, wear resistance, or appearance, as well as electrical properties. The free surface of any solid is a place of increased stress, or energy, this is due to the phase interface. The atoms within a solid that are in contact with atoms in another phase are at a higher energy than the atoms within the bulk of the material. This increased energy will cause reactions that will help to lower the total energy of the system.

One of the ways to determine the residual stress or surface tension of a solid is through the Young equation and the amount of wetting that occurs for a liquid in contact with a solid. The Young equation is $\gamma_{sv} = \gamma_{ls} + \gamma_{lv} \cos \theta$, it relates the surface tension of three phases which are in contact. By measuring the contact a liquid makes with a solid it is possible to determine the amount of surface energy that that the film exhibits. A high surface tension exists between the liquid and solid if the liquid is non-wetting with the solid, which is shown when there is a high angle θ.

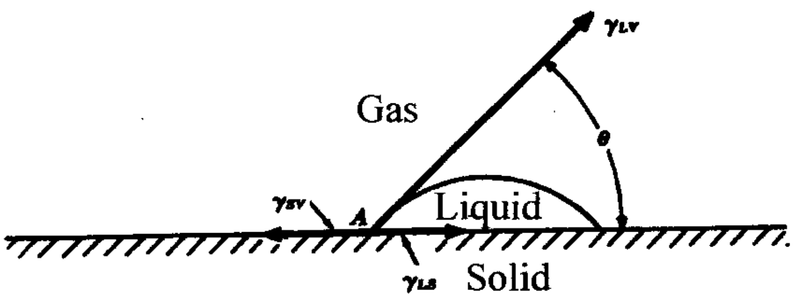

Figure 2.4: Three phase contact showing three phases, surface energy vectors, and contact angle

Often it is not desirable for the solid phase to react with the phases it is in contact with, and is often the reason that a coating is applied to a bulk material. In the application of a coating that will be contacted by a liquid, a high contact angle is an indication that the two phases will not react. If the contact angle is equal to or less than ninety degrees the surface said to be wetting and the two phases are compatible and are likely to react with each other. If the angle is greater than ninety degrees the solid is not wetting with the liquid and the surface tension of the liquid is greater than the surface tension of the solid.

3. Experimental Development

This research is directed toward the aluminum die casting industry and has the goal of finding a working layer coating, which is a good barrier to molten aluminum. The objective of these experiments is to determine which surface treatments and coatings, out of a selected set of coatings, has the largest interfacial energy and is the best barrier to selected molten aluminum alloys. A set of coatings applied using PVD techniques were tested using a sessile drop experiment. The sessile drop experiment has the advantage of allowing one to use the Young equation to help determine which of the surface treatments has a high surface energy with molten aluminum. At the same time the liquid aluminum can be left in contact with the coating for an extended period of time in order to determine which of the coatings is a good barrier to the molten aluminum.

3.1 Basis For Experiment

One of the main modes of failure of high performance H13 tool steel is known as soldering. Die soldering occurs in a series of steps, physiochemical adherence of the aluminum, pitting corrosion, diffusion, and silicon segregation. Soldering tends to occur in two main ways, impingement soldering and deposition soldering. Impingement soldering occurs in areas that experience high metal velocities, often in the vicinity of the entrance to the die cavity. Deposition soldering occurs in areas of low metal velocity (Shankar 1997, Cheng 1993). The sessile drop experiment used for this research is most like deposition soldering.

In both types of soldering the same influences are in effect. The aluminum and the iron have a high affinity and will react to form intermetallic compounds such as Fe_2Al_5, Fe_3Al, and $FeAl_3$. In the presence of alloying elements, which are prevalent in most modern aluminum alloys, other intermetallic compounds will form as well (Shankar 1997). The molten aluminum is highly alloy able and the aluminum droplet will absorb a large amount of elements until it reaches a saturation point. If the coating is a good barrier to the aluminum it will not be able to absorb as much iron from the substrate as a coating that is not a good barrier to the aluminum. The further the aluminum is able to penetrate the substrate the less likely it is a good working layer film.

3.2 Coatings and Surface Treatments Compared

The coatings chosen for this research were chosen due to their use in the die casting industry and some coatings were chosen that are theoretically non-wetting with molten aluminum. The coatings that were chosen from a theoretical standpoint were created in the ACSEL PVD laboratory. The companies that successfully produce the coatings on a commercial basis applied the rest of the coatings. To compare whether coating techniques have an effect upon the performance of a coating CrN was applied by two different companies. A complete list of the coatings selected for this evaluation can be seen in Table 3.1.

Table 3.1: Coatings chosen for the evaluation and comparison as a good working layer film for molten aluminum

Cr_3Si	Cr-C	Cr_3C_2
Cr-N	Ti-Al-N	Ti-C-B
Ti-C-B-N	Ti-B-N	Ti-N
$Ti\text{-}B_2$	Ti-Cr	Ti-Zr-Ni
Ni-Al	Ni-Al-N	$Cr(CO)_6$
Mo-Si-C-N	Ni-Fe	B-N
Zr-N	Mo-N	Mo-Zr-N

All of the coatings were applied to the same fully characterized H13 tool steel. The steel substrates were cleaned before application of the coatings but no polishing was done. In a normal coating process often the substrate will be prepared with a polishing step. The polishing step was avoided due to the polishing practices of the die casting companies, and to make sure that all of the samples have the same roughness. The roughness of the surface of the samples, have an effect upon the wetting nature of the aluminum and could influence the perceived interfacial energy between the coating and the aluminum.

3.3 Type of Experiment Used and Considerations

The system that is being worked with is complex in many ways, and it is desirable to simplify the number of variables as much as possible while maintaining the usefulness of the experiment. The experiments must be run in a self consistent manner, and is done so that trends become apparent which can be compared and related to the interactions that control the performance of the coatings. A preliminary experimental matrix was formed to find a set of conditions such that the aluminum was wetting upon H13 tool steel. H13 tool steel is the main material used for aluminum die casting: and the goal of this research is to find a coating system which is capable of prolonging the life of this material.

The sessile drop experiment, which was used to compare the films, was done in an oxygen depleted atmosphere at 770° C, and was done because it was found that the aluminum would spread and react more with H13 tool steel under these conditions than at lower temperatures, and with higher oxygen levels; which can be seen in Figure 3.1. The iron and the aluminum as well as many of the alloying elements used for both alloys have a high affinity for oxygen and so using a consistent method for controlling the amount of oxygen was necessary, and was done using a mechanical pump and high purity argon to displace much of the oxygen.

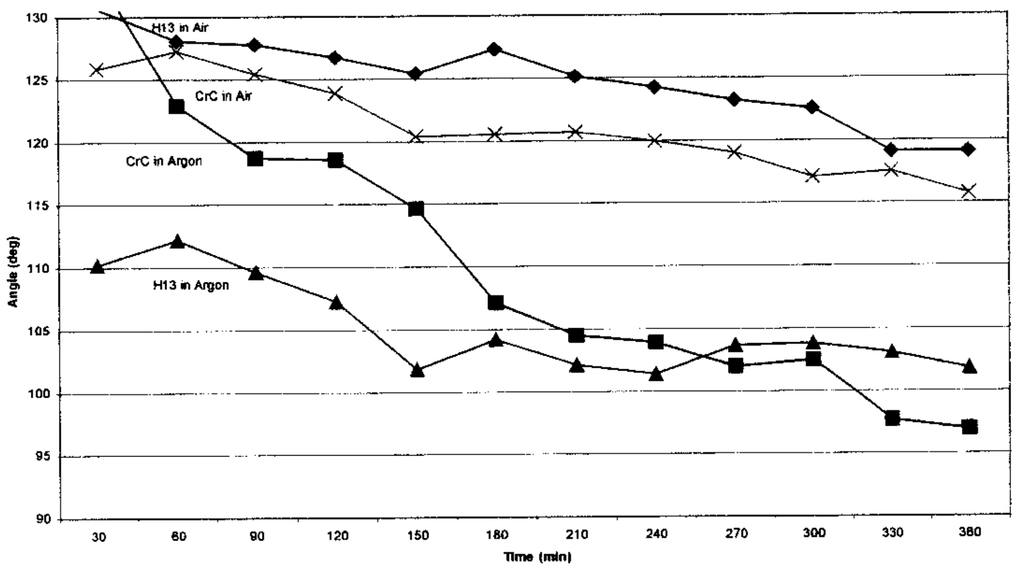

Figure 3.1: Graph of 360 Al on H13 tool steel and CrC, at 800°C, in argon and air.

The size of the aluminum droplet is a factor in the amount of spreading of the droplet due to gravity and the reaction layer. A number of tests were performed in order to determine a droplet size that was wetting and would spread upon the H13 tool steel. The surface roughness of the solid is also a contributing factor to the amount of spreading. The roughness will have an effect upon the contact angle due to the amount of surface contact between the liquid aluminum and the surface of interest. For this reason a set of H13 tool steel samples were fully characterized and used as the substrates for all of the coatings and as the raw steel the coatings and surface treatments were compared to.

Due to the high reactivity of the system being worked with, the contact angle often changes over time for the coatings being compared due to the changing surface energy for the reaction layer. For this reason the contact angle measurement is only accurate for a given moment in time. All of the samples were kept in contact with the aluminum for the same short amount of time before a measurement was made. The aluminum was left in contact with each of the coatings for a total of six hours and allowed to cool in the furnace, and was done in order leave the aluminum in contact with each of the surfaces for an extended period of time; in order to compare which of the coatings and surface treatments was the best barrier to the corrosive action of the aluminum.

After the samples were removed from the furnace the aluminum droplet was removed using an instron machine to measure the amount of force required to separate the two surfaces, and was done in order to compare the soldering strength of the samples, the lower the strength of the bond between the two materials the better. The size of the indentation left by the aluminum was then measured to determine the amount of coating and H13 tool steel that the aluminum was able to absorb while it was in a liquid state.

4. Experimental Procedure

Four aluminum cast alloys chosen for these experiments were 360, 380, 383, and 390. All of these alloys are very common in the die casting industry. All of the alloys are high in silicon content as well as other alloying elements and the H13 tool steel is also a highly alloyed metal, as can be seen in table 4.1. The aluminum was cut into ¼ inch blocks (≈ 6 mm), which was of an intermediate size that was large enough for good measurement of the contact angle, and small enough that the spreading of the aluminum over the surface of the sample was not too great.

Table 4.1 Alloying elements of H13 tool steel and the aluminum cast alloys used in this study (all amounts are in percent by weight)

H13 – 0.39 C: 0.37 Mn: 0.013 P: < 0.001 S: 1.08 Si: 5.03 Cr: 1.46 Mo: 0.95 V
360 - 9.0 to 10.5 Si: 2.0 Fe max: 0.6 Cu max: 0.5 Ni max: 0.5 Zn max: 0.4 to 0.6 Mg: 0.35 Mn max: 0.15 Sn: 0.25 others
380 – 7.5 to 9.5 Si: 2.0 Fe max: 3.0 t0 4.0 Cu: 0.5 Ni max: 3.0 Zn max: 0.1 Mg max: 0.5 Mn max: 0.35 Sn: 0.5 others
383 - 9.5 to 11.5 Si: 1.3 Fe max: 2.0 t0 3.0 Cu: 0.3 Ni max: 3.0 Zn max: 0.1 Mg max: 0.5 Mn max: 0.15 Sn: 0.5 others
390 – 16.0 to 18.0 Si: 1.3 Fe max: 4.0 to 5.0 Cu max: 0.2 Ti max: 0.65 Mg: 0.1 Mn max: 0.1 other

Each of the candidate surface coatings were applied using physical vapor deposition techniques between 3-5 μm thick onto the same fully characterized H13 tool steel. A carbo-nitriding surface treatment was also applied to the steel to be compared with the other coatings as it is currently used in commercial aluminum die casting operations. The coatings were all compared to the raw H13 tool steel as well as the carbo-nitrided surfaces that are commonly used in commercial applications.

The surface of the aluminum and the surface of the sample were cleaned using isopropyl alcohol. The samples were then loaded into a tube furnace two at a time (side be side) to lower the overall number of tests that were necessary. The samples were leveled in order to equalize the gravitational forces on both sides of the tube. The tube furnace that was used was 3 feet (0.91 m) long and 2.4 inches (60 mm) in diameter. The furnace was evacuated using a mechanical pump to 60 mTorr and then back filled with high purity argon. This was done three times and then the argon was allowed to flow at 2.6 standard cubic feet per hour ($\approx$ 1 m^3/hr) for the duration of the experiment.

The furnace was started and it took thirty minutes to reach the melting temperature of aluminum. Just before this time a video recorder was started to ensure the actual melting of the aluminum block was recorded. The furnace would continue to increase in temperature until it reached 770°C. The furnace would maintain this temperature for six hours and then the furnace would be shut off, as would the flow of argon gas. The samples would be allowed to cool back to room temperature and the samples would be removed from the furnace and another set of samples would be tested. A schematic and a picture of the experimental setup can be seen in figures 4.1 and 4.2 respectively. Figure 4.3 shows a picture of the samples when they are in the chamber.

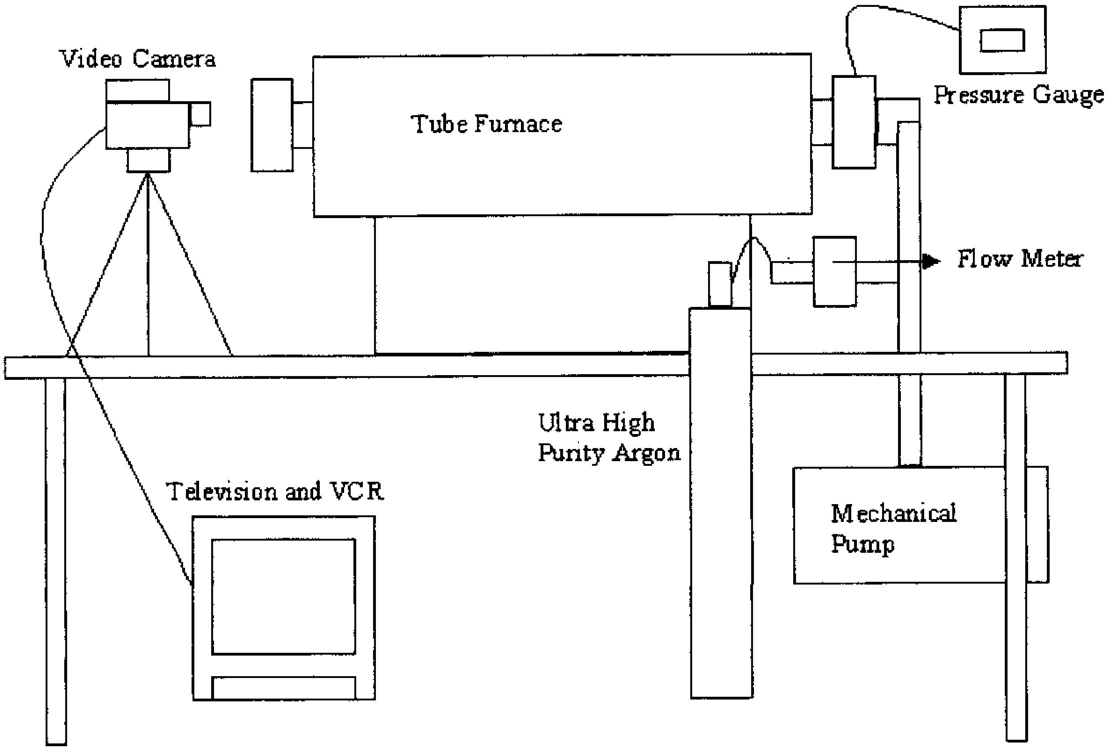

Figure 4.1: Schematic of the equipment used for the sessile drop experiments.

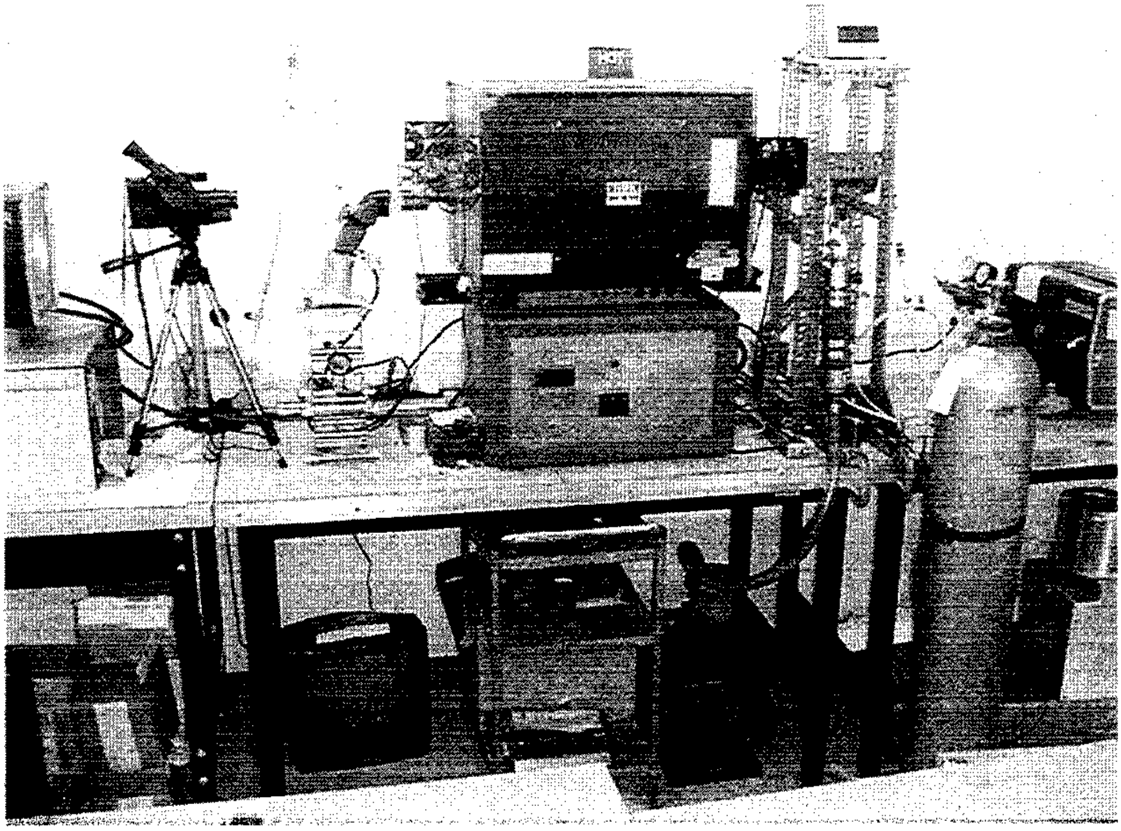

Figure 4.2: Picture of the equipment used for the sessile drop experiments.

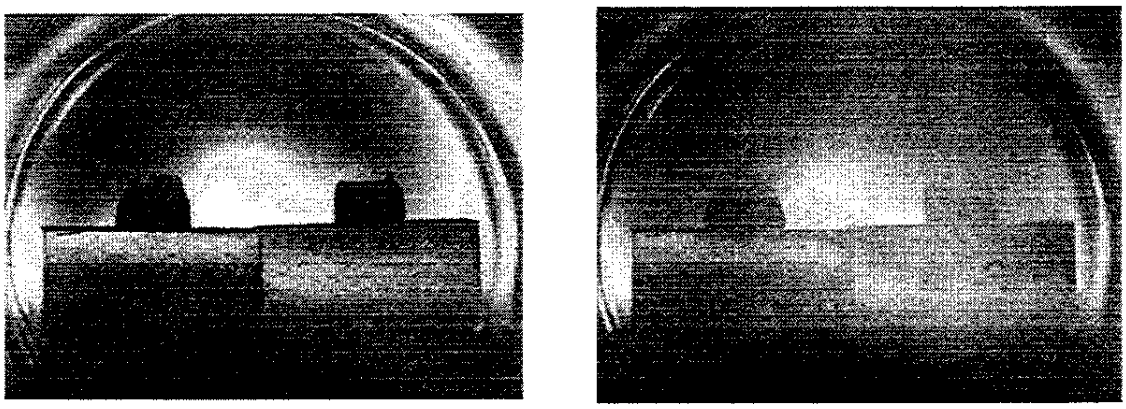

Figure 4.3: Pictures of the samples in the furnace at five minutes and four hours
H13 tool steel is on the left and CrN is on the right
with 360 aluminum cast alloy on both

5. Experimental Results

5.1 Wettability and Surface Spreading

The contact angle measurements, as well as the measurements for the spreading of the aluminum droplet, was recorded using a video recorder that was placed at one end of the tube furnace, which had a window. The recording was done onto VHS videotapes, which were capable of recording a little more than six hours each. The tapes were then taken to an image analysis computer, which was able to make all of the measurements with a ±5 degree range of variance.

To make the contact angle measurements two distances would be used to determine the angle through algebra. The first distance is at a point in the center of the droplet. The other distance that must be known is the length of the interface between the molten aluminum and the solid surface. These distances are labeled "A" and "B" respectively and can be seen in figure 5.1.

The measurements were done five minutes after the aluminum melted for each of the samples. This time was allotted for the liquid aluminum to come to a state of equilibrium with the solid. As the aluminum alloy reacts with the solid surface a reaction layer will occur and there will be a change in the interfacial energy of the two phases. The initial measurement "B" was then used along with the final distance of "B" to determine the amount of spreading of the aluminum droplet. All of the measurements are relative for each of the samples due to the variances in camera position, and the specific system that is being worked with.

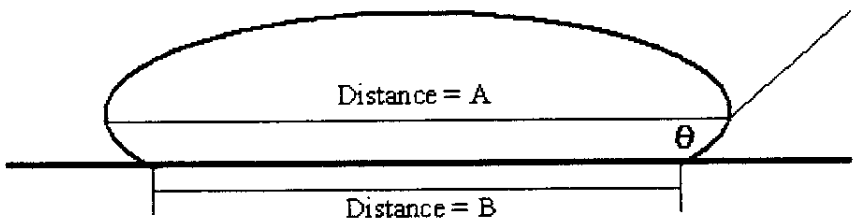

Figure 5.1: Sessile drop showing the two distance measurements that were used to determine the contact angle θ.

5.1.1 Wettability

All of the coatings and surface treatments are compared using H13 tool steel as the baseline. It was found that most of the coatings and surface treatments had a higher contact angle and thus a higher interfacial energy than the H13 tool steel. The initial contact angle and the final contact angle can change in both directions or stay the same. The less wetting the surface is with the aluminum alloy the higher the angle. Depending on the reactions that occur, between all of the alloying elements that exist within the system that is involved, the shape of the droplet changes over the duration of the experiment.

Some of the systems have a droplet that remains very much the same shape throughout the experiment, and shows very little interaction between the aluminum alloy and the surface it is in contact with: and it would seem gravity seems to have very little effect as well. Some of the samples showed very little increase in contact area between the aluminum droplet and the solid surface but the contact angle increases throughout the experiment. This increase is due to gravity and does not necessarily mean that the interfacial energy between the two phases is increasing.

For the majority of the coating and alloy combinations the interfacial area between the aluminum droplet and the surface increased. This increase normally caused the angle θ to decrease, making the surface more wetting over the duration of the experiment. This increase in surface area is due to the chemical driving force as well as the gravitational driving force. In the case of the NiAl and NiAlN coatings the combination of the two driving forces caused the aluminum droplet to completely lose shape and spread completely over the surface of the sample.

When the interfacial area between the aluminum droplet and the coating or surface treatment decreases the driving force due to gravity is less than the chemical driving force for the reactions between the two phases. This contraction of the droplet often caused the angle θ to increase, which does mean the interfacial energy of the two phases increases over the time the experiment was conducted. Due to the high level of corrosive action of molten aluminum, and the high level of alloying elements that can be absorbed by aluminum, it is ideal when the aluminum droplet is non-wetting with the solid surface when it melts, and after it has been in contact with the solid for an extended period of time.

Table 5.1: Contact angles of melted aluminum cast alloys (360,380,383,390) on H13 tool steel and selected coatings.

Coating or Surface Treatment	360 Al Beginning Ang. (deg)	360 Al Finishing Ang. (deg)	380 Al Beginning Ang. (deg)	380 Al Finishing Ang. (deg)	383 Al Beginning Ang. (deg)	383 Al Finishing Ang. (deg)	390 Al Beginning Ang. (deg)	390 Al Finishing Ang. (deg)
H13	98	< 90	114	101	106	< 90	108	125
CrN (P)	99	123	109	117	94	121	94	126
CrN (IB)	118	122	117	112	112	110	118	124
CrC	94	98	116	117	94	94	117	114
TiAlN	105	109	107	111	111	105	104	116
ZrN	99	105	112	118	106	117	107	111
MoZrN	112	111	101	107	105	112	110	112
MoNx	116	107	108	103	102	102	101	111
Al_2O_3	91	107			114	115	105	111
TiN-TiCN	99	103	116	118	114	113	107	114
Cr_3Si	117	106			109	118	107	< 90
Dynablue	112	107	98	110	110	105	108	103
TiB_2-TiC	109	119			107	115	107	113
TiBCN	98	110			118	117	108	125
$MoSi_2$-SiC	98	123			107	115	107	113
NiAl	< 90	< 90			< 90	< 90	< 90	< 90
NiAlN	< 90	< 90			< 90	< 90	< 90	< 90
H13	98	< 90			107	94	101	< 90
H13	96	< 90			106	94	102	< 90
	383 Al		**383 Al**		**383 Al**		**383 Al**	
Al_2O_3	113	109	113	108	114	109	114	109

As can be seen in Table 5.1, there are some coatings or surface treatments that do not have values, and is due to the lack of samples necessary to conduct the experiments. At the bottom of the table there are repeated experiments that were conducted to verify the results and to ensure consistency. The variance or rang of error is ± 5 degrees for the image analysis done on the computer, and is known due to the measurements having been done by more than one person and some of them done on more than one occasion.

The Al_2O_3 was produced at a different time for the repeated experiments, so other influences (such as hardness, adhesion, defect amount due to contaminants etc.) may have had an effect upon the repeatability of the values.

5.1.2 Surface Spreading

The amount of spreading of the aluminum droplet, with each of the surface treatments and coatings, is an indication of the amount of chemical driving force for the aluminum alloy to react with the solid surface. If the liquid spreads upon the surface of the solid it is likely due to gravity and the chemical reaction layer between the two materials. If the alloy does not spread, it does not have a way to lower the energy of the system by reacting with the surface it is in contact with and the gravitational pull upon the liquid is not enough to make the liquid spread. If the aluminum droplet decreases its surface area, then the elements within the aluminum alloy droplet are more attracted to one another than the elements within the solid. For this system the lowest energy state for the system is when the liquid has the least amount of contact area with the solid, and is the type of material is likely to be a good working layer for a die casting die material.

Table 5.2: Spreading percent of melted aluminum cast alloys (360,380,383,390) on H13 tool steel and selected coatings.

Coating or Surface Treatment	360 Al Growth Percent at Interface	380 Al Growth Percent at Interface	383 Al Growth Percent at Interface	390 Al Growth Percent at Interface
H13	6	10.8	13.4	17.8
CrN (P)	-11.7	-2.1	-9.1	-18.9
CrN (IB)	-1.2	2.2	-2.4	1.3
CrC	6.1	1.1	2.5	14.7
TiAlN	0	0.26	0	0.7
ZrN	3.7	-3.5	-2.5	3.6
MoZrN	6.1	-2.2	-3.7	0
MoNx	9	5	0	-4.5
Al_2O_3	1.1	0	4.1	0
TiN-TiCN	13.2	0.93	1.6	0.27
Cr_3Si	16.6	0	1.1	19.5
Dynablue	7.5	4.9	1.1	5.1
TiB_2-TiC	-1.4	0	-3.2	-3.3
TiBCN	2.4		4.8	-8.6
$MoSi_2$-SiC	-11.9	0	0.5	2
NiAl	>100		>100	>100
NiAlN	>100		>100	>100
H13	6.5		14.2	19.8
H13	4.9		13.8	20.6
	383 Al	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	2.8	2.8	3.1	2.9

5.2 Soldering Strength

The aluminum used in a die casting operation is not supposed to stick to the die material. Ideally the aluminum will take the shape to the die upon cooling and eject without difficulty from the die, the aluminum will not adhere to the die casting die and remain in the die. The problem is some aluminum will adhere to the die surface after a number of die casting shots. This problem is known as soldering and is discussed in section 3.1.

When aluminum solders to the surface of the die it becomes the surface the incoming molten aluminum will come into contact with during solidification, instead of the steel, and it the part will be defective. If the aluminum that was soldered to the steel remains after ejection, the part will not have the correct shape in the region of contact. If the aluminum detaches from the surface with the new part, then the part will have an extra interface in this region that will likely fail leaving a defect in the part. The latter condition is preferable for many reasons, ignoring the fact that two or more parts are defective.

When the aluminum that soldered to the surface of the die casting die is removed by the part following the occurrence of the event, there are advantages. The advantage that is immediate is the fact that all of the parts produced after the removal of the aluminum will not be defective. Many of the defective parts from this type of problem are cosmetic and not structural, which is a good thing unless the surface that is defective will be visible.

When the aluminum is not easily removed the die casting operation must be stopped in order to remove the aluminum. If the aluminum is adhered to the steel by physical adhesion it will be removed more easily than if it is adhered chemically. If the aluminum remains attached to the surface for a long enough period of time, due to the corrosive action of aluminum and the high temperature, the physical adhesion will become chemical adhesion. The aluminum will cause cavitation of the die steel and is time consuming and expensive to repair.

The amount of force required to separate two materials is related to the strength of the bond between the two materials. The bond strength that was evaluated in this investigation was between H13 tool steel and various surface treatments and coatings.

The lower the force required to remove the aluminum the better the surface is for aluminum die casting. The parts that are formed in contact with the die surface are more easily ejected from the die and the aluminum is less likely to solder to the surface. If soldering does occur there is a higher probability that the next casting will adhere and remove the soldered aluminum from the die.

For this investigation an instron mechanical tester was used to measure the amount of weight required to remove a solidified droplet from the surface of the test sample. Each of the samples had a droplet that was large enough that it could be pushed off of the surface by a piece of steel. The substrate for each of the samples was one inch (24.5 mm) square and one half inch (12.25 mm) thick and a special rig was designed and built in order to hold it in place. The setup can be seen in Figure 5.2.

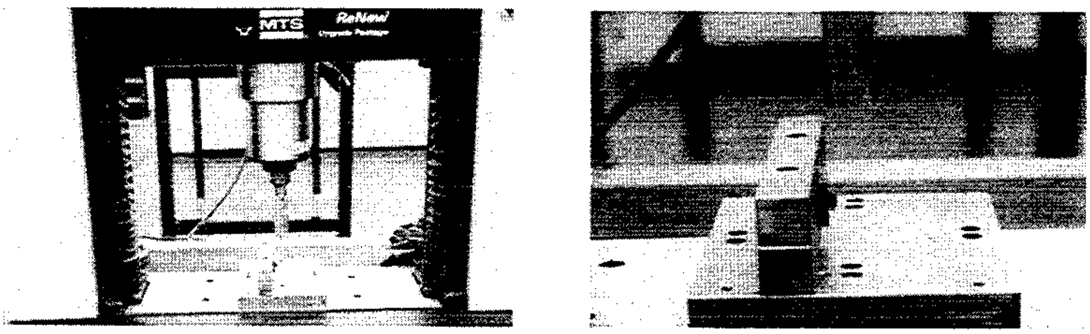

Figure 5.2: Setup for the determination of the soldering strength of the aluminum alloys to the various surface treatments and coatings.

The samples would each be loaded into the clamping device and the aluminum would be sheared from the sample. The amount of weight required to remove the aluminum would be recorded. The sample would then be investigated in order to determine the amount of surface area that was in contact between the two surfaces. The area was determined using a copy machine to increase the size by eight hundred percent and a copy of grid paper was decreased in size by fifty percent and copied onto a view graph. The number of blocks that covered the area would be counted and then knowing how many blocks make a centimeter it was possible to determine the size of the area. Knowing the amount force required when separating the two surfaces, and the area of contact between them it was possible to determine the bond strength between them.

As can be seen in Table 5.3, there are a number of values of zero reported, and is due to the fact that some of the samples would simply come apart as they were removed from the furnace. Where there are spaces with no values it is due to the lack of necessary samples to run the experiments. When one looks at the soldering strength of the droplet, the area is very small and so the strength in Newton's per meter squared is a very large number.

There are a number of assumptions that are made; the first is that the aluminum droplet was removed at the interface between the steel, or the coating, and the aluminum. The droplet will separate from the substrate at the point that is weakest and this could be due to weak intermetallics or defects in the region of fracture. Another assumption that was made is that the surface of contact is smooth, which as can be seen in section 5.3, and is not always the case. Many of the samples are very rough along the interface of fracture, which means that the contact area is much larger than one that has a very smooth surface. For the above stated reason the main thing concentrated upon for this area of investigation is the force rather than the soldering strength in deciding which treatments are good candidate working surfaces.

Table 5.3: Force to remove droplet and the soldering strength of aluminum cast alloys (360, 380, 383, 390) on H13 tool steel and selected coatings.

	360 Al		380 Al		383 Al		390 Al	
Coating or Surface Treatment	**Force to Remove Droplet (N)**	**Soldering Strength Droplet (N/m2)**	**Force to Remove Droplet (N)**	**Soldering Strength Droplet (N/m2)**	**Force to Remove Droplet (N)**	**Soldering Strength Droplet (N/m2)**	**Force to Remove Droplet (N)**	**Soldering Strength Droplet (N/m2)**
H13	236	43,703	0	0	42	6,269	489	94,039
CrN (P)	178	247,222	0	0	0	0	396	99,000
CrN (IB)	258	78,181	0	0	10	83,333	98	23,902
CrC	0	0	0	0	49	7,903	36	5,714
TiAlN	0	0	0	0	7	2,058	0	7
ZrN	51	10,625	4	7	859	357,917	89	37,083
MoZrN	0	0	0	0	0	0	10	1,887
MoNx	0	0	0	0	0	0	0	0
Al_2O_3	0	0	0	0	0	0	36	63,158
TiN-TiCN	0	0	6	1,114	0	0	0	0
Cr_3Si	311	47,498			18	3,473	622	61,002
Dynablue	578	147,017	5	2,719	27	8,631	889	161,616
TiB_2-TiC	0	0			0	0	0	0
TiBCN	667	456,623			0	0	222	54,200
$MoSi_2$-SiC	222	60,550			111	56,116	222	282,723
H13	286	42,058			36	6,207	423	52,222
H13	252	38,769			51	8,793	457	54,405
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	7	4,861	27	7,200	15	6,726	4	11,111

5.3 Surface Analysis

After the aluminum was removed from the substrate the substrate was analyzed using a mechanical profilometer to evaluate the fracture surface, and was done in order to determine the depth and roughness of the fracture. The depth of the fracture was determined using an average value that the profilometer was able to calculate. The roughness along with the depth of the various regions makes it difficult to determine the overall depth of the crater without using the profilometer to average the value.

For the investigation, one scan was insufficient to ensure the reliability of the information gathered. If one does two scans within a very short distance of one another the depths could change significantly for the deepest valleys on the scan, and is why multiple scans were done and they were done in four directions.

Most of the coatings failed, and the resulting crater that is left when the aluminum is removed is large and extends much below the depth of the coating, an example of this type of scan can be seen in Figure 5.3. All of the coatings were applied at three to five micrometers thick and the average depth of the craters for the coatings that failed was around on hundred micrometers deep. In most cases the crater edge would have a lip that had soldered aluminum upon it, and is the outer material in the spreading action of the droplet. This material is most likely a reaction product and precedes the dissolution of the coating into the molten aluminum.

Some of the coatings had penetration by the aluminum in some area but not the entire surface area where the aluminum was in contact with the coating failed. In most cases where the coating did not fail completely, regions of deposition accompanied the crater, where aluminum remained soldered to the coating after the bulk aluminum was removed, an example of this type of scan can be seen in Figure 5.4. This type of coating is not an ideal candidate for the working layer film, even though the coating did not fail completely.

Some of the samples have no crater to investigate, the coating or surface treatment was able to withstand the corrosive action of the aluminum and was a good barrier to the aluminum and it did not penetrate the coating, an example of this type of scan can be seen in Figure 5.5. All of these coatings had some regions with aluminum soldered to the surface but the amount of soldered aluminum was minimal, on the order of micrometers, and would likely not affect the casting that would be produced with the surface in a die casting operation. These coatings are likely to be the best working layer films for aluminum die casting dies.

The main information that was gathered using this data is the volume of coating and substrate that was removed when the aluminum was sheared from the surface. The volume of material removed of an indication of how quickly the aluminum was able to penetrate the coating or surface treatment. The molten aluminum is capable of absorbing iron and other alloying elements in the H13 tool steel at the same rate from one sample to the next. If the volume of material that was absorbed by the aluminum is large, then the coating failed quickly and the aluminum was able to attack the steel for a longer time than if the coating was able to withstand the aluminum and not let it penetrate it.

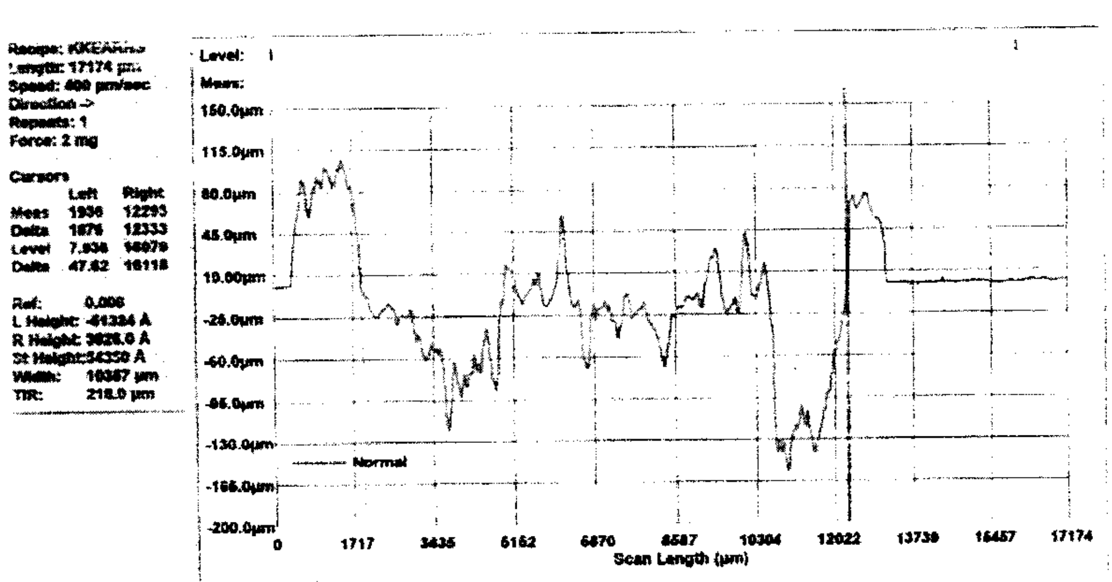

Figure 5.3: Profilometer scan of sample with a large crater and deposition surrounding the crater.

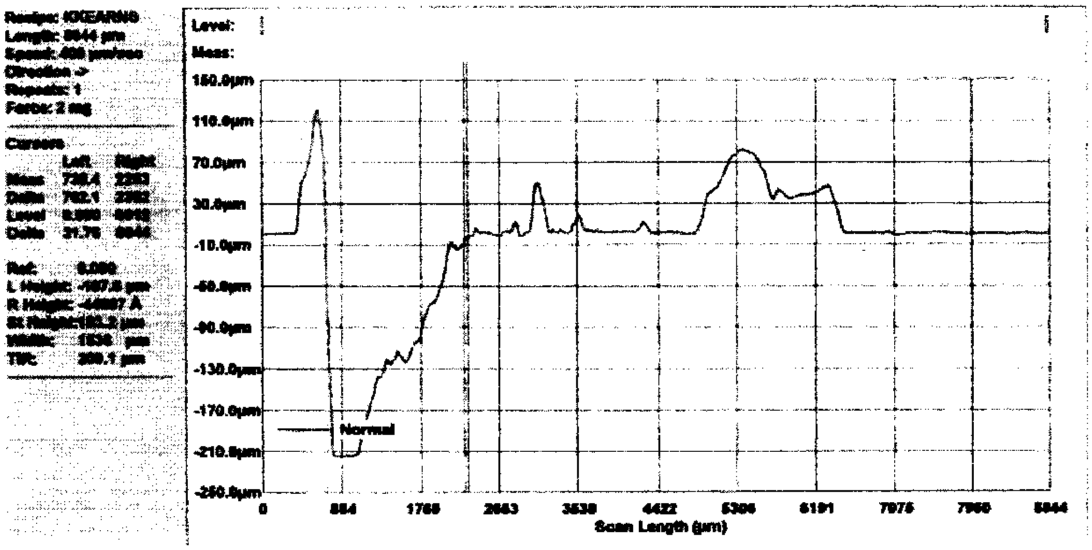

Figure 5.4: Profilometer scan of sample with a crater where the coating failed in some places and in other places did not fail and deposition soldering occurred.

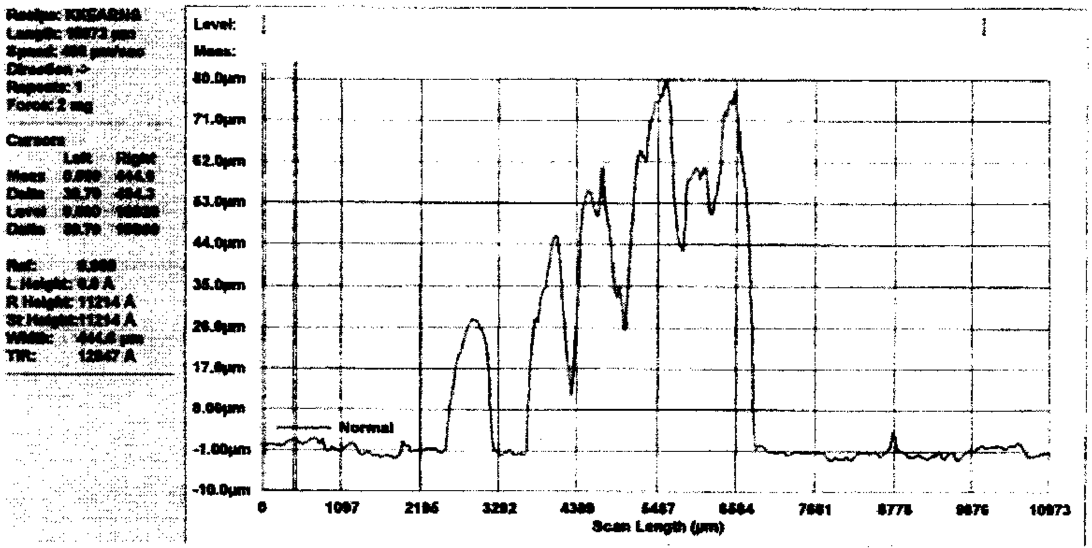

Figure 5.5: Profilometer scan of sample with deposition in some places along the interface between the aluminum and the coating with no coating failure.

Table 5.4: Volume removed (mm^3) from coatings and substrate by molten aluminum cast alloys (360, 380)

Coating or Surface Treatment	360 Al Fracture Surface Average Depth (x10-6m)	Fracture Surface Area (x10-5 m2)	Volume Removed (mm3)	380 Al Fracture Surface Average Depth (x10-6m)	Fracture Surface Area (x10-5 m2)	Volume Removed (mm3)
H13	70	5.4	3.78	118	5.8	6.844
CrN (P)	0	0.72	0	0	0	0
CrN (IB)	0	3.3	0	138	2.9	4.002
CrC	88	5.3	4.664	116	6.3	7.308
TiAlN	128	3.6	4.608	129	4.3	5.547
ZrN	109	4.8	5.232	94	6.6	6.204
MoZrN	82	4.9	4.018	122	4.5	5.49
MoNx	134	5.6	7.504	136	3.8	5.168
Al_2O_3	0	0	0			0
TiN-TiCN	82	3.9	3.198	128	5.2	6.656
Cr_3Si	84	6.6	5.544			0
Dynablue	154	3.9	6.006	91	2	1.82
TiB_2-TiC	91	3.66	3.33			
TiBCN	182	1.5	2.73			
$MoSi_2$-SiC	112	3.7	4.144			
H13	59	6.8	4.01			
H13	82	6.5	5.33			
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	88	1.44	1.26	64	3.75	2.40

Table 5.5: Volume removed (mm^3) from coatings and substrate by molten aluminum cast alloys (383, 390)

Coating or Material	383 Al Fracture Surface Average Depth (x10-6m)	Fracture Surface Area (x10-5 m2)	Volume Removed (mm3)	390 Al Fracture Surface Average Depth (x10-6m)	Fracture Surface Area (x10-5 m2)	Volume Removed (mm3)
H13	69	6.7	4.623	73	5.2	3.796
CrN (P)	0	0	0	78	4	3.12
CrN (IB)	0	0.12	0	88	4.1	3.608
CrC	82	6.2	5.084	91	6.3	5.733
TiAlN	125	3.4	4.25	169	4.2	7.098
ZrN	55	2.4	1.32	58	2.4	1.392
MoZrN	63	4.8	3.024	93	5.3	4.929
MoNx	118	7	8.26	116	5.4	6.264
Al_2O_3	0	0	0	110	0.57	0.627
TiN-TiCN	92	3.8	3.496	118	5.1	6.018
Cr_3Si	129	5.1	6.579	105	10	10.5
Dynablue	167	3.1	5.177	215	5.5	11.825
TiB_2-TiC	142	3.5	4.97	140	3.2	4.48
TiBCN	152	2.45	3.724	187	0.89	1.6643
$MoSi_2$-SiC	170	1.98	3.366	182	0.8	1.456
H13	84	5.8	4.87	69	8.1	5.59
H13	77	5.8	4.47	61	8.4	5.12
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	73	2.23	1.6	88	0.36	0.31

Table 5.6: Relative roughness of fracture surface and depth of crater left when molten aluminum cast alloys (360, 380, 383, 390) were removed form surface

Coating or Surface Treatment	360 Al Relative roughness of fracture	360 Al (+) Above (-) Below Fracture Surface (microns)	380 Al Relative roughness Of fracture	380 Al (+) Above (-) Below Fracture Surface (microns)	383 Al Relative roughness of fracture	383 Al (+) Above (-) Below Fracture Surface (microns)	390 Al Relative roughness of fracture	390 Al (+) Above (-) Below Fracture Surface (microns)
H13	Very	-100	Moderate	-150	Very	-110	Very	-110
CrN (P)	Hills & Pitts	60	Smooth	0	Hills & Pitts	-4.5	Hills & Pitts	-1
CrN (IB)	Hills & Pitts	- 70 to + 60	Smooth	-190	Hills & Pitts	15	Hills & Pitts	-125
CrC	Very	-120	Smooth	-220	Very	-130	Very	-150
TiAlN	Moderate	-190	Moderate	-220	Moderate	-190	Moderate	-200
ZrN	Moderate	-105	Moderate	-180	Pitted	-110	Pitted	-110
MoZrN	Very	-85	Moderate	-150	Moderate	-160	Very	-120
MoNx	Very	-85	Moderate	-180	Very	-95	Moderate	-135
Al_2O_3	Smooth	0			Smooth	0	Pitted	-90
TiN-TiCN	Moderate	-95	Very	-210	Moderate	-120	Moderate	-130
Cr_3Si	Smooth	-135			Smooth	-180	Moderate	-140
Dynablue	Pitted	-150	Pitted	-170	Pitted	-145	Pitted	-200
TiB_2-TiC	Very	-160			Moderate	-200	Very	-170
TiBCN	Hills & Pitts	-210			Pitted	-200	Pitted	-215
$MoSi_2$-SiC	Pitted	-200			Pitted	-210	Pitted	-200
H13	Very	-120			Very	-105	Very	-110
H13	Very	-115			Very	-115	Very	-105
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	Pitted	70	Pitted	30	Pitted	45	Pitted	50

5.4 Discussion, Index of Experimental Results, and Future Work

The experiments conducted were used to find a good working layer film, for a thin film system, that will be used to increase the life of H13 die steel used for aluminum die casting dies. The experiments are similar in properties to one of the main modes of failure for aluminum die casting dies. This mode of failure is called soldering and is responsible for a considerable amount of the overall down time for a die casting operation. The prevention of this problem has been the subject of a considerable amount of research.

The problem of soldering is not a simple one to prevent. This is due to the high temperatures and pressures developed when molten aluminum is injected into a die, as well as the high chemical reactivity of all of the materials that are within the system. The conditions within a die casting die are hard to reproduce in a laboratory setting. For this reason the influences that surround the performance of the coating or surface of the die must be projected.

A set of experiments was designed to consider different aspects of the performance of selected coatings and surface treatments. The areas of consideration were the surface energy of the interface between the molten aluminum and the solid surface, the bond strength between the aluminum and coating or surface treatment, and the amount of dissolution of the solid surface into the molten aluminum.

The higher the energy is between an aluminum alloy and a coating, the less wetting the alloy is, and the affinity for the two phases is low. The contact angle for the majority of systems considered was very close and hard to distinguish one from another: but the spreading action of the aluminum is a close relation to the affinity of the elements within the systems considered, and was noticeably different from one coating to another. The spreading was both negative and positive and the coatings that had a negative spreading had a system of elements that had a lower affinity for one another than the coatings with a large amount of spreading, which also means that the interfacial energy between the two materials is high.

The next area that was explored was related to the strength of the bond between the two materials. After the aluminum was allowed to cool the aluminum was removed from the surface of the sample that was being tested. The amount of force that was required to remove the aluminum was recorded using an instron mechanical tester. The higher the force required to remove the aluminum the stronger the bond is that exists between the two materials.

The last area of investigation for this research is related to the ability of the coatings and surface treatments to act as a barrier to molten aluminum alloys. The amount of material that was removed, when the aluminum was sheared from the sample, was an indication of the coatings ability to withstand the corrosive action of the molten aluminum.

In order to ensure reproducibility a set of H13 tool steel samples were tested more with the aluminum cast alloys 360, 383, 390. The values can be seen for these three alloys which were tested two more times, at the bottom of the tables. The variance for the tool steel is within a range that the index is the same for the different samples. The 390 aluminum alloy is the exception and the index is one point higher than the initial experiments that were run. The other tests that were done to ensure reproducibility were done with the alumina coating and the aluminum alloy of 383. The samples reacted in a very similar fashion and the variance that was found was not significant enough to affect the index by more than one point.

An index was developed in order to compare all of the surface treatments and coatings. With so many coatings and alloy combinations it is necessary to correlate all of the information in order to compare which coatings performed well compared to the other coatings that were investigated as can be seen in Tables 5.7 and 5.8. To determine which coatings performed the best with all of the alloys investigated the index totals were averaged, which can be seen in Table 5.9.

For the work that can be done in the future, the dunk tester that is described in the next sections will be able to test the coatings in a manner which eliminates the oxidized layer of aluminum in contact with the surface treatment or coating. For the dunk tester, when the sample is "dunked" into the aluminum, pure aluminum alloy is in contact with the surface. The amount of interaction of the aluminum with the various coatings and surface treatments is an indication of the wetting and the ability of the samples to withstand the corrosive action of the aluminum.

If one were to continue with sessile drop tests in the future, I would recommend using a different experimental setup that would reduce the amount of oxidation of the materials that are in the furnace. The amount of oxygen in the chamber affects the wettability of the aluminum and influences the outcome of the experiments. The amount of oxidation can be controlled further with the system that was used by adding an oxygen getter. Another way to reduce the amount of oxidation that is affecting the experiment would be to redesign the experiment in a way that the aluminum drips from a small hole, after it melts, and comes into contact with the surface treatment or coating as a liquid. By not having contact between the sample and the aluminum as it is melting the amount of oxide that exists between the sample and the molten aluminum would be reduced.

Table 5.7: Index for the interactions of molten aluminum cast alloys (360, 380) with various surface treatments and coatings.

Coating or Material	360 Al Force	Vol	Spread	**Total**	380 Al Force	Vol	Spread	**Total**
H13	4	3	3	**10**	1	4	3	**8**
CrN (P)	3	1	1	**5**	1	1	1	**3**
CrN (IB)	4	1	1	**6**	1	3	1	**5**
CrC	1	3	3	**7**	1	5	1	**7**
TiAlN	1	4	1	**6**	1	4	3	**8**
ZrN	2	4	3	**9**	2	4	3	**9**
MoZrN	1	3	3	**7**	1	4	3	**8**
MoNx	1	5	3	**9**	1	4	3	**8**
Al_2O_3	1	1	1	**3**				
TiN-TiCN	1	3	5	**9**	2	4	4	**10**
Cr_3Si	4	4	5	**13**				
Dynablue	5	4	4	**13**	2	2	2	**6**
TiB_2-TiC	1	3	1	**5**				
TiBCN	5	2	2	**9**				
$MoSi_2$-SiC	4	3	1	**8**				
H13	4	3	3	**10**				
H13	4	3	3	**10**				
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	**2**	**2**	**2**	**6**	**2**	**2**	**2**	**6**

Force = 0	1	Volume Removed = 0	1
Force = 0 - 100	2	Volume Removed = 1-2	2
Force = 100 - 200	3	Volume Removed = 3-4	3
Force = 200 - 400	4	Volume Removed = 5-6	4
Force = > 400	5	Volume Removed = 7 and <	5

Spreading % < 1	1
Spreading % = 1-3	2
Spreading % = 4-6	3
Spreading % = 7-9	4
Spreading % = 10 and >	5

Table 5.8: Index for the interactions of molten aluminum cast alloys (383, 390) with various surface treatments and coatings.

Coating or Material	383 Al Force	Vol	Spread	Total	390 Al Force	Vol	Spread	Total
H13	2	3	5	**10**	5	3	5	**13**
CrN (P)	1	1	1	**3**	4	3	1	**8**
CrN (IB)	2	1	1	**4**	2	3	5	**10**
CrC	2	4	2	**8**	2	4	2	**8**
TiAlN	2	3	1	**6**	1	5	2	**8**
ZrN	5	2	1	**8**	2	2	2	**6**
MoZrN	1	3	1	**5**	2	3	1	**6**
MoNx	1	5	1	**7**	1	4	1	**6**
Al_2O_3	1	1	3	**5**	2	1	1	**4**
TiN-TiCN	1	3	2	**6**	1	4	1	**6**
Cr_3Si	2	4	2	**8**	5	5	5	**15**
Dynablue	2	4	2	**8**	5	5	3	**13**
TiB_2-TiC	1	3	1	**5**	1	3	1	**5**
TiBCN	1	3	3	**7**	4	2	1	**7**
$MoSi_2$-SiC	3	3	1	**7**	4	2	2	**8**
H13	2	3	5	**10**	5	4	5	**14**
H13	2	3	5	**10**	5	4	5	**14**
	383 Al	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**	**383 Al**
Al_2O_3	**2**	**2**	**2**	**6**	**2**	**1**	**2**	**5**

Force = 0	1	Volume Removed = 0	1
Force = 0 - 100	2	Volume Removed = 1-2	2
Force = 100 - 200	3	Volume Removed = 3-4	3
Force = 200 - 400	4	Volume Removed = 5-6	4
Force = > 400	5	Volume Removed = 7 and <	5

Spreading % < 1	1
Spreading % = 1-3	2
Spreading % = 4-6	3
Spreading % = 7-9	4
Spreading % = 10 and >	5

Table 5.9: Average of the Index for the interactions of molten aluminum cast alloys (360, 380, 383, 390) with various surface treatments and coatings.

Coating	or Material
H13	10.75
CrN (P)	4.75
CrN (IB)	6.25
CrC	7.5
TiAlN	7
ZrN	8
MoZrN	6.5
MoNx	7.5
Al_2O_3	4
TiN-TiCN	7.75
Cr_3Si	9
Dynablue	10
TiB_2-TiC	5
TiBCN	7.7
$MoSi_2$-SiC	7.7

6. Conclusions

The goal of the research was to narrow down a large group of coatings and surface treatments, that were considered good candidates for use as a working layer to protect aluminum die casting dies from the corrosive action of molten aluminum, to a small number of coatings, which could be incorporated into a multi layer thin film system, that could be used to increase the life of aluminum die casting dies. Die casting dies fail in three main ways and through the use of coatings and surface treatments it is possible to decrease down time and increase the productive life of die casting dies and their components.

It was found that there is likely a coating system for each alloy that is ideal. When one averages the values that were gained through the experiments that were conducted it is clear that all of the coatings perform better than raw H13 tool steel, and the carbo-nitriding (Dynablue) surface treatment is also out performed by all of the coatings. When looking for a good working layer film that will be used in contact with more than one alloy, an all around good working layer, the Al_2O_3 coating from ACSEL, Tib_2 – TiC coating from ACSEL, and the CrN coating from Phygen have performed the best and would be the best choice.

7. Development of the Dunk Tester

A good method of determining the durability of various coatings, to be used on aluminum die casting components, is a test where the coating is held, or rotated, in a molten bath of aluminum. By having the samples immersed in the molten aluminum there is no gas to influence the results of the experiment and this allows the corrosive action of the aluminum to deteriorate the coatings. Emulating the aluminum die casting process in the laboratory is not easily accomplished, but it is desirable to predict which coatings are most likely to perform well for any specific situation and why. The dunk test has many advantages over other experiments used in the analysis of coatings and surface treatments, but it still has limitations when one is trying to recreate what is occurring within an aluminum die casting die.

The aluminum die casting process is one that is very hard on the components that come into contact with the molten aluminum. The corrosive action of the aluminum and the thermal cycling that the components are subjected to, along with the high impingement velocities of the aluminum, are the main reasons die casting dies and components fail. Finding a coating or surface treatment that can be subjected to these conditions and remain intact for long periods of time, which can be used as a barrier between the die casting components and the molten aluminum, is very desirable.

If the coatings are tested in a laboratory it is possible to test coatings more quickly and at a lower price than if the coatings are tested in a die casting operation. The coatings can be compared with one another in order to learn which coatings or surface treatments performed the best and why. The information that is gathered can then be used to make predictions as to which are more likely to perform well in an aluminum die casting operation.

In order to test the coatings it is desirable to emulate the die casting operation as much as possible. The pressures that are developed, and the velocity of the aluminum, are not easily reproduced. It is possible to emulate the thermal gradients that the coatings and the substrate are subjected to and it is also possible to put the molten aluminum metal in direct contact with the potential working surface, instead of the oxide layer that forms on aluminum very rapidly when any oxygen is present.

7.1 Design Parameters and Goals

It was desired to design and build a multi-functional dunk tester that is capable of testing coatings in a thermal cycling and corrosive environment that can be done very consistently from one sample to the next. The dunk tester must be capable of putting a sample through a series of stations, one of the stations is a molten bath of aluminum, one station is a spray chamber, which is used to cool and clean the sample, and the system should have room for expandability.

The dunk tester is used to cause the coatings to fail, and then various techniques are used to determine which of the coatings withstood the harsh environment with the least amount of damage. Core pins are one of the small components in a die casting die which are prone to failure causing the entire operation to shut down, which makes these parts a good candidate for applying coatings and surface treatments to. Core pins also have a geometry that is ideal for use in a dunk tester.

Computer control is the best way to ensure consistency between experiments. The computer is used to control switches, which in turn control motors that are used to move the sample from one station to another. The initial design can be seen in Figure 7.1. The design offers one the ability to have three stations on the table and two free standing stations, allowing a total of five stations. If one were to use the machine for more than one experiment it is not necessary to change the entire setup each time the experiments are changed.

When one has computer control, experiments can be run the exact same way each time, and it is possible to make small changes to the experiments very quickly and easily. An ideal type of computer interface is one where it is possible to use the system without having to spend much time learning how to use it. A basic desktop computer with a point and click type of software package was desired for that reason. This type of system is user friendly and very consistent, along with the flexibility to test coatings in a variety of experimental conditions.

An industrial robot was chosen to manipulate the samples. A used industrial robot was purchased that was capable of the speeds and weight requirements and was versatile enough to complete all of the tasks necessary to accomplish the goals set out upon. The initial design was designed to be made of servo motors, switches and a computer to control it, and can be seen in Figure 7.1. The industrial robot that was purchased has the same basic design and is capable of more than the initial design allowed and it was more economical. A picture of the machine can be seen in Figure 7.2.

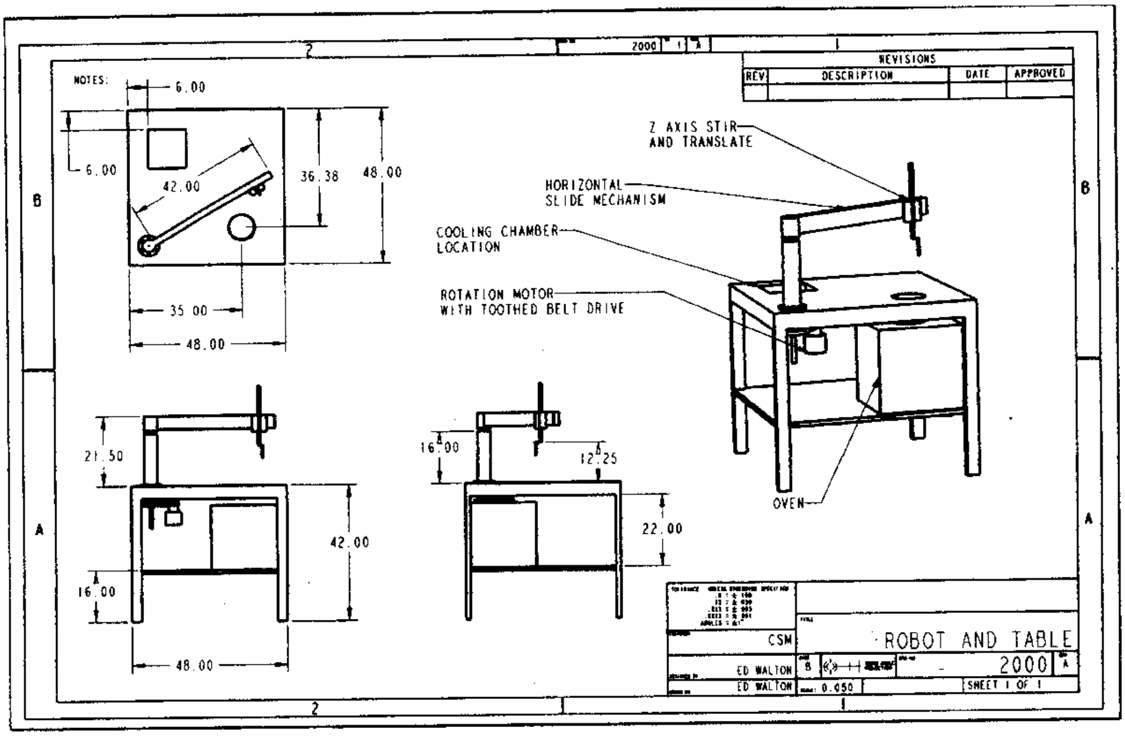

Figure 7.1 Schematic of the initial design for the dunk tester.

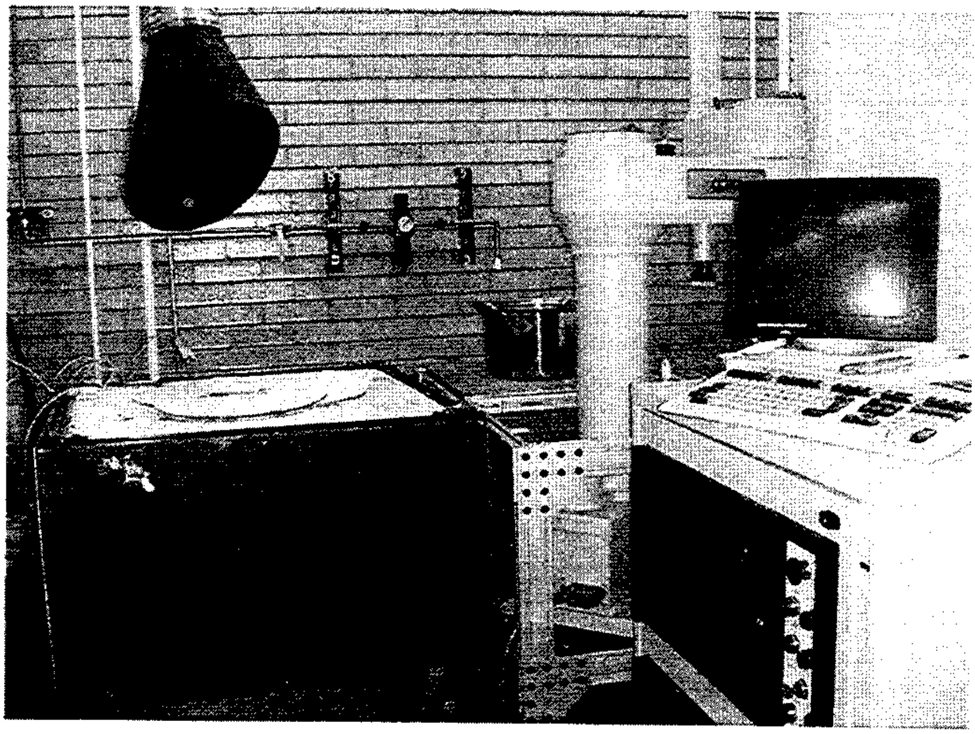

Figure 7.2 Picture of the dunk tester and the crucible furnace as well as the control system.

8. References

Ahraronov, R. R., Chellapilla, S., Janoss, B.: "An Investigation of the Corrosion of H13 Steel Coated with CrN in Molten Aluminum Alloys: Effect of Steel Surface Preparation and Coating Thickness"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Apelian, D., Shankar, S.: "Die Soldering – A Metallurgical Analysis if the Molten Aluminum/Die Interface Reactions"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Apelian, D., Shankar, S.: "Soldering Tendencies of Alternate Non-Ferrous Die Materials"
North American Die Casting Association, Cincinnati, 2001
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Aria, T.: "Research and Application of Carbide and Nitride Coatings onto Aluminum Die Casting Molds in Japan"
North American Die Casting Association, Indianapolis, 1995
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Asthana, R.: "An Empirical Correlation Between Contact Angles and Surface Tension on Some Ceramic – Metal Systems"
Metallurgical Transactions, Volume 25A, pp 225 - 230, January, 1994

Asthana, R., Soboczak, N.: "Wettability, Spreading, and Interfacial Phenomena in High_Temperature Coatings"
The Minerals Metals and Materials Society JOM 2000
JOM-e, 52(1)(2000),
http://www.tms.org/pubs/journals/JOM/0001/Asthana/Asthatna-0001.html

Bauer, A. F.: "The First Water-Cooled, Die Cast, Six Cylinder Automobile Engine Block"
Society of Die Casting Engineers, Inc. Paper No. 9C
Detroit Artillery Armory, November 8-11, 1960

Balasubramaniam, S., Rajan, R., Shivpuri, R.: "A Study of the Cast Alloy Die Surface Interactions in Aluminum Die Casting"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Bergstrom, J., Burman, C., Persson, A.: "Experimental Simulation of Heat Checking Using H13 Tool Steel"
North American Die Casting Association, Cincinnati, 2001
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Berry, R. W., Hall P. H., Harris, M. T.: "Thin Film Technology"
Van Norstrand Company Ltd. Princeton, New Jersey 1968 D.

Bhat, D. G., Gorokhovsky, V., Bhattacharya, R.: "Development of a Coating for Wear and Cracking Prevention in Die Casting Dies by the Filtered Cathodic Arc Process"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Birks, N., Meier, G. H.: "Introduction to High Temperature Oxidation of Metals"
Edward Arnold (Publishers) 1983,
41 Bedford Square, London WC1B 3DQ

Cahn, J. W.: "Critical Point Wetting"
The Journal of Chemical Physics,
Vol. 66, No 8, April 15, 1977

Chalker, P. R., Bull, S. J., Rickerby, D. S.: " A Review of the Methods for the Evaluation of Coating Substrate Adhesion"
Materials Science and Engineering, A140 (1991) pp 583-592

Chellapilla, S., Shivpuri, R., Balasubramaniam, S. "Coatings for Die Casting: A Comprehensive Review of Performance Evaluation Including Current and Future Research"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Chu, Y., Cheng, P. S., Shivpuri, R.: "A Study of Erosive Wear in Die Casting Dies: Surface Treatments and Coatings"
North American Die Casting Association, Cleveland, 1993
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Chu, Y., Cheng, P. S., Shivpuri, R.: "Soldering Phenomenon in Aluminum Die Casting: Possible Causes and Cures"
North American Die Casting Association, Cleveland, 1993
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Clark, W. A. T., Dahmen, U., Briant, C. L.: "Structure and Properties of Interfaces in Materials"
Materials Research Society Volume 238, (1991), pp 775 – 780

Devereux, O. F. "Topics in Metallurgical Thermodynamics"
Krieger Publishing Company , Malibar, Florida 1983
Reprint with corrections 1989

Eustathopoulos, N., Nicholas, M. G., Drevet, B.: "Wettability at High Temperatures"
Pergamon Materials Series 1999
Elsivier Science Ltd.
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB, UK

Finnis, M. W.: "The Theory of Metal – Ceramic Interfaces"
Journal of Physics and Condens. Matter 8, (1996) pp 5811 – 5836

Fujii, H., Nakae, H., Okada, K.: "Four Wetting Phases in AlN/Al and AlN Composites/Al Systems, Models of Nonreactive, Reactive, and Composite Systems"
Metallurgical Transactions, Vol. 24A, June 1993, pp 1391 - 1397

Fujii, H., Nakae, H., Okada, K.: "Interfacial Reaction Wetting in the Boron Nitride Molten Aluminum System"
Acta Metall. Mater., Vol. 41, No 10, pp 2693 – 2971, 1993

Gulizia, S., Jahedi, M. Z., Doyle, E. D.: "Performance Evaluation of PVD Coatings for High Pressure Die Casting"
Surface Coatings and Technology 140 (2001) 200 - 205

Guo, J., Zhu, H., Jia, J.: "Computer Simulation of the Formation and Growth of Fe-Al Intermetallic Phase Layers during Die Casting of Aluminum Alloy"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Hairy, P., Richard, M.: " In-Plant Trials of Four Die Surface Coaitngs"
Die Casting Engineer 1996
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018
www.diecasting.org/dce

Hanliang, Z., Jingjie, G., Jun, J.: "Energy Analysis of Die Soldering in Aluminum Die Casting"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Javernick, D.: "Critical Wetting Phenomena in the Cu-O/Al_2O_3 System"
Thesis, Colorado School of Mines

Jones, D. A.: "Principles and Prevention of Corrosion"
Prentice-Hall, inc Simon and Schuster/
A Viacom Company 1996

Koch, H., Franke, A. J.: "Use of Low Iron Die Casting Alloys for the Automotive Industry: Properties and Applications"
Die Casting Engineer 1998
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018
www.diecasting.org/dce

Kowalczyk, J. E.: "Materials That Enhance Wear Resistance in Tooling For Aluminum Castings"
North American Die Casting Association, Cincinnati, 2001
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Kristsalis, P., Coudurier, N., Eustathopoulos, N.: "Contribution to the Study of Reactive Wetting in the $CuTi/Al_2O_3$ System"
Journal of Materials Science 26 (1991) 3400 - 3408

Laidler, Kieth J. Meiser, J. H.: "Physical Chemistry Second Edition"
Houghton Mifflin Company,
222 Berkley St. Boston, MA 02116-3764
1995

Lakare, A., Gopal, S., Shivpuri, R.: " Coatings and Surface Treatments for Die Casting Dies: Composition, Coating Techniques and Causes for Failure"
North American Die Casting Association, Clevleand, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Lanning, Bruce R.: "A Method for Predicting Wettability and Interfacial Bond Strengths at Metal/ Ceramic Interfaces"
Colorado School of Mines 1990

Laurent, V., Chatain, D., Estathopoulos, N.: "Wettability of SiO_2 and Oxidized SiC by Aluminum"
Materials Science and Engineering A135 (1991) 89 - 94

Lewin, M.: "H13 Die Life – Finding the Missing Link"
Die Casting Engineer 1988
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018
www.diecasting.org/dce

Maissel, L., Glang, R.: "Handbook of Thin Film Technology"
McGraw-Hill, Hopeville Junction, New York 1983

Mattox, D. M.: "Handbook of Physical Vapor Deposition (PVD) Processing"
Noyes Publications 369 Fairview Avenue, Westwood,
New Jersey 1998,

McMurry, J. Fay, R. C.: "Chemistry"
Prentice-Hall Inc. 1995

Meier, A., Chidambaram, P.R., Edwards, G. R. "Generation of Isothermal Spreading Data and Interfacial Energy Data for Liquid Reactive Metals on Ceramic Substrates – The Copper Titanium Alumina System"
Journal of Materials Science 1995
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018
www.diecasting.org/dce

Moore, J.J. "Chemical Metallurgy Second Edition"
Reed Educational and Professional Publishing Ltd 1990
Butterworth-Heineman
Linacre House, Jordan Hill, Oxford OX2 8DP

Nicholas, M. G., Moritimer, D. A., Jones, L. M., Crispin, R. M.: "Some Observations on the Wetting and Bonding of Nitride Ceramics"
Journal of Materials Science 25 (1990) 2679 - 2689

Nogi, K., Iwamoto, N., Ogino, K. "Wetting Phenomena at High Temperature"
Welding Research Institure, JWRI 1992
Welding Research Institute, Osaka University,
Ibaraki, Osaka 567 Japan

Raj, R.: "Cavitation of Interphase Interfaces at High Temperatures"
Diloque De Physique 1990
Diloque Cl, supplement au n°1, Toma 51 janvier 1990,
Cl – 393 – Cl - 401

Ranganathan, M., Shivpuri, R.: "Reducing Scrap and Increasing Die Life in Low Pressure Die Casting Through Flow Simulation and Accelerated Testing"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Schmauser, H. R.: "Salt Bath Nitriding of Die Casting Dies and Tool Elements to improve Properites"
Die Casting Engineer 1982
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

www.diecasting.org/dce

Schwam, D., Wallace, J. F.: " Improvemetn of Die Life in Aluminum Die Casting"
Die Casting Engineer 1992
North American Die Casting Association
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018
www.diecasting.org/dce

Shankar, S., Apelian, D.: "The Role of Aluminum Alloy Chemistry and Die Material on Die Soldering"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Shankar, S.: "A Study of the Interface Reaction Mechanism Between Molten Aluminum and Ferrous Die Materials"
Doctor of Philosophy Thesis,
Worchester Polytechnic Institute 2000

Shimbo, M., Okamoto, M. N. I.: "Wettability of Silicon Carbide by Aluminum, Copper and Silver"
Journal of Materials Science Letters 8 (1989) 663 – 666

Shivpuri, R. Joshi, V., Srivastava, A.: "Soldering and Ejection Behavior of Duplex and Multilayer Filtered Arc PVD Coatings"
North American Die Casting Association, Cincinnati, 2001
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Shivpuri, R., Kulkarni, K.: " Development of a Coating for Wear and Cracking Prevention in Die Casting Dies by the Filtered Cathodic Arc Process"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Smith, D. L.: "Thin Film Deposition, Principles and Practice"
McGraw-Hill 1995
R. R. Donnelley & Sons Company

Sundqvist, M., Bergstrom, J., Bjork, T., Westergard, R.: "Corrosive Wear of Duplex Coatings in Die Casting of Aluminum"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Tsuchiya, Y., Kawaura, H., Hashimoto, K., Hikoichi, I. Arai, T: "Core Pin Failure in Aluminum Die Casting and the Effect of Surface Treatment"
North American Die Casting Association, Minneapolis, 1997
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Vendatesan, K. Shivpuri, R. "An Investigation of the Effect of Process Parameters on the Washout in Die Casting Dies"
North American Die Casting Association, Indianapolis, 1995
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Vossen, J. L., Kern, W.: "Thin Film Processes"
Academic Press, 111 Fifth Ave. N.Y., N.Y. 1978

Wallace, J. F., Schwam, D., Zhou, Q.: " Die Materials for Demanding Applications and Increased Productivity"
North American Die Casting Association, Cincinnati, 2001
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Wahid, A., Olson, D. L., Matlock, D. K. "Corrosion of Weldments"
ASM Handbook Volume 6 Welding, Brazing, and Soldering
First Printing, December 1993

Wang, Y.: "Effects of Die Geometry and Hard Coatings on Heat Checking and Soldering of Die Casting Dies"
North American Die Casting Association, Cleveland, 1999
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Wills, Barry A.: "Mineral Processing Technology"
Butterworth Heinemann 1997
Linacre House, Jordan Hill, Oxford OX2 8DP

Woolverton, A.: "Plasma Characterization and Tribological Evaluation of Sputter Deposited Molybdenum Disulfide-Based Solid Lubricating Coatings"
Thesis, Colorado School of Mines

Xue, X. M., Wang, J. T., Sui, Z. T.: "Wettability and Interfacial Reaction of Alumina and Zirconia by Reactive Silver – Indium Base Alloy at Mid-Temperatures"
Journal of Materials Science 1993

Xue, X. M., Wang, J. T., Quan, M. X.: "Wettability and Spreading Kinetics of Liquid Aluminum on Boron Nitride"
Journal of Materials Science 28 (1993) 1317 - 1322

Yu, M., Chu, Y., Shivpuri, R.: "A Study of Corrosion of Die Materials and Die Coatings in Aluminum Die Casting"
North American Die Casting Association, Cleveland, 1993
9701 West Higgins Rd, Suite 880, Rosemont, IL 60018

Zhong, D.: "Synthesis, Processing and Modeling of a Graded Coating Architecture for Glass Molding Dies and Forming Tools"
Thesis, Colorado School of Mines 2001