Direct manufacture of wear resistant and corrosion resistant coatings for the paper, mining and materials industries

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Abstract

At the present time there are various thermal spray coatings in use for wear and corrosion protection, these coatings contain inherent porosity which could be detrimental to their performance. Plasma sprayed chromium oxide coatings are currently used within the paper, mining and materials industries; they provide good wear and corrosion resistance, although they are still susceptible to failure.

This work focuses on thermal sprayed nickel based coatings deposited using flame spray and High Velocity Oxy-Fuel (HVOF) techniques. They were then processed with a flame or laser heat treatment process called fusing to create a dense, pore free and strongly bonded microstructure. This is to overcome the shortcomings present in the chromium oxide thermal spray coatings to provide a good wear and corrosion resistant coating.

Laser cladding of the Ni-based coatings was also performed to observe the potential use in depositing these coatings. Dense, pore free microstructures were produced with laser cladding process.

A coating adhesion testing method was developed to determine the bonding strength of these fused coatings (thermal sprayed followed by fusing process). The coatings were placed in a salt spray fog corrosion chamber to observe their corrosion resistance; to rank and compare them to coatings currently used in the paper and mining and materials industries. The same coatings were subjected to a pin-on-disk wear test to observe their wear resistance performance.

Corrosion testing showed that flame and laser fused coatings had good corrosion resistance along with Cr$_2$O$_3$. The majority of coatings had performed well and the coatings that failed showed corrosion had occurred at the coating and substrate interface, where corrosion had initiated at the sample edges.
Wear testing demonstrated the low wear of chromium oxide coatings, while it was possible to obtain comparable wear results with laser fused nickel based coatings. Some flame fused coatings demonstrated high wear due to pull out of tungsten carbide particles present in the coating.

The study shows that nickel based fused coatings demonstrated very high bonding strength as well as showing good corrosion and wear resistance. These coatings can replace the currently used chromium oxide coatings. Laser fusing was able to provide coatings that could compare with the wear resistance of chromium oxide. Laser cladding coatings showed a favourable microstructure that could also be used to replace current coatings, however further testing is required before they can be utilised in industry.
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My family and friends whom have supported me during my studies.
Student Declaration

I, Mathew Giacomantonio, declare that this body of work:

Contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text and to the best of my knowledge contains no material previously published or written by another person except where due reference is made in the text.

Signed

Mathew Giacomantonio
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Chapter 1 Introduction

Surface coatings are utilised for many reasons including wear and corrosion resistance, which are of particular importance in regards to prolonging the working life of various components.

There are various materials and compositions of coatings used and their methods of deposition are also varied. In this work, only thermal, cold spray and laser technologies are discussed because of their relevance in the project. Thermal spray [1] is a common process to deposit metal coatings onto a wide range of substrates. It is an established process with a long history, and types of deposition include flame spray, high velocity oxy-fuel (HVOF), plasma spray as well as cold spray. These methods are able to produce coatings that can resist wear and corrosion; however coatings produced by thermal spray inherently contain porosity. Porosity can be detrimental to the corrosion resistance of a coating as a path to the substrate can be formed and lead to failure of the coating and substrate.

One method to eliminate porosity in certain coatings is to fuse them. Fusing [2] involves heating the coating to about 1000°C, this causes the microstructure to change from one that is porous and contains oxide inclusions and cracks to a dense almost pore free coating. While fusing can create a suitable coating for wear and corrosion resistance there are a number of drawbacks [3, 4]. The current methods of fusing are flame, furnace and induction fusing. These fusing processes are limited in the size that can be fused. It is difficult to fuse large geometries. While flame fusing can be adapted to large geometries it is a manual process that is influenced by an operator. The substrates that can be processed are also limited by the high temperatures involved.

More recent methods of fusing involved laser fusing and laser cladding which both processes that can potentially create a pore free coating, while overcoming the aforementioned drawbacks present in the other fusing processes. Lasers are able to be utilised in many situations that allow large and complex geometries to be
processed, lasers can also an automated thus eliminating the errors than can occur in the other techniques.

Currently, chromium oxide is used for protection of components used with the mining and paper industries. It provides excellent wear resistance although it is still susceptible to failure; it is also a noxious material for the environment.

In this study, the coatings to be investigated are Nickel-based self-fluxing coatings and to determine if they can replace the usage of Cr$_2$O$_3$ while still possessing good wear and corrosion resistant properties. Ni-based self-fluxing coatings are less noxious than Cr$_2$O$_3$ [5], although the current manual processes involving depositing and fusing of these coatings are unable to provide a consistent finish, an aspect which warrants further investigation. The study of the use of lasers is to overcome the inconsistent finish of the manual process of flame fusing and to bypass the limits in size and form of objects that can be processed. The further reduction in porosity is also a potential benefit in the use of lasers.

The thesis is structured with Chapter 2 as the literature review of the current methods and coatings used. Chapter 3 is the methodology and experiments carried out. Chapter 4 presents the results and discussion and finally Chapter 5 the conclusion.
Chapter 2 Literature Review

2.1 Introduction
Surface coatings are used to enhance a material by utilising its properties that are beneficial to the reduction in wear and corrosion, as well as achieving desired conditions for friction, and electrical and thermal conductivities. There are several methods to coat a surface, a general classification from Holmberg and Matthews [6], Figure 1, groups methods by the form of the coating deposited. These are gaseous, solution and molten/semi-molten states where CVD – Chemical Vapour Deposition, PVD - Physical Vapour Deposition and IBAD – Ion Beam Assisted Deposition. The main surface coating method to be investigated in this project is in the predominantly molten or semi-molten state; namely thermal spraying. Only, the latter will be discussed in great length as the other coating methods are not involved in this work.

![Figure 1: Diagram of various forms of surface coating methods available [6].](image)

2.2 Thermal Spray Overview
Thermal spray is a type of process where metals and non-metals are deposited onto a substrate to form a coating. The coating material, in either a form of powder, wire or arc, is heated to a molten or semi-molten state and then propelled towards a
substrate by gases where it impacts on the substrate and is deposited onto it. Coatings can be used to protect the substrate material from wear and corrosion [2].

Thermal spray has been around since the 1910s, the earliest forms were developed by Max Ulrich Schoop from Zurich, Switzerland [7], which was a flame spray process as well as an electric arc process [8]. Since then a number of various processes have been developed.

Thermal spray coatings are made up of splats, these splats are individual particles that have struck the substrate and adhered to it, many of the splats build up to form layers. Within the layers are present along with splats are oxides, unmelted particles and pores; this is illustrated in Figure 2. The structure of the coating is dependent on a number of factors, including the process and its parameters, the type of material for coating and its particle size.

![Figure 2: Illustration of thermal spray splats and the built up layers [2].](image)

2.2.1 Flame Spray
Combustion gases, usually oxygen and acetylene enter the gun and are ignited to produce a flame at the exit of the nozzle. Powder, wire or rods of the desired coating material are fed into the path of the flame where they are then melted and propelled to the substrate. Figure 3 shows a powder fed flame spray gun while a schematic of the process is illustrated in Figure 4.
Powder can be gravity or axially fed via carrier gas, usually air, while wires and rods are fed through axially. Flame spray is able to use a wide variety of materials including metals [9], ceramics [10] and even polymers [11].

Particle speeds for flame spray are normally less than 100 m/s [2] which is quite low compared to other forms of thermal spray; high temperatures of 2600°C spray rates vary from 0.5-9 kg/h depending on the spray material.

Nickel based self-fluxing coatings (NiCrBSi) are commonly flame sprayed material [12-14], these are usually treated post spraying by fusing. This technique leads to a microstructure that is dense, mostly porous free and is suitable for corrosion and wear resistance, unlike as-sprayed flame spray coatings which typically have a high amount of porosity [2]. Commercially pure titanium wire has been used by Ishikawa et al [9]. They learned that it was unable to resist corrosion by chloride due to the porosity of the as-sprayed condition; however corrosion resistance was improved by sealing the coating with resins after spraying.

![Image of a vertically fed flame spray gun.](image)
2.2.2 Electric Arc Spray

The process [15] involves two wire electrodes with opposing polarities of the desired spray material that are fed through together with a current; an electric arc is formed at the gap between the two wire tips creating sufficient heat to melt the wires. The molten material is carried towards the substrate by a flow of atomising gas, commonly air, where it will form a coating, Figure 5 shows an electric arc gun and Figure 6 is a schematic of the electric arc spray process.

Spray rates widely differ for each material due to various conductivity and melting points, for example 23 g/min for titanium, 45 g/min for Aluminium and 182 g/min for Zinc [2]. As there are no burning gases present the substrate temperature is therefore lower compared to flame spray, thus limiting any metallurgical changes for substrates that are sensitive to temperature.

Aluminium is frequently used to increase corrosion resistance [15, 16]. Due to porosities arising from arc spraying, Liu et al [15] found its corrosion resistance can be improved by applying a hydrothermal sealing coating, this method involves boiling samples in deionised water which reacts with the oxides present filling and sealing the pores.
Figure 5: Image of a twin wire electric arc spray gun.

Figure 6: Schematic drawing of the electric arc process.
2.2.3 Plasma Spray

Plasma is ionised gas; gases are heated to over 10,000°C to form a plasma jet where powder material is introduced. There are variations of the plasma spray process [17]; these include atmospheric and vacuum conditions of spray.

An electric arc discharge between the anode and cathode is formed; working gases are fed into this and ionised and expand rapidly to form a plasma jet. Powder is then fed into the jet where it is melted and directed to the substrate, an atmospheric plasma spray gun is shown in Figure 7, Figure 8 illustrates this process which is also known as atmospheric plasma spray (APS).

Argon, helium, nitrogen and hydrogen, or a mixture of these gases is mostly used as working gases for plasma spraying. Molecular gases have greater thermal conductivity while monatomic gases can reach higher velocities which are usually why a mixture of both types of gases is used. Plasma temperatures can reach around 14,000°C and particle velocities can reach over 800 m/s.

The anode geometry and diameter have an effect on the plasma flow and pattern, and such would alter the jet temperature and the velocity distribution. Vacuum plasma spray (VPS) also known as low pressure plasma spray (LPPS) was first developed in the 1970s. The main difference to APS is the plasma jet which streams into a vacuum chamber. Advantages of VPS when compared to APS are: longer and larger spray jets, substrate cleaning, low oxide coatings, high coating densities, low residual stresses and thicker coatings [2].
Figure 7: Image of a plasma spray gun.

Figure 8: Schematic drawing of the plasma spray process.
2.2.4 High Velocity Oxy-Fuel (HVOF)

In the HVOF process, fuel and oxygen are combusted under high pressure, while powder is fed in axially where it is heated and accelerated down through a narrow nozzle exiting at very high speeds (200-1000 m/s) [2]. A schematic of this process is shown in Figure 9; Figure 10 shows an image of a HVOF gun. Due to its high kinetic energy it is able to produce dense and well adhered coatings. Another similar process is High Velocity Air Fuel (HVAF) where air is substituted for oxygen. There have been studies [18-20] to reduce the particle temperatures to help increase deposition efficiency.

Figure 9: Schematic drawing of the HVOF spray process.

Figure 10: Image of a HVOF spray gun.
Barletta et al [21] sprayed WC-10%Co-4%Cr powder onto grit blasted Al substrates using HVOF. They found that the number of passes had large influences on the coating properties. The cermet particles deformed the surface rather than splat completely therefore creating defects. The coating hardness increased and thus improves the wear and corrosion resistance. WC-CoCr coatings possess these properties which make them suitable for wear resistance. However it is noted that these cermet coatings contained interconnected porosity that can lead to corrosion.

Benegra et al [22] deposited NiCrAlC of 0.3 mm thickness onto 316L stainless steel substrates under different gas flow rates. It was found that porosity was low in reducing atmospheres and corrosion resistance was at its highest; although all coatings provided protection against corrosion, wear behaviour were not varied significantly for each sample. However the wear resistance of the coating was lower than that of cast and aged NiCrAlC.

Gorlach [20] developed a hybrid HVAF process. The constraint was to retain high spray rates resulting from wire and a de Laval nozzle was designed. The Zn-Al coating was found to have low porosity, good adhesion and corrosion resistance. This process is suitable for low melting temperature materials as it is not a high temperature process.
2.2.5 Detonation Gun

Fuel, oxygen and powder are fed into a long tube and ignited by a spark plug at frequencies of 3-6 Hz [2]; the resulting pressure forces the coating particles out of the tube at high velocity impinging to the substrate, an illustration of this process is shown in Figure 11. This produces dense and adhesive coating with low oxide content. It was developed by Union Carbide after studying oxyacetylene explosions in pipelines [23]. Lv et al [24] reported that the high particle velocity leads to a high bond strength, hardness and low porosity coatings. The bond strength can range from 70-80 MPa with coating thickness of 300 µm and porosity of 0.5% [1]. Particles velocities are more than 800 m/s [2] and flame temperatures are around 3000°C [25].

Lv et al [24] detonation sprayed Mo-Co-CrB alloy to 316L stainless steel with thicknesses of 150-350 µm. Spray parameters were O₂C₂H₂ ratio of 1.2:1, 4-6 shots per second, spray distance of 100 mm, spot diameter of 0.6 mm and powder flow rate of 0.5-1.4 g/s. They found that the microhardness and bond strength of a detonation gun sprayed coating was higher than a HVOF sprayed coating of the same powder.

Computer controlled detonation spray (CCDS) allows for optimal parameters to be applied when spraying and is noted for a high precision gas supply and has a twin powder feeding system. Composite cermet-ceramic, metal-ceramic and ceramic-ceramic and regular multilayered ceramic-ceramic, metal-metal and cermet-ceramic coatings could be sprayed. CDDS has higher microhardness and higher ceramic content compared to cold spray [26].
2.2.6 Cold Spray

The cold spray process is a relatively new process and was developed in the 1980s at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Science in Novosibirsk. It differs to other types of thermal spraying as powder is sprayed below its melting temperature which is between 0-700°C. The coating powder, particle sizes ranging from 1-50 µm, is fed through a de Laval type nozzle at high velocities (300-1200 m/s) [27]. The high velocities are sufficient for the particles to plastically deform on the substrate and adhere to it; a schematic of the process is in Figure 12. Figure 13 is an image of a cold spray gun.
The negative effects, compared to other forms of thermal spraying, of high temperature oxidation, evaporation, melting, recrystallisation and residual stresses are limited or removed due to much lower processing temperatures [2].

Particle size and temperature, substrate material and the coating materials properties have a large influence on the deposition efficiency and the formation of the coating [28]. Temperature, pressure and particle size have an effect on limiting porosity and temperature also have an effect of eliminating oxidation [29]. Cold spray can be used where it is necessary to avoid oxidation and retain the properties of the powder.

Critical velocity is a fundamental of cold spraying, above this velocity particles will adhere to a surface, below this velocity they will either reflect of the surface or erode it [30]. Critical velocity is defined as [31]:

$$v_{\text{crit}} = \frac{Ag}{\rho} + Bc_p(T_m - T)$$
Where $\sigma$ is the temperature dependant flow stress, $\rho$ is the density, $c_p$ is heat capacity, $T_m$ is the melting temperature, $T$ is the mean temperature of the particles at impact and $A$ and $B$ are constants. Furthermore by using Helium or a mixture of helium and nitrogen as a process gas it is possible to obtain high deposition efficiencies for certain materials.

For the use of multi-component coatings, location of injection has an effect on the temperature and velocity hard sprayable powders should be injected into the subsonic area of the nozzle while the easy-sprayable powders injected in the supersonic area [32]. This enables optimal spraying conditions for both materials.

By using this technique cold spray is able to deposit composite metal-metal and metal-ceramic coatings, the ceramic content however is restricted to 20-30% [26]. Low pressure cold spray is a variation of cold spray that takes place under pressures of 0.5-0.9 MPa, it is able to be sprayed onto substrates of metal, ceramic and polymer [33]. Stoltenhoff et al [34] noted that materials with a melting temperature above 2300°C and those with ordered crystal lattices need to have high particle velocities for them to be able to plastically deform.

Koivuluoto et al [28] designed an experiment using a CGT Kinetiks 3000 with tantalum powder with particle size of 38+10 µm and a CGT Kinetiks 4000 using an improved tantalum powder of particle size of 30+10 µm. Nitrogen was used as the process gas. The powders were sprayed onto Grit-blasted carbon steel sheet substrates. They found that process parameters were crucial to obtain a good quality coating. Particle size was found to affect particle velocity and consequently the ability to plastically deform. They found that the improved powder particle size of 30+10 µm with a more advanced machine produced a dense coating with no visible pores or defects. Whereas the initial powder used (38+10 µm) and with an earlier generation (Kinetiks 3000) machine produced a coating with pores and weak particle boundaries. Under corrosion testing, the improved powder coating was impermeable and showed a rapid and high passivation range, exhibiting a good corrosion resistance.
Wang et al [35] experimented spraying titanium powder (particle size: 5-45 µm) onto a sandblasted carbon steel substrate. The process gases used were nitrogen and compressed air (up to 3 MPa). They observed that high gas temperatures and pressures led to low porosity. Coatings deposited using compressed air showed much higher porosity compared to nitrogen deposited coatings, this is due to the titanium reacting with oxygen. The open circuit potential test showed a higher corrosion resistance than the steel substrate.

Jeandin et al [36] attached a laser to a cold spray gun for pre and post spraying surface treatment in order to improve coating adhesion. They found that for Al and Ni based surfaces coating adhesion had been improved, due to oxide cleaning and substrate heating.

2.2.7 Powder Feeding
Generally there are four types of powder feeding systems [37], namely, gravity fed, volumetric fed, fluidised bed fed and rotating wheel feeders. Gravity fed system allows powder to fall freely into the stream. This process is not accurate but low cost and simple to use. Volumetric fed system is where powder falls into a carburettor and is then brought into the stream using a gas flow system. Fluidised bed feeding is where the powder is held in a bed with a fluidising gas, which then enters the stream via a venturi. Rotating wheel feeders work by powder entering a rotating disc that feeds a certain amount of powder into a carrier gas stream that is transported to the thermal spray gun. In the project, a gravity feed system was used for flame spraying, while HVOF, plasma spray and cold spray processes utilised rotating wheel powder feeding systems.

2.2.8 Spray Fuse Coatings
Thermal sprayed coatings generally contain inherent porosity as well as oxides and unmelted particles. To eliminate these features a post-spraying treatment called fusing is utilised. Fusing [38] involves heating a sprayed coating to create a dense microstructure, largely devoid of porosity and other inclusions with metallurgical bonding to the substrate. Usually these coatings are of nickel or cobalt based alloys and contain certain amounts of silicon and boron which make the coating self-fluxing. Figure 14 demonstrates a coated cylinder is undergoing fusion process.
Fusing can be performed with flame torches, furnaces, or induction coils. Typically flame fusing is the most common method owing to its low cost and adaptability for various work piece shapes.

![Figure 14: Oxyacetylene fusing of a flame sprayed coating on a steel cylinder.](image)

The coating is heated to a temperature in between its solidus and the liquidus, at this point the surface shows a shiny, bright appearance. This is the optimal point for fusion where particles melt, gaps close and fluxing of oxides occurs [39]. Fusing reduces the porosity to 0.3-5% and coating volume shrinks by 20% [40] therefore the spraying process must take this into account. Over-fusing can bring about excessive fluxing which depletes silicon and boron and then creates slag residue, it also leads to voids and poor bonding resulting in the coating to spall. Spalling can also occur due to coating and substrate having large differences in thermal mismatch.

Hard materials, such as tungsten carbide, are added to give increase in hardness and wear resistance. Cooling the coated substrate slowly eliminates cracking, due to the high expansion coefficient and its brittleness. Porosity can occur if the coating has been under- and over-fused, as well as possible contaminants during spraying [39]. Fusion can be performed using oxyacetylene torches, furnace or induction. Furnace method allows for a better controlled atmosphere compared to torch fusing.
which is left to operator judgement. In recent times, laser has been gaining more ground for use in fusing [41-44] as it is more precise and easier to control the parameters.

In a study on fusing processes, Gonzalez et al [42] sprayed and fused a NiCrBSi coating with flame, laser and by laser cladding. They mentioned that flame fusing was imprecise due to poor parameter control. They also concluded that there was no great difference in wear behaviour between any of the processes.

An initial trial experiment by the present author was to analyse a spray fused coating that had failed. It was determined that the coating had spalled due to incorrect surface preparation, the coating shows low porosity and demonstrated high corrosion resistance with only some evidence present at the surface of the coating, Figure 15.

Figure 15: SEM image showing a cross-section of a spray fused coating demonstrating low corrosion and low porosity.
2.2.9 Laser Fusing
Laser fusing [38] is a relatively recent development, with laser having become widespread. Laser fusing works the same way as other fusing methods, however, lasers provide benefits in comparison. It is a precise method with minimal distortion, controlled penetration, no need for preheating and can be utilised on a larger range of materials and various geometries [38]. Lasers can be automated and their parameters can be finely controlled. For example laser power, traverse speed; spot sizes can all be selected to the suitable values to achieve the optimal fusing condition.

2.2.10 Laser Cladding
Laser cladding is a one step process that offers a similar coating to thermal spraying plus laser fusing. Powder is deposited and heated at the same time to provide a dense microstructure with very low porosity, low dilution and good bonding between coating and substrate [45]. Oberländer and Lugscheider [46] found that laser cladding allowed for easier control of processing parameters and dimensions. Compared to plasma spray coatings had smoother surfaces, increased adhesion, low dilution and high cooling rates. They also found that cladding over large areas had disadvantages in an increased heat affected zone with increased surface temperatures and decreased cooling rates. Gómez-del Rió et al [44] compared laser cladding with other forms of fusing reported that laser cladding led to harder coatings with higher wear resistance. Vuoristo et al [47] also reported laser cladding can produce coatings with high density, low heat and input, strongly bonded coatings due to metallurgical bonding as well as improved corrosion resistance.

2.2.11 Thermal Spray Applications in the Industry
The ideal coating would have eliminated or reduced porosity so as to limit corrosion. Therefore a suitable process and coating must be chosen.

Calender rolls should have surface coatings that are hard and well bonded to limit abrasive wear and corrosion [48]. Pawłowski [1] stated that plasma spray coatings have been used on dryers, while HVOF was used for calender rolls and flame spray for boiler tubes.
HVOF sprayed coatings were investigated by Fedrizzi et al [49] as replacements for hard chromium coatings which have been recently banned in the European Union due to carcinogenic effects, these coatings were used in the mining industry among others. A standard sized and a finer sized Cr3C2 cermet powder was employed, it was found that the thermal sprayed coating with finer sized powder had better wear and corrosion performance mainly due to lower porosity and roughness, and better carbide distribution.

Sari and Yilmaz [50] assessed the wear performance of various coatings and methods including thermal spray, flame and HVOF spraying. An additional study of remelting of NiCrBSi coatings was carried out. They found that composite based coatings compared to ceramic coatings had performed better. The thermal spray coatings weight loss rated better than the other processes and the remelted coatings performed even better than the sprayed coatings.
2.3 Properties of Thermal Spray Coatings

2.3.1 Splats
Splats are individual particles of a coating material that have hit, plastically deformed and adhered to a substrate. All thermal spray coatings are made up of layers of splats, see Figure 2.

2.3.2 Porosity
Porosity is a gap or pocket of void in a coating. It is undesirable for wear and corrosion resistant coatings. Most of the porosity in thermal spray coating is a result of unmelted or resolidified particles in the coating leaving gaps between splats. It is possible for corrosion to initiate and deteriorate the coating, or in the case of through porosity, reach the substrate. For wear resistant coatings porosity leads to low hardness and poor surface finish. The coating can also break up and become an abrasive [2].

Porosity arises from a number of factors, these being:
Shrinkage as a result of cooling, unmelted or resolidifed particles and large voids that are not filled form under these particles, poor splat cohesion, poor wetting, intersplat cracks, spraying from angles deviating from 90°, porosity of the powder.

Porosity can be limited by controlling the jet temperature, jet and particle heat transfer effectiveness, jet and gas properties, particle size and the morphology, thermal properties, dwell time and dwell time of the particles [2].

2.3.3 Oxide Inclusions
When thermal spraying, hot particles react with the air to form oxide layers on the substrate. These inclusions can increase hardness of a coating however it also creates brittle coatings; high oxide content and also results in poor coating cohesion. Ways to limit oxide inclusions include removing the reacting environment,
lowering the particle temperature, lowering particle dwell time by reducing spray distance or increase spraying velocity, lowering the interface temperature and using optimal particle size.

2.3.4 Microhardness
Microhardness test on a coating is performed to determine its wear resistance [1]. Hardness test involves indenting a surface and analysing the indentation, the hardness value is determined by measuring the size and depth of the indentation on the surface, a smaller and shallower indentation signifies a higher hardness [3]. There are a number of hardness tests and scales, Vickers hardness is a microhardness scale, commonly used for small samples where a microscope is used. It is a popular testing method owing to its ease of use, low cost and non-destructive [51].

2.3.5 Bond Strength
The bonding between the coating and substrate interface can be measured as bond strength. It is controlled by residual stresses and most failures occur at the interface. Contaminants can cause problems with the coating bonding and a number of failures are due to improper bonding through poor preparation, poor material choices or oxide inclusions. The first splats fill the asperities present on the surface and form the first layer, this is adhesive bonding. Subsequent layers of splat build up on top, this is cohesive bonding.

Thickness of coatings can have an adverse effect on the bonding strength as Greving et al [52] learned that for Ni5Al coatings, bond strength decreased with increasing coating thickness.

2.3.6 Stresses
When thermal spray splats cool and solidify they contract, leading to tensile stress within the splat. It is possible for thick coatings to have stresses higher than the bond strength of the coating. However excessively thick coatings can lead to stress cracking [53].
Dense coatings usually have greater stress than porous coatings. HVOF and cold spray processes are able to provide stress free and dense coatings due to compressive stress from splat deformation, activated by high kinetic and low thermal energy processes.

### 2.3.7 Grain Boundaries

Grain boundaries separate two grains with different crystalline orientations. Bonding is less frequent along grain boundaries owing to the grain boundary energy nearer to the surface energy. As a result the grain boundaries are more chemically reactive than the grains [51].

### 2.3.8 Tested Coatings

Casteletti et al [54] sprayed WC-12%Co and WC-10%Ni onto AISI 1645 by HVOF and analysed by optical and SEM microscopy, performed tests for microhardness, porosity deformation and dry sand/rubber wheel abrasive tests. The HVOF coatings had low porosity and high average hardness of around 1100 HV. The abrasive test began with removal of the binder by the abrasives.

WCNi had recorded the highest wear resistance due to its high compaction and few partially melted particles. The wear rate was the same for both coatings but at high revolutions the WCo performed better due to carbide and binder interaction. The smooth surface finish gave greater wear resistance, as a rough surface would have less contact area due to asperities therefore there resulted in greater wear.

The corrosion behaviour of thermal sprayed coatings in boiler tubes was studied by Rezakhani [55], FeCrAl and Tafaloy 45CT were electric arc sprayed while 50Ni-50Cr and Cr3C2-NiCr were HVOF sprayed. The substrates used are commonly used for boiler tubes and these were SA213TP 347 H, SA213 T11 and SA213 T22. Samples were tested in cyclic corrosion and synthetic salt deposit. The thermal spray coatings were attacked via the oxides and voids present at the splat boundaries. Rezakhani’s finding showed that Tafaloy 45CT performed well and Cr3C2-NiCr 80/20 was mostly intact in the corrosion test.
2.4 Surface Preparation

It is imperative to correctly prepare a surface prior to applying any coatings to ensure the coating would bond to the substrate and not prematurely fail.

The first step in surface preparation is to clean the substrate from all contaminants. Vapour degreasing involves soaking the component in degreaser solvent for about 15-30 minutes in order to remove oils and grease from the surface and pores. Porous materials would require a longer soaking time. Sometimes steam or manual cleaning is required to remove residue off from larger components [39].

Vapour blasting is another method of cleaning. It involves blasting abrasive slurry at the substrate. Rust inhibitors and anti-solidifying additives are also included in the slurry. The substrate then requires rinsing after blasting [39].

Oven baking will remove contaminants from deep within porous materials, baking occurs at about 330°C [2]. Ultrasonic cleaning is used to remove embedded contaminants. A cleaning solution is placed in a container that has ultrasonic vibrations through it. Dry abrasive blasting is used to remove scale, oxides, burrs and old coatings. Abrasive is projected to the surface by air jets.

2.4.1 Roughening

Dry abrasive grit blasting is a roughening of a surface by directing abrasive grit particles to the surface at high velocities. The impact of the grit roughens the surface by plastic deformation and gives a large surface area to allow for coating adherence. As a result the outer layer of the substrate is in residual compressive stress while the inner layer is in tension. The amount of deformation is defined by a number of variables and they are grit size, particle hardness and density, velocity and angle of the process [2].

Aluminia, iron, steel, sand and SiC are the most common materials used for grit blasting. It is important to select a suitable grit for the material to be blasted. For example it is possible that SiC would embed into softer metals due to its high
hardness. The biggest factor in determining the surface roughness is the grit size, coarse grit is ideal for thick coatings and provides better adherence. Fine grit gives smooth finish and suitable for thin coatings. After roughening it is important to clean the surface, usually by spraying with compressed air, and then to quickly commence thermal/cold spraying otherwise the surface would be contaminated once again. Grit residue affects the diffusion and thermal stresses between coating and substrate therefore lowering the residue would be beneficial. Wigren [56] found that grit blasting at 45° compared to 90° left less residue while the average surface roughness was lower.

Bond coats are another way to roughen a surface and allow for coating adhesion. It is employed in situation where minimum surface preparation is required, surfaces that cannot be machine blasted and to account for a difference in thermal expansion coefficient between coating and substrate [2].

Surface roughness is usually measured as an average of the asperities over a length of a surface. Figure 16, is a plot showing the average surface roughness (Ra) and the average maximum height of profile (Rz) values.

![Roughness profile](image)

\[
R_z = \frac{1}{5} (Z_1 + Z_2 + Z_3 + Z_4 + Z_5)
\]

\[
R_a = \frac{1}{l_m} \int_{x=0}^{x=l_m} |y| \, dx
\]

Figure 16: Surface roughness profile demonstrating Ra and Rz [57].
Further Roughness parameters of use are Rq – Root mean square, Rp – maximum profile peak height and Rt – maximum height of profile.

Rz is the roughness averaged over five different lengths; this method takes into account of maximum peaks.

2.5 Adhesion of Thermal Spray Coatings

Adhesion is the bonding between two different materials, in thermal spray this is the bonding at the coating and substrate interface. Cohesion is bonding within the same material that is the bonding between each layer of splats.

Failure of the coating in the cohesive area is called cohesive failure, while failure at the interface is called adhesive failure.

Adhesion of thermal spray coatings occurs due to mechanical bonding of splats to the surface irregularities of the substrate. The overall structure of the coating, as well as the properties mentioned in 2.3 has an effect on the adhesion of thermal spray coatings.

2.5.1 Forms of Bonding

Mechanical bonding is a type of bonding occurs from the impact of splats on a substrate surface, due to kinetic energy of the molten particle deforming the particles and forming splats, the splats surround the asperities on the substrate, and subsequent cooling enables the material to adhere.

Metallurgical bonding occurs due to high contact temperature between coating and substrate. Diffusion of the materials occurs and thus forms a strong bond between the two surfaces.

Chemical bonding forms due to reaction between the substrate and coating materials.

Chicot et al [58] found that for NiCr coatings annealing after spraying led to improved adhesion. They also mention that thermal shock and thermal cycling process can increases adhesion as a reinforcement of the metallurgical bond present.
2.5.2 Testing Methods

It is necessary to determine the testing method required based on the type of adhesion and the failure method of the coatings. There are various methods that can be employed in determining the adhesion of coatings; these can be seen in Table 1.

<table>
<thead>
<tr>
<th>Mechanical methods</th>
<th>Non-mechanical methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct pull-off method</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Laser pallation test</td>
<td>Thermal method</td>
</tr>
<tr>
<td>Ultracentrifugal test</td>
<td>Nucleation test</td>
</tr>
<tr>
<td>Scratch test</td>
<td>Capacitance test</td>
</tr>
<tr>
<td>Cellophane tape test</td>
<td></td>
</tr>
<tr>
<td>Abrasion test</td>
<td></td>
</tr>
<tr>
<td>Bend and scratch test</td>
<td></td>
</tr>
</tbody>
</table>

Common methods of determining coating adhesion, for example ASTM C633 standard, involve gluing two coated samples together with an adhesive and then pulling both samples apart.

The tensile pull-off testing method has limitations in the strength of the adhesive, for some coatings the adherence exceeds the current available adhesives. Such limitations were observed by Bergant et al [60] who used the tensile test method for fused NiCrBSi coatings and determined that coating adhesion was higher than the adhesion of the glue. Era et al [61] proposed a shear test method that can determine adhesion of strongly bonded thermal spray coatings. Otsubo et al [62] utilised a shear test for Ni-based fused coatings. Marot et al [63] compared interfacial indentation testing with shear testing to tensile adhesion testing. They found that indentation test was a cheap method to obtain adhesion results; the shear test was able to provide a real time result and did not suffer the problems encountered with the adhesives used in tensile testing. The shear test more accurately represents real stress for present in components used in industry, although this method of testing requires relatively thick coatings and specific testing equipment.
2.6 Wear Behaviour of Coatings

Wear is the removal of material from a surface due to relative motion at the surface. Wear can lead to component failure and downtime, thus it is beneficial to reduce the effects of wear.

There are a number of mechanisms of wear; those of particular importance to the paper and mining industries are abrasive and impact wear, erosion and cavitation [2].

2.6.1 Abrasive Wear

Abrasive wear, as shown in Figure 17 [64], is classified into four types:

Gouging abrasion is when large abrasive particles move under high load between surfaces and also under impact, this can lead to deformation, cutting or chipping of the materials. This form of abrasion occurs during crushing and grinding processes for example during rock crushing, grinding mills and machinery used to collect rocks.

High stress abrasion occurs when abrasives are squashed and crushed under high load between two materials, this leads to a grinding type of material removal. High stress abrasion occurs in ball and rod mills where the balls, rods and liners are affected.

Low stress abrasion occurs when small abrasive particles move across a surface under low loads leading to a scratching of the surfaces. Low stress abrasion exists in chutes and screens.

Similar to low stress abrasion is erosion-corrosion, where it differs is the smaller particles that are in a slurry or fluid mixture, wearing the surface and also enable corrosion to commence. This form of wear is prevalent in pumps.
Figure 17: The classification of abrasive wear [64].
There are many parameters that have an effect on abrasive wear, it is important for the design and selection of a coating to keep these in mind, these parameters are listed in Table 2 as follows:

Table 2: Parameters than effect the behaviour of abrasive wear [64].

<table>
<thead>
<tr>
<th>Abrasive Properties</th>
<th>Contact Conditions</th>
<th>Wear Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Force/impact level</td>
<td>Hardness</td>
</tr>
<tr>
<td>Particle shape</td>
<td>Velocity</td>
<td>Yield strength</td>
</tr>
<tr>
<td>Hardness</td>
<td>Impact/impingement angle</td>
<td>Elastic modulus</td>
</tr>
<tr>
<td>Yield strength</td>
<td>Sliding/rolling</td>
<td>Ductility</td>
</tr>
<tr>
<td>Fracture properties</td>
<td>Temperature</td>
<td>Toughness</td>
</tr>
<tr>
<td>Concentration</td>
<td>Wet/dry</td>
<td>Work-hardening characteristics</td>
</tr>
<tr>
<td>pH</td>
<td>Fracture toughness</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Microstructure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corrosion resistance</td>
</tr>
</tbody>
</table>

Velocity is an important parameter concerning slurries; the wear rate, $W$, is proportional to the velocity, $V$, influenced also by abrasive properties.

$$W \propto V^n$$

Where $n$, ranging from a value of 2-3, is determined by the abrasive size, material and the angle of impingement [64].

An important parameter for abrasive wear is the hardness ratio ($H/H_a$), which is the wear material hardness over the abrasive hardness. The abrasive wear rate drops when the wear material hardness nears the abrasive material hardness [65]. An important study on abrasive wear was conducted by Khruschov [66], he found that the wear resistance for pure metals was proportional to the materials hardness, Figure 18 demonstrates the linear increase in wear resistance with the increase in material hardness.
Figure 18: Relationship between hardness and wear resistance of commercially pure metals adapted from [66].

An equation to estimate the wear volume \( V \) for the abrasive wear of ductile materials has been proposed by Stachiowak [67]:

\[
V = \alpha \beta \frac{WL}{H_v}
\]

Where \( W \) is the load, \( L \) the sliding distance and \( H \) is the hardness. \( \alpha \) is the asperity shape factor and \( \beta \) is the degree of wear by the abrasive asperity. The equation is only suitable for single abrasive scratching.

2.6.2 Erosive Wear
Erosive wear is the impact of particles against a surface being in the solid or liquid form. The influences for erosive wear are the size and material of the particles, the impingement angle and the impact velocity.

Low impingement angles can lead to a similar form of wear as abrasive type wear whereas high angles are more characteristic for erosive wear, the impingement angles varies for the material properties, where the highest wear rate for ductile materials occur at 30°. While for brittle materials the maximum wear rate occurs and
angles from 80-90°, this is demonstrated in Figure 19. In a study by Santa et al [68] a nickel based coating, and a steel and Al mix coating were thermally sprayed on steel substrates. They found that the Ni based coating had the better slurry erosion resistant due to its higher hardness and ductile matrix. Particle sizes conducive to erosive wear tend to be within the range of 5-500 µm [69].

![Figure 19: Effect of impingement angle on the wear rate for ductile and brittle materials](image)

In erosion by slurry, that is a mix of liquid and solid particles, the viscosity, density and turbulence of the fluid all contribute to the erosion occurring, the corrosivity of the fluid would also cause the material to undergo corrosion, while the lubrication properties of the fluid can also limit the wear rate of erosion.

### 2.6.3 Wear of Thermal Spray Coatings

The wear behaviour and performance of thermal spray coatings including along with post spraying treatments can vary. Garrido et al [70] found that surface texturing of NiCrBSi coatings reduced the friction coefficient. The wear behaviour can be improved by using mall diameter dimples combined with optimised density and contact area. Liu et al [71] observed that HVOF sprayed Inconel coatings combined with laser treatment led to improved wear behaviour due to removal of porosity and the dense strongly bonded microstructure. The wear resistance was also improved by increasing the amount of WC. Kumari et al [72] found that HVOF sprayed WC-10Co-4Cr coatings abrasive wear mechanism was due to pull out of
WC particles from the coating, they mention that have fine and uniform WC grain sizes will improve the wear performance. Laser clad NiCrBSi coatings were observed under a block-on-ring test performed by Fernandez et al [45], the coatings were found to have wear mechanism by oxidation under all their testing conditions, adhesive wear was observed under higher loads.

Benegra et al [22] reported the wear mechanism for HVOF sprayed NiCrAlC coatings was severe abrasion with ploughing and cutting, a rubber wheel testing method was employed. Surzhenkov et al [73] compared wear performance for iron and nickel based self-fluxing coatings, they found that iron-based coatings had high abrasion resistance due to their higher hardness, while nickel-based coatings had higher erosive wear resistance.

2.7 Corrosion Properties of Coatings

Corrosion is the chemical reaction between a surface and its surroundings causing damage to the surface. The surroundings refer to the state of matter, whether it is a gas, liquid or solid, the chemicals present and the temperature, further factors can include velocity of the surrounding matter and loading on the surface [74].

Costs related to corrosion are high due to replacement of damaged components and/or costs associated with preventative measures. Furthermore, it can lead to other effects such as machine downtime or even plant shutdowns, and defective and inefficient production, and loss of products [75].

2.7.1 Atmospheric Corrosion

Atmospheric corrosion is the degradation of a material that is exposed to air and its environment. Roberge [76] specifies the environments into four atmospheres; these are industrial, marine, rural and indoor. Despite this specification it is possible for them to vary and be a mix of either one. Industrial atmosphere is made up of pollution typical of emissions from industry such as sulphur, nitrogen and chlorine compounds. These compounds along with a moist environment would react to produce corrosion. Marine atmosphere consists of salts blown by the wind from sea and deposited onto surfaces. This atmosphere exists at sea and along coast,
diminishing in effect the more distance inland. Rural atmospheres are the least conducive to corrosion due to being a lack of contaminants. Indoor atmospheres depend on contaminants and conditions. The presence of chemical compounds or a high amount of humidity and condensation could lead to corrosion.

### 2.7.2 Galvanic Corrosion

Galvanic corrosion [77] occurs when a metal or alloy exists together in an electrolyte with a conducting material. It is necessary that both materials have differing potential; there is a common electrolyte as well as a common electrical path.

Potential differences cause electrons to flow between the two materials. The more active material is anodic, where current flows into, while the more noble material is cathodic, where current flows from. The relationship for metals is shown in Figure 20 for materials in seawater.

Area, distance and geometry all play a role in galvanic corrosion. When the area of the cathode material is larger than the anode material corrosion would take place at a greater rate. In the reverse situation the effect is only slightly increased. The closer together both materials are then the greater the effect of galvanic corrosion would be, the type of solution the materials are in would also contribute to the corrosion rate.

Ways to control galvanic corrosion include selection of materials, controlling the environment, using coatings and electrochemical methods. It would be ideal to select materials that are close to each other in the galvanic series to limit the rate of corrosion. Insulating the materials from each other would also assist against corrosion; this can be achieved by using washers, sleeves and bushes of polymers or other metals. Surface coatings may also provide assistance against corrosion, although pores can still lead to a galvanic effect [78-80]. Liu et al [71] found that laser surface treatments of HVOF sprayed coatings removed crevices and pores limiting paths for galvanic corrosion to take place.
Figure 20: Galvanic series for seawater [81].
2.7.3 Localised Forms

Localised corrosion occurs at specific locations on a surface that would deteriorate and give way to perforation or cracking of the material. Common forms of localised corrosion include crevice, pitting and intergranular.

2.7.3.1 Crevice

Corrosion that commences at tight gaps between two materials is called crevice corrosion in the presence of an electrolyte; types of locations where it can occur are for example at flanges, joints and washers. Factors that influence corrosion on steels can be geometric, environmental, metallurgical and electrochemical. The geometry is the most important factor as it is what determines crevice corrosion, that is the gap and depth between the two materials, and usually the corrosion is more prominent on tighter crevices. This is represented in Figure 21.

![Figure 21: Schematic diagram of a crevice [81].](image)

An example of the effect of crevice corrosion can be seen in Figure 22, where a crevice former was placed onto 316L stainless steel and immersed in artificial seawater, the corroded area appears as discoloured rings.

Limiting crevice corrosion involved changing the geometry widening the gap of the crevice, the choice of materials also play a role as alloyed metals, namely chromium and molybdenum would increase the corrosion resistance. Roberge [76] gave several methods to design for crevice corrosion resistance: Use of butt joints instead of lap joints, eliminate or seal lap joints, enable total drainage, frequent inspection and cleaning and careful use of packing and insulation materials. Ferreira et al [82] had laser alloyed regions that were susceptible to crevice corrosion with an aluminium alloy with additions of chromium. They found that this had improved
the resistance against crevice corrosion due to the chromium; it creates a passive film that is less soluble in acidic solution. Aluminium, titanium and scandium have also shown to help improve resistance to crevice corrosion by Bombara et al [83]; the three elements were ion implanted onto 316L stainless steel and then tested in a NaCl solution.

![Figure 22: Example of crevice corrosion on 316L stainless steel [84].](image)

### 2.7.3.2 Pitting

Pitting is the localised formation of pits on the surface on the passive film of a metal due to reaction with aggressive anionic substances, chlorine ions being most predominant [85]. It is one of the most damaging types of corrosion as it can cause failure with minimal weight loss and the pits are usually covered with corrosion material making it hard to detect [86]. Pits generally propagate downwards into a material and take a relatively long time to show any signs of attack.

Pitting corrosion is an autocatalytic process meaning that it leads to conditions that support and sustain the corrosion activity. Figure 23 shows an example of a pit and its autocatalytic nature. Metal is dissolved which creates a positive charge in the pit where chloride ions would flow to maintain neutrality, oxygen is reduced on the surface around the pit and the chloride in turn dissolves the metal sustaining the pitting.
Figure 23: The autocatalytic nature of a pit [81].

The environment, potential, temperature, types of metal and the condition of the surface have an effect on crevice corrosion, usually pitting occurs in liquids that are stagnant or at low velocity. Methods to limit pitting involve using more resistant materials, change in design of the system and making the conditions less favourable to corrosion. Figure 24 shows the characteristic form of pitting corrosion on the surface of a stainless steel substrate.

Pitting occurrence and diameter both decreased when solution droplets also decreased in diameter and thickness according to [87] due to a smaller cathode area.

Pardo et al [88] studied the effects manganese and molybdenum additions in stainless steels on pitting corrosion in a solution of NaCl. They found that Mn had an undesirable effect on the pitting corrosion as MnS would tend to form which result in corrosive attack. The Mo inclusions reduced the rate of corrosion by making the passive film more stable against the Cl ions. In addition to Mo, Pohjanne et al [89] also found that Cr and nitrogen also increased pitting resistance.
2.7.3.3 Intergranular

Intergranular corrosion is a localised attack at or adjacent to grain boundaries with only minor corrosion of grains [86].

A form of corrosion that forms at grain boundaries, grains would be displaced and the surface became rough. It begins when the corrosion rate of the boundaries is greater than the interiors; this is due to the different compositions between the two.

In stainless steels the different composition can be attributed to precipitation of carbides at high temperatures. By limiting the carbon in the steel it is possible to prevent intergranular corrosion. Figure 25 illustrates the attack on the grain boundaries on stainless steel, clearly outlining the grains. In their investigation on intergranular corrosion on stainless steels Pardo et al [90] found that titanium provided an increase in resistance to corrosion. They noted that decreasing the carbon content has a greater effect than increasing the amount of titanium. They also compared 316Ti and 321 stainless steels and found the intergranular corrosion resistance was higher for 315Ti due to its high molybdenum content. The Mo readily forms carbides in place of the chromium present; as such negative effects of Cr depletion are avoided. Niobium, tantalum and titanium also provided resistance for Ni-Cr-Fe alloys [91].

Figure 24: Example of pitting corrosion on stainless steel [88].
2.7.4 Corrosion Observed in Thermal Spray Coatings

Corrosion behaviour of thermal coatings and their post spraying treatments has been observed in the literature. Hussain et al [92] performed electrochemical and salt spray testing on cold sprayed titanium on carbon steel substrates. They found that the corrosion occurred at the substrate due to interconnected porosity. NiCrBSi coatings remelted with laser were tested using potentiodynamic polarization method; Serres et al [5] reported that the coatings corrosion resistance had improved due to the change into a dense microstructure. Tuominen et al [93] observed that laser fusing HVOF sprayed high chromium and nickel-chromium coatings led to an increase in the corrosion resistance compared to in the as-sprayed state. They also discussed that excessive specific energy can lead to iron dilution from the substrate into the coating, reducing the pitting corrosion resistance. Zhao et al [94] found that HVOF sprayed NiCrBSi coatings main mechanism of failure was exfoliation or laminar peeling off. They noted corrosion first occurred at the superficial unmelted particles then pores and defects in the coating and subsequent paths through these defects to the substrate. WC-Co and Tribaloy 400 HVOF sprayed coatings were corrosion tested against hard chromium coatings by Natishan et al [95], the found that the corrosion resistance on steels were equivalent. On aluminium substrates, the WC-Co coating showed pitting corrosion along the edges whereas the hard chromium coating had no signs of corrosion visible. The Tribaloy 400 coatings showed corrosion on all substrates, the main mechanism was pitting.
Chapter 3 Methods and Materials

3.1 Introduction
This chapter describes the methods and materials used in the experimental work. The materials composition and particle sizes are also tabulated. The thermal and cold spray processes and the operating parameters used are presented, as well as the conditions used for laser fusing and laser cladding. The testing machines and methods used for wear, adhesion, corrosion and metallography are also discussed.

The experimental method covers a variety of coatings in order to determine the best coating and deposition process that can fulfil the wear and corrosion resistance for such applications, to potentially replace current coatings used within the industries as they may still suffer from corrosion and difficulty to deposit repair coatings.

3.2 Materials
Materials selected for substrates were 316 stainless steel and 1040 mild steel. These are the most commonly used materials used in industries. The samples were rectangular in form with dimensions of 50 mm x 40 mm and 15 mm thick for the wear and corrosion testing, while adhesion testing samples were 24 mm in diameter and 5 mm thick.

A number of powders were employed in the project to determine their suitability for wear and corrosion resistance. Within the industry, chromium oxide (Cr₂O₃) is currently employed. The coating offers an extremely hard wear resistant coating as well as providing good corrosion resistance. Ni-based coatings were selected as potential replacements.

Nickel based self-fluxing powders were studied due to their ideal microstructure once fused, which lends to greater wear and corrosion resistance. The powders used were Metco 36C and Metco 34F and their compositions are shown in Table 3. 36C has a particle size of 150+45 µm and 34F has a particle size of 53+15 µm.
Table 3: Composition of nickel-based coatings in weight percentages.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni (%)</th>
<th>Cr (%)</th>
<th>WC/Co (%)</th>
<th>Fe (%)</th>
<th>B (%)</th>
<th>Si (%)</th>
<th>C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metco 36C</td>
<td>46.5%</td>
<td>11%</td>
<td>35%</td>
<td>2.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metco 34F</td>
<td>33%</td>
<td>9%</td>
<td>50%</td>
<td>3.5%</td>
<td>2%</td>
<td>2%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Metco 450</td>
<td>93%</td>
<td>4.5%</td>
<td>2.5%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TLS Gr2 Ti</td>
<td>99.71%</td>
<td>0.19%</td>
<td>0.04% N</td>
<td>0.03%</td>
<td>0.02%</td>
<td>0.005%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The self-fluxing coatings require heat treatment after spraying onto the substrate. This process is called fusing. The fusing was performed using an oxyacetylene torch held over the work piece until the coating glows an orange colour. This signifies that the fusing has taken place.

Chromium oxide coatings were also corrosion and wear tested as a comparison to other coatings. In addition, Amperit 704.054 (particle size of 45+10 µm, composition 99.5% fused Cr$_2$O$_3$ [98]) was plasma sprayed with a Metco 450 (particle size 90+45 µm) bond coat, its composition is described in Table 3.

TLS Grade 2 commercially pure titanium powder, particle size of 25 µm, was used as an undercoat for some Cr$_2$O$_3$ coatings to act as a further barrier to corrosion. Cr$_2$O$_3$ coatings were subsequently sprayed on top of the cold sprayed titanium. The composition of the titanium powder is presented in Table 3.
3.3 Processes

The following is a series of 5 experiments employed in this study, various types of coatings were investigated utilising different coating deposition processes and treatments. This is necessary in order to determine the best wear and corrosion resistance for rollers in the paper production and mining industries.

- Nickel-based coatings using flame and HVOF spray, fused by oxyacetylene flame
- Chromium oxide coating using plasma spray
- Titanium undercoat using cold spray
- Nickel-based coatings fused using laser
- Nickel-based coatings using laser cladding

The parameters of each experiment are discussed as follows - Self-fluxing coatings were fused using oxyacetylene torch as well as laser. Flame spray, HVOF, plasma spray and cold spray were all thermal spray systems used for depositing coatings. These are described in the following sections.

All substrates were chemically cleaned with ethanol initially by hand with cotton to remove most of the larger contaminants and subsequently cleaned in an ultrasonic bath for 15 minutes; the substrates were then dried in a furnace oven at 70°C for 5 hours. All surfaces of the substrates were then mechanically prepared prior to spraying by grit blasting with #30 Alumina grit. Substrates were held in place on a steel rack, the blasting nozzle was held at 45° to limit the amount of grit residue embedding in the surface of the substrate.

The adhesion of fused coatings was tested using different grit sizes, 16, 30 and 46. There was no difference noticed in adhesion, depending on the different grit used in surface preparation. Alumina #30 grit and surface ground finishes were utilised, these conditions are what are currently being used to prepare components for industrial use.
3.3.1 Nickel Based Coating using Flame and HVOF Spray, Fused by Oxyacetylene Flame

Nickel based coatings were deposited using flame spray and HVOF thermal spray systems. Flame spraying was carried out using a Metco Type 5P spray gun, shown in Figure 28. The operating parameters used for spraying 36C and 34F are displayed in Table 4.

Table 4: Parameters used for flame spraying 36C and 34F.

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Spray distance (mm)</th>
<th>Lighting Pressure setting</th>
<th>Flow meter readings</th>
<th>Consumption per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>P7G for 36C</td>
<td>180-205</td>
<td>1.08 C₂H₂, 2.07 O₂</td>
<td>34 (for O₂ and C₂H₂)</td>
<td>1.7 m³/h (O₂) 0.93 m³/h (C₂H₂) 9 kg/h Powder</td>
</tr>
<tr>
<td>P7-B for 34F</td>
<td>75-150</td>
<td>2.07 for O₂ and air 1.03 for C₂H₂</td>
<td>33 (for O₂ and C₂H₂)</td>
<td>1.6 m³/h (O₂) 0.91 m³/h (C₂H₂) 4.5 kg/h Powder</td>
</tr>
</tbody>
</table>
HVOF was carried out using a Jetkote II system the nozzle in action is shown in Figure 29, the parameters used are shown in Table 5. Only 34F coatings were utilised as the particle size for 36C proved to be too large to successfully deposit using HVOF.

Table 5: Parameters for spraying 34F by HVOF.

<table>
<thead>
<tr>
<th>LPG Pressure (kPa)</th>
<th>Oxygen Pressure (kPa)</th>
<th>Gas Pressure (kPa)</th>
<th>Flow Pressure (kPa)</th>
<th>Powder Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>379</td>
<td>6858</td>
<td>1034</td>
<td>20.68</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Some of the nickel-based samples were then flame fused. These samples were directly flame fused after spraying using an oxyacetylene torch, the torch was passed over the surface of the coated samples and heated until an orange glow had emitted from the coating, signifying that fusion had occurred.
3.3.2 Chromium Oxide Coatings using Plasma Spray

Plasma spraying utilised a Plasmadyne SG100, the nozzle used is shown in Figure 30. It is necessary to apply a bond coat prior to spraying Cr$_2$O$_3$ so that the coating can adhere without debonding. Metco 450, a NiAl powder was deposited onto the work piece to a thickness of around 25 µm. HC Starck Amperit 704 was then sprayed on top of the bond coat to a thickness of 500 µm. Substrates were preheated with oxyacetylene torch to around 180°C. The parameters used in plasma spraying for both the NiAl bond coat and Cr$_2$O$_3$ coating are shown in Table 6.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Argon Pressure (kPa)</th>
<th>Helium Pressure (kPa)</th>
<th>Carrier Pressure (kPa)</th>
<th>Current (A)</th>
<th>Stand off distance (mm)</th>
<th>Cooling air pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metco 450</td>
<td>344</td>
<td>0.44</td>
<td>241-275</td>
<td>650</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Amperit 704</td>
<td>344</td>
<td>689</td>
<td>241-275</td>
<td>900</td>
<td>95</td>
<td>551</td>
</tr>
</tbody>
</table>

Table 6: Plasma spraying parameters used for bond coat and coating deposition.
3.3.3 Titanium Undercoat using Cold Spray
Kinects 4000GT cold spray system was used to deposit titanium onto stainless and mild steel substrates. The operating parameters used for cold spraying are listed in Table 7. An image of the setup used is shown in Figure 31.

<table>
<thead>
<tr>
<th>Standoff (mm)</th>
<th>Nozzle traverse (mm/sec)</th>
<th>Gun temperature (°C)</th>
<th>Gun pressure (kPa)</th>
<th>Powder feeder speed (RPM)</th>
<th>Powder feeder gas flow rate (m²/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>150</td>
<td>800</td>
<td>4000</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 7: Operating parameters for cold spraying of titanium.
3.3.4 Nickel Based Coatings Fused using Laser

Laser fusing is a heat treatment process that modifies the microstructure of a coating. Traditional methods utilise flame, furnace or induction heating to fuse a coating, laser is a relatively recent method that can provide good results with a more controllable and automated process. Some of the nickel-based 34F and 36C coatings that were flame and HVOF sprayed were later fused by laser.

Laser fusing was carried out at Swinburne University, using a POM DMD 505 unit with a Trumpf CO\textsubscript{2} laser. It was necessary to determine the ideal laser fusing parameters that would lead to best result. The parameters used are shown in Table 8. These parameters were kept constant apart from the laser power which varied from 0.5 kW to 3 kW.

<table>
<thead>
<tr>
<th>Stand Off (mm)</th>
<th>Spot Size (mm)</th>
<th>Overlap (mm)</th>
<th>Power (kW)</th>
<th>Traverse Speed (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.8</td>
<td>1.5</td>
<td>0.5 - 3</td>
<td>500</td>
</tr>
</tbody>
</table>
3.3.5 Nickel Based Coatings using Laser Cladding

A POM DMD 505 with a Trumpf CO₂ laser at Swinburne was used for the laser cladding of 36C onto 316 stainless steel. Substrates were preheated in a furnace at a constant 400°C; samples were placed in vermiculite to slow down the rate of cooling. The parameters used for cladding are shown in Table 9.

Table 9: Laser cladding parameters.

<table>
<thead>
<tr>
<th>Stand Off (mm)</th>
<th>Spot Size (mm)</th>
<th>Overlap (mm)</th>
<th>Power (kW)</th>
<th>Traverse Speed (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.8</td>
<td>1.5</td>
<td>1 - 2.5</td>
<td>500</td>
</tr>
</tbody>
</table>
3.4 Characterisation and Analysis of Coatings

In order to analyse the coatings, light optical microscope (LOM) and scanning electron microscope (SEM) were used to visualise the coatings on a microscopic scale. Electron beam dispersion (EDS) detector was used to characterise the elemental composition of coatings and substrates. A perthometer was used to obtain the roughness profile of sample surfaces. A new adhesion test was developed to determine the bonding strength of the fused coatings. To investigate corrosion resistance a salt spray chamber corrosion test was used. A pin-on-disk wear test was used to analyse wear resistance. The details of this equipment are discussed in the following.

3.4.1 Optical Microscope Studies

Olympus PMG 3, Figure 33, was use to magnify and observe samples before and after experiments were finalised. Optical magnification ranges used were 50-500x.

Figure 33: Olympus PMG 3 LOM for optical analysis.
3.4.2 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscopes enable visualisation of surfaces at very high magnifications compared to traditional light microscopes. A Leica 440 SEM, Figure 34, was used for imaging the surfaces of the samples. The microscope uses a Tungsten filament, with acceleration voltage from 300V – 300 keV, electron beam current 1 pA to 1 µA.

3.4.3 Energy-Dispersive X-ray Spectrometer (EDS) Analysis

Oxford X-Max silicon drift detector EDS, Figure 34, was used. Elemental analyses for samples in SEM, samples are bombarded with electrons, the resulting x-ray spectrum emissions correspond to each element. The energy of emission is electron volts (eV). Quantitative analysis can also be performed.

Figure 34: Leica 440 SEM with Oxford X-max EDS.
3.4.4 Roughness Measurements

Roughness measurements were taken with a Mahr Perthometer with a PRW pickup, Figure 35. The surface profile was scanned over a length of 2 mm with reading intervals at every 0.1 µm, a measuring speed of 0.1 mm/s.

Figure 35: Mahr Perthometer for roughness testing.

3.4.5 Microhardness Studies

Microhardness testing was performed utilising a Buehler MMT-3, Figure 36. A Vickers indentation head was used with a 300 g mass.

Figure 36: Buehler MMT-3 microhardness tester.
3.4.6 Adhesion Testing

As fused coatings microstructures have been altered from a mechanical bond to a metallurgical bond. The adhesion strength between the coating and interface would significantly improve. Currently there is no specific method to determine the adhesion strength of fused coatings; therefore a new adhesion test was developed in this project. Traditional adhesion testing method included the pull off test, for example ASTM C633. This method is constrained to the strength of the adhesive which has a maximum bonding strength of around 100 MPa. Metallurgically bonded coatings have adhesion strengths that exceed this value. The solution to this problem was to develop a test that would be able to separate the coating from the substrate by shear failure. Stainless steel rods of 24 mm diameter were coated and fused with self-fluxing coating of 0.5 mm thick. The rods were sectioned into buttons of 5 mm thickness, with the coating having been machined off to leave 2 mm thickness of coating around the button, a button used in testing is shown in Figure 37.

![Figure 37: Coated button used in adhesion testing showing 2 mm of coating on the button after the remainder had been machined off.](image)

A stainless steel holder was made with a hole large enough to accommodate the button with the coating, a hole of smaller diameter to allow the button to fall through once the coating had been sheared.

The testing machine utilised was an Instron 5500R load frame with a load cell of 100 kN in compression mode a custom punch and holder were made to be able to compress the button against the testing block. The testing setup is shown in Figure 38.
Figure 38: Adhesion testing setup showing the load cell, testing block and punch.

The testing block is shown below in Figure 39; a machined button is placed on the block resting on the counterbore.

Figure 39: Testing block for adhesion testing with testing sample button loaded.
3.4.7 Corrosion Testing

The salt spray corrosion test was performed according to ASTM B117, the test was conducted in a Vötsch SC1000 salt spray chamber, Figure 40, and the salt solution used was 5% NaCl with a pH of 6 - 7. The temperature and humidity conditions were 35°C and 46% respectively.

Samples were prepared for testing by scrubbing them in a neutral cleaning agent, rinsed in deionised water and followed by ethanol. Samples were then dried in an oven at 110°C for 15 minutes. Once dried, the sides and rear of each sample were painted with a water based paint to leave only the coated front of the samples exposed to the corrosive media. All samples were approximately 50 mm x 40 mm.

The testing ran for 5000 hours, images of corroded samples were taken periodically. Small samples were sectioned from the salt spray testing samples after 1161 hours for microscopical analysis, remaining samples were then repainted and returned to testing, due to the destructive nature required for analysis this was only later performed on samples that had failed and at the end of corrosion testing. Analysis were performed at 1161, 2290 and 4673 hours, these intervals were chosen to be at approximately 1000 hours, where it was possible to perform analysis.

Figure 40: Salt spray chamber used for corrosion testing.
3.4.8 Pin-on-Disk Wear Testing

The pin-on-disk wear testing method was employed based on ASTM G99 standard, a ruby (Al₂O₃) sphere of 3 mm diameter was used as the pin. The wear tests were conducted on a pin-on-disk machine fabricated at CSIRO, Figure 41.

All samples were sectioned to approximately 50 mm x 40 mm and then surface ground to an average roughness of 0.8 µm. Each test was run for 1 km under a loading of 10 N and sample rotation of 96 RPM with a wear diameter of 19 mm and subsequently for 2 km with a wear diameter of 23 mm and rotation of 82 RPM. Linear speed was kept constant at 0.1 m/s.

The wear tracks on each sample were profiled using the Mahr perthometer, the data was then placed in Microsoft Excel to graph and analyse the tracks. Wear volume was calculated by the area of the wear track profile, obtained as a graph, multiplied by the circumference of the wear track.

Figure 41: Pin-on-disk wear testing machine.
Chapter 4 Results and Discussion

4.1 Introduction
This chapter firstly covers adhesion testing results, followed by microstructure analysis of fused coatings to determine its suitable parameters. Salt spray corrosion test and pin-on-disk wear test results are also presented.

4.2 Adhesion Testing
Flame sprayed and HVOF sprayed Ni-based coatings in as-sprayed condition and flame fused conditions were tested for their adhesion strength. The results recorded from the adhesion testing are presented in Table 11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating</th>
<th>Adhesion Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame sprayed as-sprayed</td>
<td>36C</td>
<td>29 ± 1.29 MPa</td>
</tr>
<tr>
<td>HVOF sprayed as-sprayed</td>
<td>34F</td>
<td>49 ± 12.55 MPa</td>
</tr>
<tr>
<td>Flame sprayed flame fused</td>
<td>36C</td>
<td>497 ± 12.47 MPa</td>
</tr>
<tr>
<td>HVOF flame fused</td>
<td>34F</td>
<td>465 ± 6.06 MPa</td>
</tr>
<tr>
<td>Flame sprayed laser fused</td>
<td>36C</td>
<td>386 ± 22.63 MPa</td>
</tr>
<tr>
<td>Flame sprayed laser fused</td>
<td>34F</td>
<td>199 ± 22.45 MPa</td>
</tr>
</tbody>
</table>

There was only a moderate difference in bond strength between the coatings produced by flame spray and HVOF in the as-sprayed conditions, that is, 29 and 49 MPa respectively. The bond strength increased significantly when the coatings were fused, to over 400 MPa respectively. All coatings failed in the pure shear mode based on the design, using the new test methodology, the failure occurred at the coating substrate interface and thus the mode of failure can be considered as adhesive failure. Another observation was that the coating produced in the as-sprayed condition had a rough appearance at the substrate/coating interface whereas the fused coatings had sheared cleanly at the substrate/coating interface, indicating a degree of metallurgical bonding. Laser fused samples still exhibited high bond strength but were generally lower than the flame fused samples.
It is clear the difference in adhesion strength between the as-sprayed coatings compared to the fused coatings. These results are consistent with the literature; Hjörnhede et al [99] found that HVOF coating failed at 55-61 MPa while laser deposited coatings exceed the adhesive strength of the tensile pull-off test. Otsubo et al [62], using a shear test, found that Ni-based self-fluxing flame fused coatings had adhesion strengths between 400-500 MPa. Capp and Rigsbee [100] reported that laser fusing of plasma sprayed coatings also improved cohesion and adhesion bonding after having performed adhesion tests. This improvement was due to the microstructure becoming dense and the interface having a stronger bond.

4.3 Microstructure of Flame Fused Coatings

Nickel based self-fluxing coatings on stainless and mild steel were flame fused. Their typical microstructure is seen in Figure 42. Porosity is evident throughout the microstructure as well as unfused particles and oxides.

![Figure 42: Back scattering electron SEM image of flame fused 36C on stainless steel substrate.](image-url)
4.4 Microstructure of Laser Fused Coatings and Fusing Parameter Selection

Initial laser fusing tests were carried out with 36C flame sprayed, 34F HVOF sprayed and 34F flame sprayed on stainless steel. 34F HVOF sprayed stainless steel plate is shown in Figure 43, each track was fused using a different power output ranging from 0.5 kW to 3 kW. Cracking is clearly visible at the 1.5 kW tracks; also some melting can be seen as the laser fusing power increases.

Figure 43: Laser fusing parameter test tracks on 34F HVOF on stainless steel substrate.
Fusing of stainless steel samples using power ranges from 0.25 kW to 0.5 kW, demonstrated incomplete fusion with about half the coating had undergone a change in microstructure, while the bottom half remained in the as-sprayed condition, illustrated in Figure 44.

Figure 44: LOM cross-section image of the microstructure of Ni-based coating 36C flame sprayed after laser fusing at 0.5 kW showing partial fusion.
Fusing between 1 - 1.5 kW lead to cracking and trapping of porosity in the coating despite most of the coating microstructure had changed. The interface still retained its mechanical bonding; overall a poor, unusable coating was produced. Figure 45 shows 34F HVOF fused at 1.5 kW the coating having cracked and lifted from the substrate.

![Figure 45: LOM image of the cross-sectioned 34F HVOF 1.5 kW at 500 mm/min sample showing the coating having separated from the substrate.](image)

Figure 46 shows a cross-section of the microstructure of 36C laser fused at 1.5 kW. The coating had transformed to a dense microstructure with lower porosity than before fusing. The interface between the coating and substrate still demonstrates the mechanical bonding present in the as-sprayed condition as opposed to a metallurgical bond of fused coatings.
Figure 46: LOM image of the cross-sectioned 36C laser fused at 1.5 kW showing a change in the coating microstructure and unfused coating/substrate interface.

Figures 47 and 48 are 34F and 36C flame sprayed Ni-based coatings, they show a fused dense microstructure where porosity had been reduced and a good metallurgical bonding between coating and substrate, such microstructures occurred at laser fusing power parameters of 2 - 3 kW.

Figure 47: LOM image of microstructure of Ni-based coating of 34F flame sprayed and laser fused with laser power of 3 kW.
Figure 48: LOM image of the microstructure of Ni-based coating 36C flame sprayed and laser fused at 2.5 kW.
Figure 49 is an EDS map of a 36C coating on stainless steel laser fused at 3 kW, showing the distribution of Cr, Fe, Ni and W. Chromium is shown throughout the coating and also in the substrate. Iron is present in the coating in a small amount but forms the majority of the substrate, on the other hand nickel forms the majority of the coating while only a small amount is present in the substrate. The tungsten is highlighted as random pieces within the coating.

Figure 49: EDS map of cross-section of 36C laser fused at 3 kW showing the distribution of Cr, Fe, Ni and W throughout the coating and substrate.
4.5 Microstructure of Laser Cladded Coatings

The particle size of 36C (150+45 µm) was suitable for laser cladding, whereas 34F had a particle size (53+15 µm) that was too fine to be processed by the equipment. Optical analysis determined the suitable parameters for cladding this material.

Test tracks were cladded onto stainless steel plate, the power of the laser was varied for each track within the ranges of 1 to 2.5 kW, the plate after cladding is shown in Figure 50. Metallographic analysis showed cladding at all parameters produced a dense microstructure, with a barely visible interface. At 1 kW only a small amount of power was deposited leading to a relatively thin coating (100 µm), Figure 51, while the cladding at 1.5, 2 and 2.5 kW provided a thicker coating (>1 mm), Figures 52-54.

Laser cladding on mild steel, however, constantly showed cracked coatings. After preheating the substrate to 450°C and controlling the cooling rate of the work piece once cladded, it was possible to eliminate cracking on the coating.

![Figure 50: Stainless steel plate with laser clad 36C tracks of differing parameters.](image-url)
Figure 51: LOM image of cross-sectioned laser clad 36C onto stainless steel using 1 kW.

Figure 52: LOM image of cross-sectioned laser clad 36C onto stainless steel using 1.5 kW.
Figure 53: LOM image of cross-sectioned laser clad 36C onto stainless steel using 2 kW.

Figure 54: LOM image of cross-sectioned laser clad 36C onto stainless steel using 2.5 kW.
4.5.1 Discussion of fused coatings

The microstructures of fused coatings present a much more dense structure compared to as-sprayed coatings. All processing methods utilised, flame and laser fusing and laser cladding demonstrated this. It was possible to eliminate porosity by laser fusing and laser cladding once the correct processing parameters had been determined, this was also observed by Gonzalez et al [42]. Laser cladding also has the benefit of being a one stage process as opposed to a two stage involving spraying and then fusing.

The elemental distribution shows the majority of the nickel, chromium and tungsten carbide to be in the coating layer, there is a slight diffusion of the elements and the interface, this is characteristic of metallurgical bonding as per fused coatings. Bergant et al [60] observed that fusing over 1000°C led to diffusion between particle interfaces and uniform distribution throughout the microstructure as well as a reduction in porosity. Gómez-del río et al [44] found that NiCrBSi fused coatings contained diffusion of iron from the steel substrate into coatings. They concluded that laser cladding led to a uniform distribution of small and rounded precipitates, while flame fusing had similar sizes but was non-uniform. Laser fusing contained larger sizes as well as being non-uniform. Serres et al [101] observed that plasma sprayed and laser fused Ni-based coatings showed a fine dendritic microstructure with no porosity.
4.6 Corrosion Testing

Salt Spray testing is a visual form of identification of corrosion. Images were taken periodically (at 1161, 2290 and 4673 hours) to track the formation and propagation of corrosion. Figure 55 shows the prepared samples in the salt spray chamber prior to commencing the test, the sample name and their corresponding coating and substrate is presented in Table 12, Samples A and B are uncoated substrates Mild Steel and Stainless Steel, these were included in the testing as control samples. The coated samples were sprayed onto mild steel and stainless steel substrates, as these are the commonly used substrates within the industries.

Three laser fused samples on mild steel with 34F (Flame, P, and HVOF sprayed, Q) and 36C (Flame sprayed, R) coatings, were introduced in the chamber at a later stage and were tested for 428 hours. The samples after 24 hours of testing are shown in Figure 56, it is clear the uncoated mild steel sample (A) which is a benchmark test sample had already begun corroding. The parameters that produced the most consistently well fused coatings were 2 kW at 500 mm/min. Consequently the laser fused samples used in the testing were all processed at these parameters.
Table 12: Sample names with their respective coating, substrate and fusing method.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Coating, Substrate and Fusing Method</th>
<th>Corrosion Observation</th>
<th>Sample name</th>
<th>Coating, Substrate and Fusing Method</th>
<th>Corrosion Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mild Steel</td>
<td>Yes</td>
<td>J</td>
<td>34F Flame Spray Stainless Steel Laser Fused</td>
<td>Surface</td>
</tr>
<tr>
<td>B</td>
<td>Stainless Steel</td>
<td>No</td>
<td>K</td>
<td>34F HVOF Stainless Steel Laser Fused</td>
<td>No</td>
</tr>
<tr>
<td>C</td>
<td>34F Flame Spray Stainless Steel Flame Fused</td>
<td>Yes</td>
<td>L</td>
<td>Cr₂O₃ Mild Steel Plasma Sprayed</td>
<td>Yes</td>
</tr>
<tr>
<td>D</td>
<td>34F Flame Spray Mild Steel Flame Fused</td>
<td>No</td>
<td>M</td>
<td>Cr₂O₃ Stainless Steel Plasma Sprayed</td>
<td>No</td>
</tr>
<tr>
<td>E</td>
<td>34F HVOF Stainless Steel Flame Fused</td>
<td>Yes</td>
<td>N</td>
<td>Plasma Sprayed Cr₂O₃ and Cold Sprayed Ti under layer Mild Steel</td>
<td>Yes</td>
</tr>
<tr>
<td>F</td>
<td>34F HVOF Mild Steel Flame Fused</td>
<td>No</td>
<td>O</td>
<td>Plasma Sprayed Cr₂O₃ and Cold Sprayed Ti under layer Stainless Steel</td>
<td>No</td>
</tr>
<tr>
<td>G</td>
<td>36C Flame Spray Mild Steel Flame Fused</td>
<td>No</td>
<td>P</td>
<td>34F Flame Sprayed Mild Steel Laser Fused</td>
<td>Yes</td>
</tr>
<tr>
<td>H</td>
<td>36C Flame Spray Stainless Steel Flame Fused</td>
<td>Surface</td>
<td>Q</td>
<td>34F HVOF Mild Steel Laser Fused</td>
<td>Yes</td>
</tr>
<tr>
<td>I</td>
<td>36C Flame Spray Stainless Steel Laser Fused</td>
<td>Surface</td>
<td>R</td>
<td>36C Flame Spray Mild Steel Laser Fused</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Figure 55: Samples in salt spray chamber prior to testing with blue acrylic paint on the uncoated areas of the samples.

Figure 56: Salt spray corrosion samples after 24 hours of testing.
4.6.1 Salt Spray Testing after 1161 Hours

Bench mark test samples A and B were not metallurgically analysed. Only sample C to sample R were sectioned and characterised by optical microscopy. After 1161 hours it was noted that corrosion was present in a number of samples. The sectioned sample C can be seen in Figure 57 showed no sign of corrosion indicating the coating has high corrosion resistance. A majority of the coatings testing showed the same integrity and corrosion resistance.

Figure 57: LOM of cross-section of flame fused Ni-based coating 34F flame sprayed on stainless steel sample C after 1161 hours of salt spray testing.
Figure 59 below is light optical micrographs of Ni-based coating E respectively. Corrosion appears to have taken place on the surface of sample E; however the coating has remained intact after 1161 hours of testing.

![Surface Corrosion](image)

Figure 58: LOM of cross-section of flame fused Ni-based coating 34F HVOF sprayed on stainless steel sample E after 1161 hours of salt spray testing.

The chromium oxide coated samples (L and N) on mild steel substrate corroded at the substrate interface in the case of sample N (CS Ti MS), resulted the coating to spall off from the substrate, these are illustrated in Figures 59 and 60. The corrosion fluid was able to penetrate the acrylic paint covering the sample edges. Corrosion appears at the interface, due to the large difference in potential between the mild steel substrate because the NiAl bond coat behaves as a galvanic cell. Crevice corrosion prevailed once the fluid penetrated and stagnated in the gap between coating and substrate.
Figure 59: LOM of cross-section of sample L after 1161 hours of salt spray corrosion testing, showing corrosion had entered from the side of the sample, resulting in corrosion at the interface between the substrate and coating.

Figure 60: LOM of cross-section of sample N the chromium oxide coating showing NiAl bond coat and titanium under layer that had spalled from the substrate/coating interface after 1161 hours of salt spray corrosion testing.
4.6.2 Salt Spray Testing of Ni-based Laser Fused on Mild Steel Samples after 428 Hours

Nickel based laser fused coating on mild steel substrate (Sample P 34F flame sprayed) after salt spray corrosion testing for 428 hours is shown in Figure 61. Corrosion fluid was able to penetrate the coating via cracks present. Since mild steel being more anodic than the coatings, pitting corrosion had occurred at the substrate. This corrosion was also observed on the other two laser fused on mild steel samples (Q and R).

Figure 61: LOM of cross-section of 34F flame sprayed laser fused sample on mild steel, sample P after 428 hours of testing showing corrosion of the substrate and fluid has entered through a crack in the coating.
4.6.3 Salt Spray Testing after 2290 Hours

After 2290 hours, corrosion had appeared on sample C, in a similar method of corrosion observed in the samples L and N, which corrosion had occurred between the coating and substrate, as shown in Figure 62.

![Figure 62: LOM of cross-section of flame fused 34F flame sprayed on stainless steel sample C after 2290 hours of salt spray testing, showing corrosion has penetrated between the coating and substrate interface.](image)

For the rest of the samples, the observation of the corrosion test showed no significant corrosion on them. Subsequently at 4673 hours of testing, the samples were then sectioned and observed.
4.6.4 Salt Spray Testing after 4673 Hours

The corrosion test ran for 4673 hours, the cross section of each sample was metallographically prepared. The reference benchmark sample B (stainless steel) showed no corrosion after 4673 hours of salt spray testing.

Figure 76 shows sample E at the completion of salt spray testing after 4673 hours. Corrosion has penetrated along the coating and substrate interface, some parts of the substrate has also corroded in a form similar to intergranular corrosion [102].

Figure 63: LOM of cross-section of 34F HVOF flame fused on stainless steel sample E showing corrosion at the substrate after 4673 hours of salt spray testing.

Figure 64 shows the cross-section of Ni-based coating 34F HVOF sprayed on mild steel (Sample F) at the end of salt spray corrosion testing. There appears to be little or no signs of corrosion on samples F and G, while sample H showed some minor surface corrosion.
Figure 64: LOM of cross-section of 34F HVOF flame fused on mild steel sample F showing no sign of corrosion after 4673 hours of salt spray testing.

Figure 65 is a light optical microscope images of the cross-section of Ni-based coating on stainless steel (Sample I 36C flame sprayed laser fused) after 4673 of salt spray testing showing little sign of corrosion.

Figure 65: LOM of cross-section of 36C flame sprayed laser fused on stainless steel sample I showing no sign of corrosion after 4673 hours of salt spray testing.
Figure 66 is a light optical micrograph of chromium oxide coated sample M at the end of salt spray corrosion testing after 4673 hours. There was little to no presence of corrosion visible.

Figure 66: LOM of cross-section of plasma sprayed chromium oxide on stainless steel sample M showing no visible corrosion after 4673 hours of salt spray testing.
4.6.5 Summary of Corrosion Test

Mild steel sample A had corroded after 24 hours of testing, while the stainless steel sample B showed no sign of corrosion after the testing was completed. Samples C and E, both 34F flame fused coatings on stainless steel, had exhibited corrosion after 2290 hours at the coating and substrate interface, in a similar fashion to samples L and N. Sample E also exhibited intergranular corrosion of the substrate.

The coatings that had exhibited corrosion along the interface demonstrated the integrity of the coating as corrosion did not penetrate through the coating itself, however the weak point was at the edges where the coating and substrate intersected.

The remaining samples, D, F, G, H (Ni-based flame fused samples) and I, J, K (Ni-based laser fused samples), M and O (Cr₂O₃ samples) had not corroded when test completed at 4673 hours, these particular coatings are showing encouraging results of corrosion resistance, although some superficial corrosion was present on Sample H and I, which has not affected the integrity of either coating. The stainless steel sample had not shown signs of corrosion on test completion.

The laser fused nickel based coated on mild steel samples P, Q and R exhibited corrosion after 428 hours of testing, due to cracking present, salt solution was able to reach the substrate and corrosion initiated. Chromium oxide coated samples L and N had spalled from their mild steel substrates after 1161 hours. Crevice corrosion had occurred at the coating and substrate interface having penetrated from the covered edges.
4.6.6 Discussion of Corrosion Test

The salt spray corrosion tests showed that the majority of the coatings had good corrosion resistance upon completion after a total exposure period of 4673 hours. The dense, mostly pore free structure provided resistance from corrosion penetrating the coating. Li et al [4] stated that uniform distribution and high solubility of chromium lends to high corrosion resistance for laser fused coatings.

The coatings that had failed (Samples C, E, L and N) demonstrated corrosion had occurred from the edges of the coated sample at the coating and substrate interface. Despite C and E were fused coatings, both these samples were 34F coated stainless steel samples, it is possible that the corrosion had occurred due to dilution of cobalt with the substrate according to Crook [103] which reduces corrosion resistance. Navas et al [104] found that corrosion fluid was able to penetrate through pores and defects formed after laser fusing, while some cracks and defects were observed in some of the laser fused coatings. Evidence of crevice corrosion and intergranular corrosion were observed see Figures 68, 69, 73 and 76. The failure of the coatings can be attributed to the difference in potential particularly between the Cr₂O₃ and bond coat for sample L and titanium for sample N and the mild steel substrate forming a galvanic cell. Monticelli et al [105] and Li et al [106] observed a similar effect although mentioned that the corrosion was able to penetrate through the porous coating. Tuominen et al [93] observed that high specific energy from laser fusing can lead to iron dilution from the substrate to coating this reduces the resistance to pitting corrosion.

Chromium oxide coatings L and N that had failed crevice corrosion at the coating/substrate interface and bond coat/substrate interface, as opposed to Li et al [106], who observed corrosion fluid to have penetrated through the porous chromium oxide coating causing crevice corrosion between the coating and NiCr under layer used.

In other research, Li et al [4] found that under hot corrosion testing, corrosion resistance for Ni-based coatings was improved when laser fused compared to flame fused. Similarly Serres et al [5], using potentiodynamic polarisation tests, found that laser fusing had improved corrosion resistance of Ni-based coatings over as-sprayed and flame fused conditions.
4.7 Wear Testing

Pin-on-disk wear testing results are presented. The wear profiles for 1 km and 2 km runs with light optical micrographs of the corresponding wear track on the coated surface and on the ruby ball are presented.

The wear volume losses for all the samples are presented in Table 13.

Table 13: Wear volume loss after 1 km and 2 km pin-on-disk testing.

<table>
<thead>
<tr>
<th>Sample - Description</th>
<th>Wear volume loss after 1 km (mm$^3 \times 10^{-3}$)</th>
<th>Wear volume loss after 2 km (mm$^3 \times 10^{-3}$)</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Mild Steel</td>
<td>9.80</td>
<td>24.83</td>
<td>271±4</td>
</tr>
<tr>
<td>B Stainless Steel</td>
<td>432.11</td>
<td>1572.56</td>
<td>278±6</td>
</tr>
<tr>
<td>C 34F Flame Spray Stainless Steel Flame Fused</td>
<td>3.36</td>
<td>6.05</td>
<td>911±44</td>
</tr>
<tr>
<td>D 34F Flame Spray Mild Steel Flame Fused</td>
<td>2.84</td>
<td>6.32</td>
<td>915±38</td>
</tr>
<tr>
<td>E 34F HVOF Stainless Steel Flame Fused</td>
<td>1.63</td>
<td>24.06</td>
<td>1036±24</td>
</tr>
<tr>
<td>F 34F HVOF Mild Steel Flame Fused</td>
<td>2.29</td>
<td>2.85</td>
<td>896±19</td>
</tr>
<tr>
<td>G 36C Flame Spray Mild Steel Flame Fused</td>
<td>11.67</td>
<td>8.27</td>
<td>661±53</td>
</tr>
<tr>
<td>H 36C Flame Spray Stainless Steel Flame Fused</td>
<td>1.99</td>
<td>19.87</td>
<td>771±49</td>
</tr>
<tr>
<td>I 36C Flame Spray Stainless Steel Laser Fused</td>
<td>2.26</td>
<td>27.76</td>
<td>990±11</td>
</tr>
<tr>
<td>J 34F Flame Spray Stainless Steel Laser Fused</td>
<td>3.12</td>
<td>1.02</td>
<td>1162±20</td>
</tr>
<tr>
<td>Sample</td>
<td>Coating Description</td>
<td>Wear Rate</td>
<td>Wear Depth</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td><strong>K</strong></td>
<td>34F HVOF Stainless Steel Laser Fused</td>
<td>0.04</td>
<td>1.61</td>
</tr>
<tr>
<td><strong>L</strong></td>
<td>Chromium Oxide Mild Steel Plasma Sprayed</td>
<td>1.57</td>
<td>2.77</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>Chromium Oxide Stainless Steel Plasma Sprayed</td>
<td>1.12</td>
<td>2.26</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>Plasma Sprayed Chromium Oxide and Cold Sprayed Titanium under layer Mild Steel</td>
<td>2.63</td>
<td>2.12</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>Plasma Sprayed Chromium Oxide and Cold Sprayed Titanium under layer Stainless Steel</td>
<td>1.37</td>
<td>3.02</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>34F Flame Sprayed Mild Steel Laser Fused</td>
<td>8.99</td>
<td>9.41</td>
</tr>
<tr>
<td><strong>Q</strong></td>
<td>34F HVOF Mild Steel Laser Fused</td>
<td>4.57</td>
<td>19.52</td>
</tr>
<tr>
<td><strong>R</strong></td>
<td>36C Mild Steel Laser Fused</td>
<td>0.77</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Pin-on-disk wear test was carried out over a distance of 1 km, most of the coatings had a similar wear profile and depth, indicating that there was not a large difference in wear performance over 1 km between coatings. The relatively low wear for all coatings indicated most of them had good wear resistant behaviour. Although the 36C flame fused coating (Sample G) had a much larger wear, this may be due to tungsten carbide particle having been embedded in the wear track augmenting the wear profile.
The wear test was also carried out on the same coatings over a distance of 2 km. The results showed more variation in wear over 2 km between coatings. The Chromium Oxide coatings performed consistently (Samples L, M, N, and O); while the Ni-based coatings were generally slightly higher wear volume. Again, the 34F HVOF coating (Sample E) exhibited a large wear profile in relation to the rest; this may be due to large tungsten carbide particles embedding in the track augmenting the wear profile.

4.7.1 Summary for Pin-on-Disk Wear Test Results

The results for the 1 km wear test demonstrated similar results with low wear reported for most of the samples. Stainless steel (sample B) exhibited the greatest wear, with the highest volume loss. Sample A and sample G also showed that while having greater wear resistance than the stainless steel, and sample G is 36C flame sprayed which this coating contains large tungsten carbide particles that are susceptible to pull out from the matrix of the coating. The Ni-based samples and Cr₂O₃ samples all demonstrated similar wear results, with the Cr₂O₃ showing slightly greater wear resistance. Also laser fused Ni-based coatings demonstrated lower wear loss in comparison to the flame fused Ni-based coatings.

Rank of wear resistance based on 1 km wear volume losses from lowest to highest are as follows: Sample K > Sample R > Sample M > Sample O > Sample L > Sample E > Sample H > Sample I > Sample F > Sample N > Sample D > Sample J > Sample C > Sample Q > Sample P > Sample A > Sample B.

The results for the 2km wear test showed Stainless steel (sample B) had the highest wear volume loss. Cr₂O₃ coatings performed consistently with lower wear losses than the other coatings in general. The Ni-based coatings showed varying results. C, D, F, G, R showed wear losses from .02 mm³ to .08 mm³. E, H, I, P and Q demonstrated higher wear loss and are believed to be due to the pull out of WC particles from the coating matrix. Overall Cr₂O₃ coatings demonstrated consistently higher wear protection along with the laser fused Ni-based coatings, while the flame fused Ni-based coatings showed similar performance; they generally exhibited higher wear loss, and at times slightly higher losses due to possible WC pull out.
The best performing coating was Sample J with the lowest wear volume loss of 0.01 mm$^3$. The rank of the coatings based on 2 km wear volume losses from lowest to highest are as follows: Sample J > Sample K > Sample N > Sample M > Sample R > sample L > Sample F > Sample O > Sample C > Sample D > Sample G > Sample P > Sample Q > Sample H > Sample E > Sample A > Sample I > Sample B.

4.7.2 Wear Testing of Ni-based Coatings on Stainless Steel Substrates

The Ni-based coatings on stainless steel had varying wear test results.

Figure 67 shows 34F HVOF laser fused on stainless steel sample K after 1 km pin-on-disk wear testing. This was one of the best performing samples in the wear testing; the wear track was narrow, at 100 µm. The wear volume loss was 2.26 x10$^{-2}$ mm$^3$ and wear track depth was 3 µm.

Figure 67: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed laser fused on stainless steel K, wear track and (c) surface profile of ruby ball in contact with the wear track.

One of the most worn of the coated stainless steel samples is shown in Figure 68. 36C flame sprayed laser fused on stainless steel (Sample I) after pin-on-disk wear testing. The coating resulted in a wear track depth of 9 µm and track width of 800 µm, wear volume loss of 27.76 x10$^{-2}$ mm$^3$. This sample was one of the most worn in the tests.
4.7.3 Wear Testing of Ni-based Coatings on Mild Steel Substrates

One of the better performing in wear resistance was Laser fused Ni-based coating on mild steel (34F flame sprayed (Sample P)). Light wear is observed on the ruby ball and coated surface can be seen in Figure 69. Wear depths are 6 µm for the 34F coating. The sample had a wear track width of 400 µm and a wear volume loss of \(8.99 \times 10^{-2} \text{ mm}^3\).

Figure 70 shows 36C flame sprayed laser fused on mild steel sample R, wear track depth 1 µm, wear track width 400 µm, wear volume loss \(2.40 \times 10^{-2} \text{ mm}^3\). This was one of the least wear resistant coatings on mild steel tested.
Figure 70: (a) 2km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed laser fused on mild steel sample R, wear track and (c) surface profile of ruby ball in contact with the wear track.

4.7.4 Wear Testing of Chromium Oxide Coatings

Chromium oxide coatings were more consistent in their wear losses than the Ni-based coatings, the coating showing one of the least wear losses (Sample N), and the most wear loss (Sample O), of the chromium oxide coatings is shown below.

Figure 71 is showing chromium oxide with cold sprayed titanium under layer on mild steel sample N, wear track depth 3 µm, wear track width 200 µm, wear volume loss $2.12 \times 10^{-2} \text{ mm}^3$.

Figure 71: (a) 2km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide and cold sprayed titanium on mild steel N, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure 72 is showing chromium oxide with cold sprayed titanium under layer on stainless steel sample O, wear track depth 2 µm, wear track width 300µm, wear volume loss $3.02 \times 10^{-2}$ mm$^3$.

![Figure 72: (a) 2km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide and cold sprayed titanium on stainless steel O, wear track and (c) surface profile of ruby ball in contact with the wear track.](image)

**4.7.5 Discussion of Wear Test**

It appears that the 2 km wear test shows some significant wear losses for certain coatings. Namely: the Ni-based coatings E, H, I, P and Q showed severe wear profiles, this high wear volume loss was due to pull out of WC particles from the coating matrix that then act as an abrasive, as observed by Rodríguez et al [12] and Kim et al [40]. Another reason for high wear loss can be attributed to non-uniformity of the WC and Ni-based phases as reported by Guo et al [107] that this resulted in high residual stresses and removal of WC particles. Despite the occurrence of pull out Kim et al [40] found that WC content improved dry sliding wear resistance.

The laser fused coatings generally showed a higher wear resistance over flame fused coatings, this is in agreement with Felgueroso et al [108] who observed lower wear values and lower friction coefficient. Overall the laser fused Ni-based coatings and chromium oxide coatings most consistently demonstrated the highest wear resistances, Serres et al [41] found that laser remelted coatings at times lower wear
rate when compared to hard chromium coatings. Gonzalez et al [14] concluded that there was no significant difference in wear behaviour between flame or laser fused coatings.

The wear mechanism observed appear to be abrasive wear with the ruby ball removing material from the substrate, clear wear tracks in the direction of rotation are visible. Miguel et al [3] using a ball-on-disc testing method with a steel ball, found that the wear mechanism of fused Ni-based coatings was combination of adhesion, abrasion and delamination. Guo et al [109] used a steel ball and ring wear testing method and found the wear mechanism to be abrasive and adhesive for Ni-based coatings. The mechanisms appear to be similar between the chromium oxide as well as the Ni-based coatings. The chromium oxide coatings wear loss was generally lower than the Ni-based.

There did not appear to be a significant correlation between the microhardness of the coatings and the pin-on-disk wear test results.
Chapter 5 Conclusions and Future Work

The objective of the project was to find suitable wear and corrosion resistant coatings that can replace current coatings used within the paper, mining and materials industries.

Ni-based coatings were deposited onto stainless and mild steel substrates using various flame and HVOF thermal spray processes and then heat treated with a fusing process utilising flame and laser. These coatings were subjected to salt spray fog corrosion testing and pin-on-disk wear testing; their performance was compared to traditional plasma sprayed Cr$_2$O$_3$ coatings and modified Cr$_2$O$_3$ coating with cold sprayed titanium underlayer. Adhesion testing was performed to determine the adhesion strengths of fused and as-sprayed Ni-based coatings. Laser cladding was trialled to observe the ability to process these coatings.

The conclusion drawn from these experiments are presented below.

The adhesion test resulted in very high adhesion strengths for the fused coatings, the flame sprayed and flame fused coatings were the highest with 497 MPa, followed by HVOF sprayed with 465 MPa, 386 MPa for 36C Laser fused and 199 MPa for 34F laser fused. The as-sprayed coatings recorded 49 MPa for Flame sprayed and 29 MPa for HVOF sprayed.

Salt spray corrosion testing showed that the Ni-based coatings were able to perform just as well as Cr$_2$O$_3$ coatings that are currently used in industry. Corrosion occurred at the substrate coating interface causing the coating to spall from the substrate. This was readily visible on the Cr$_2$O$_3$ coatings on mild steel and present on 34F on stainless steel. A galvanic cell was created when the coating and substrate had been exposed to the corrosive media. The corrosion was only able to penetrate from the sides of the samples and not from the top through the coating, thus the integrity of the coating microstructures were sufficient to resist corrosive fluids. The best performing coatings in the corrosion test were flame fused Ni-based coatings D, F and G; laser fused Ni-based coatings I and K and Cr$_2$O$_3$ coatings M and O.

Pin-on-disk wear testing showed relatively low wear rates compared to the uncoated substrates of mild and stainless steels. The Ni-based coatings also compared
favourably to the Cr$_2$O$_3$ coatings, although Cr$_2$O$_3$ still proved to have greater wear resistance.

The best performing coatings from the pin-on-disk wear tests were laser fused Ni-based coatings K and R and Cr$_2$O$_3$ coatings M and L. The laser fused and chromium oxide coatings most consistently reported low wear volume losses.

In summary, Ni-based coatings fused by laser have shown favourable wear and corrosion resistances and, providing further development, could replace current usage of plasma sprayed Cr$_2$O$_3$ in industries.

Laser cladding of 36C provided promising results, achieving a dense, pore free microstructure in a single step process.

Laser fusing and laser cladding can be further refined to eliminate cracking, it is necessary to develop a method to easily determine suitable parameters that produce completely dense coatings. As these methods are automated compared to the manual flame fusing process, they present benefits in their ability to process larger quantity of materials and geometries. Further wear and corrosion tests particularly those simulating the use of the coating within their respective industries should be carried out.

A modified chromium oxide coating with a cold spray underlayer was tested. It had failed in a similar method to traditional Cr$_2$O$_3$ coatings. Further work into improving this modified coating could also be undertaken.
References


Appendix A - Salt Spray Corrosion Testing Images

Figure A-1: LOM of cross-section of flame fused Ni-based coating 34F flame sprayed on mild steel sample D after 1161 hours of salt spray testing.

Figure A-2: LOM of cross-section of flame fused Ni-based coating 34F HVOF sprayed on mild steel sample F after 1161 hours of salt spray testing.
Figure A-3: LOM of cross-section of flame fused Ni-based coating 36C flame sprayed on mild steel sample G after 1161 hours of salt spray testing.

Figure A-4: LOM of cross-section of flame fused Ni-based coating 36C flame sprayed on stainless steel sample H after 1161 hours of salt spray testing.
Figure A-5: LOM of cross-section of laser fused Ni-based coating 36C flame sprayed on stainless steel sample I after 1161 hours of salt spray testing.

Figure A-6: LOM of cross-section of laser fused Ni-based coating 34F flame sprayed on stainless steel sample J showing cracks running in transverse direction, after 1161 hours of salt spray testing.
Figure A-7: LOM of cross-section of laser fused Ni-based coating 34F HVOF sprayed on stainless steel sample K showing pores developed during the spray and fuse process and no corrosion effect after 1161 hours of salt spray testing.

Figure A-8: LOM of cross-section of plasma sprayed chromium oxide on stainless steel showing no effect of corrosion after 1161 hours of salt spray testing on sample M.
Figure A-9: LOM of cross-section of plasma sprayed chromium oxide and cold sprayed titanium under layer on stainless steel showing no effect of corrosion after 1161 hours of salt spray testing on sample O.

Figure A-10: LOM of cross-section of 34F HVOF laser fused on mild steel, sample Q after 428 hours of salt spray testing, showing the path of corrosion has penetrated the coating via the crack and commenced corrosion of the substrate.
Figure A-11: LOM of cross-section of 36C flame sprayed laser fused on mild steel, sample R after 428 hours of salt spray testing, showing corrosion has penetrated through the coating to the substrate where corrosion had occurred.

Figure A-12: LOM of cross-section of stainless steel sample B showing no corrosion after 4673 hours of salt spray testing.
Figure A-13: LOM of cross-section of 34F flame sprayed flame fused on mild steel sample D showing no sign of corrosion after 4673 hours of salt spray testing.

Figure A-14: LOM of cross-section of 36C flame sprayed flame fused on mild steel sample G showing no sign of corrosion after 4673 hours of salt spray testing.
Figure A-15: LOM of cross-section of 36C flame sprayed flame fused on stainless steel sample H showing minor corrosion at the surface of the coating after 4673 hours of salt spray testing.

Figure A-16: LOM of cross-section of 34F flame sprayed laser fused on stainless steel sample J showing passivity at the cracks after 4673 hours of salt spray testing.
Figure A-17: LOM of cross-section of 34F HVOF laser fused on stainless steel sample K showing no visible corrosion after 4673 hours of salt spray testing.

Figure A-18: LOM of cross-section of cross-section of plasma sprayed chromium oxide and cold sprayed titanium under layer on stainless steel sample O showing no sign of corrosion after 4673 hours of salt spray testing.
Appendix B - Pin-on-Disk Wear testing images

Figure B-1: (a) 1km wear track profile (b) LOM image corresponding to the surface of mild steel sample A, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-2: (a) 1km wear track profile (b) LOM image corresponding to the surface of stainless steel sample B, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-3: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed flame fused on stainless steel C, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-4: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed flame fused on mild steel D, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-5: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed flame fused on stainless steel E, wear track and (c) surface profile of ruby ball in contact with the wear track with some wear debris.

Figure B-6: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed flame fused on mild steel F, wear track and (c) surface profile of ruby ball in contact with the wear track showing debris coming off from the ruby ball.

Figure B-7: (a) 1km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed flame fused on mild steel G, showing rough wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-8: (a) 1km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed flame fused on stainless steel H, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-9: (a) 1km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed laser fused on stainless steel I, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-10: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed laser fused on stainless steel J, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-11: (a) 1km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide on mild steel L, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-12: (a) 1km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide on stainless steel M, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-13: (a) 1km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide and cold sprayed titanium on mild steel N, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-14: (a) 1km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide and cold sprayed titanium on stainless steel O, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-15: (a) 1km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed laser fused on mild steel, Q, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-16: (a) 1km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed laser fused on mild steel, R, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-17: (a) 2km wear track profile (b) LOM image corresponding to the surface of mild steel sample A, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-18: (a) 2km wear track profile (b) LOM image corresponding to the surface of stainless steel sample B, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-19: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed flame fused on stainless steel C, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-20: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed flame fused on mild steel D, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-21(a) 2km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed flame fused on stainless steel E, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-22(a) 2km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed flame fused on mild steel F, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-23: (a) 2km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed flame fused on mild steel G, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-24: (a) 2km wear track profile (b) LOM image corresponding to the surface of 36C flame sprayed flame fused on stainless steel H, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-25: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed laser fused on stainless steel J, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-26: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed laser fused on stainless steel K, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-27: (a) 2km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide on mild steel L, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-28: (a) 2km wear track profile (b) LOM image corresponding to the surface of plasma sprayed chromium oxide on stainless steel M, wear track and (c) surface profile of ruby ball in contact with the wear track.
Figure B-29: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F flame sprayed laser fused on mild steel sample P, wear track and (c) surface profile of ruby ball in contact with the wear track.

Figure B-30: (a) 2km wear track profile (b) LOM image corresponding to the surface of 34F HVOF sprayed laser fused on mild steel sample Q, wear track and (c) surface profile of ruby ball in contact with the wear track.
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