Effect of Substrate Temperature on Coating Adhesion

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

DEPARTMENT OF MECHANICAL AND INDUSTRIAL ENGINEERING
UNIVERSITY OF TORONTO

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Abstract

An experimental study was conducted to study the effect of preheating stainless steel specimens before depositing nickel coatings with a D.C. plasma torch.

Substrate temperature was varied from 25 °C to 650 °C. The adhesion strength and the porosity of the coating were respectively measured using a standard ASTM C 633-79 pull test and a mercury intrusion porosimeter. Coating microstructure was examined under a SEM. Oxide layer formed on the test specimens during heating was analyzed using XPS and argon ion sputtering.

The adhesion strength of the coating increased from 10 MPa to 75 MPa when substrate temperature was raised from 25 °C to 650 °C. Heating substrate slows the solidification rate of impinging particles, allowing them to make better contact with the substrate, and also produces an oxide layer on the substrate surface which can change its thermal contact resistance and wettability. Oxide layer thickness increased with substrate temperature.
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To my family
Abstract
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CHAPTER 1

Introduction

1.1 Background

In many industrial applications, material performance can be strongly affected by the exposed surfaces of the materials involved. For example, corrosion, oxidation, thermal properties and wear characteristics are all critically dependent on the surface characteristics of the material [1]. Thermal spraying technology is a versatile, well-established, cost-effective method of surface modification. It is also used to repair and refurbish worn or otherwise degraded parts, restore a part to its original dimensions and improve its surface properties. This technology can be used to create new materials such as composites with enhanced properties or completely new functional properties.

Thermal spray coatings are built up from individual particles that strike the substrate [2]. In the coating process powders of metals, alloys, polymers or ceramics with particle size from 10 -100 μm are injected into a stream of hot gas and accelerated towards the substrate. As the thermal and kinetic energy of the flow is transferred to the particles, the particles become fully or partially molten.
by the time they impact on the substrate surface where they freeze and form a dense hard coating. Thermal spray techniques derive thermal energy from either an electrical arc or gas combustion. Several techniques are grouped under the name of thermal spraying. Of these, the commonly used ones are:

**DC plasma:** This process relies on a direct current electric arc between a cathode and anode, which partially ionizes an inert gas flowing through the spray gun. Partially ionized particles of a gas exhibiting local electrical neutrality are called "plasma". Part of the energy stored in the plasma flame plume is released when the gas de-ionizes. The plasma heats up and melts the powder particles injected into it before impacting on the substrate to form the coating /1,2,3/.

**HVOF:** In this process a fuel gas such as hydrocarbon or hydrogen is mixed with oxygen, and burnt in a combustion chamber at high pressure. The gas exits the nozzle at a hypersonic velocity with values near Mach 5. The powder is injected via a carrier gas (nitrogen, argon, or helium) into the exhaust gas stream and propelled through the nozzle at high velocity. The flame temperature is relatively low because it is limited by the enthalpy of the chemical reaction of the fuel combustion /1,2,3/. However, because of the high particle impact velocity, particles do not need to be fully molten to attain high quality coatings.

**Wire Arc-Spraying:** This technique is based on the production of molten metal droplets by an electric arc between two wires that are consumable electrodes.

**Radio Frequency (RF) Plasma:** RF plasmas can be produced without electrodes. The apparatus consists of a water-cooled coil or gas-cooled
refractory (often silica glass). Energy coupling to the plasma is generated through electromagnetism and plasma gases do not come in contact with any electrodes. Therefore, contamination is largely prevented /1,3,4/.

Figure 1.1 gives an overview of different thermal spray processes. The experiments described in this thesis were all done using d.c. plasma spray technology.
The plasma spray methods

surrounding atmosphere

- Air
  - Conventional plasma spraying (APS)
  - High power plasma spraying (HPPS)
  - Shrouded plasma spraying (SPS)

- Special atmosphere
  - Underwater plasma spraying (UPS)
  - Inert gas plasma spraying (IGPS)
  - Vacuum plasma spraying (VPS)
  - Controlled atmosphere plasma spraying (CAPS)

Figure 1.1: Plasma techniques divided by their principal energy source and by surrounding atmospheres /3/
1.2 Motivation

The main motivation for this work was to gain a better understanding of the effect of substrate temperature on the strength of adhesion of plasma sprayed coatings to substrates.

Coating adhesion is one of the most important characteristics used to determine the quality of the coating /2,3/. Many studies have reported the influence of particle impact parameters (e.g., velocity, temperature) and substrate conditions (e.g., temperature, roughness) on the morphology of splats formed by the impact and solidification of molten droplets in a thermal spray. However, it is not clear what effect splat shape has on the quality of coatings.

Previous experiments and computer simulations conducted by the Centre for Advanced Coating Technology at the University of Toronto /5-9/ and by other research groups /10-16/ focused on the investigation of particle conditions in flight before their impact on the substrate and their effect on splat morphology after impact. This research has shown that substrate temperature is an important parameter in determining splat shape. When sprayed on cold substrate, splats show evidence of splashing and break-up. However, when the substrate is preheated above the so-called “transition temperature”, the splats are more likely to be disc shaped, without any splashing. The transition temperature depends on the material being sprayed: in the case of nickel powder sprayed on a stainless steel plate the transition temperature was found to be between 300 °C and 400 °C /6,16/. 
1.3 **Objectives**

The main objective of this project was to examine the effect of substrate temperature on the quality of a nickel coating applied onto a stainless steel substrate using a DC plasma gun. The initial substrate temperature before spraying was varied from 25 °C to 650 °C. Other spray parameters such as particle temperature, velocity, size and mass flow rate were kept constant.

To perform the experiments the following equipment was designed and constructed:

- a heater system for cylindrical specimens
- a fixture to hold the specimens in the oven
- a self-aligning fixture to hold the specimen for the tensile test

Coating quality was characterized using a number of different tests. Adhesion strength of the coating to the substrate was measured using a standard ASTM C633-79 tensile pull test. Substrate roughness was measured with a stylus profilometer. The microstructure of cross-sections taken through the coating and substrate was examined with a scanning electron microscope (SEM). Coating porosity was measured with an intrusion mercury porosimeter. The thickness and composition of the oxide layer developed on the substrate when it was heated were measured using argon ion sputtering and X-ray photoelectron spectroscopy (XPS).
1.4 **Thesis layout**

Chapter 1 gives a brief description of commonly used thermal spray techniques. The motivation for the project is presented along with its objectives.

Chapter 2 reviews the literature on factors influencing adhesion of thermal spray coating on preheated substrates, fracture of coatings and the effect of preheated substrates on splat morphology.

Chapter 3 presents the experimental set up. The substrate preparation method is described. The adhesion pull test, microstructure analysis method, oxide layer analysis and porosimeter tests are explained. A brief description is given of the particle sensing device, the DPV 2000, which measures in-flight particle parameters such as temperature, velocity and size.

Chapter 4 outlines the experimental test procedure and lists the conditions under which tests were done.

Chapter 5 gives the results of the coating adhesion tests, coating porosity measurements, and analyses of the oxide layers on the substrate.

Chapter 6 presents the conclusion derived from the research project and gives suggestions for future work.
CHAPTER 2

Literature review

The strength of adhesion of the coating to the substrate varies with the materials involved in the coating process, the spraying conditions and the pre-spraying treatment of the substrate. Thus, in order to understand the effect of substrate temperature on the adhesion of coating to the substrate, it is important to understand other factors influencing coating adhesion, coating fracture, the effect of the splat morphology on adhesion and the effect of substrate preheating on the splat morphology.

2.1 Adhesive/cohesive strength of coating

In practice the adhesion of thermal spray coating to substrate depends on a large number of factors. Some of the most important are:

- Thermal spraying process used
- Surface preparation before spraying. Usually surface roughness is increased by grinding or grit blasting before coating.
- Physical properties of the substrate and coating material
- Morphology of the splat after impingement onto the substrate
- Power input to the spray gun
- Powder gas pressure and feed rate
- Injection angle
- Oxidation of the interface substrate-coating
- Spray distance

The impact of molten particles onto the substrate is a key phase of the thermal spraying process. Ideally, particles flow and lock into the roughness of the substrate when they solidify. Subsequent particles interlock with one another. These interlocking forces are the main source of the adhesive strength of the coating and determine its quality /20/. To ensure good adhesion, the particles must have sufficient plasticity, high impact velocity, low viscosity and good wettability with the substrate surface. Amada /25/ showed that the adhesive strength is proportional to the average surface roughness.

Metallurgical adhesion occurs when micro-welds form between the coating and substrate and some alloying of materials occurs at the interface. This is observed in plasma sprayed coatings when very high temperature contact occurs between sprayed particles and the substrate /28/. Thus strong adhesion can result from the melting of the substrate and particle to form an alloy /12/. Adhesion can also be the result of Van Der Waals forces and diffuse bonding where chemical reactions occur due to high temperatures at the substrate/coating interface and produce intermetallic phases /26,27/. 
2.2 **Fracture of thermally sprayed coatings**

From an industrial perspective, adhesion strength is the most important property of a coating. Tensile adhesion tests that measure the strength of the bond between a thermally sprayed coating and a substrate are widely performed as a means of quality control or as an inspection method. The tensile strength of adhesion is described by the force necessary to tear off a unit area of the coating from the substrate /2,3/.

One widely used bond strength test performed by industry and research organizations is the ASTM Standard C 633-79 entitled "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings" /3/1. Figure 2.1 shows the method used. The coating is deposited on one end of a cylindrical test coupon. A matching coupon is then attached to the surface of the coating using epoxy glue. The two coupons are pulled apart until the coating fails, and the force required to fracture the coatings is recorded.

As illustrated in Figure 2.1, failure of the coating occurs most commonly as adhesive fracture at the substrate-coating interface or as cohesive fracture within the coating itself. According to ASTM standard C633-79, failure occurring entirely at the coating/substrate interface is reported as adhesive failure and the corresponding maximum tensile strength at the time the break occurs is recorded as the adhesive strength. Failure within the coating is reported as cohesive failure and the tensile strength recorded is considered to be cohesive strength.
Poor failures are those in which fracture occurs within or at the surface of the epoxy glue, in which case no conclusion can be drawn as to the strength of the coating.

Fracture occurs at various levels of deformation. If the value of deformation is low, the fracture is said to be brittle and if fracture follows necking, the fracture is said to be ductile. Brittle fracture requires low strain deformation energy whereas ductile fracture needs high energy and its occurrence can take a long time. Failure within the coating or at the interface coating/substrate can be generated by cracks or porosity and, in general, sprayed coatings are more brittle than their corresponding bulk materials. The adhesion strengths of sprayed layers are considerably lower than the tensile strength values of the corresponding materials and the adhesion of sprayed layers decreases with increasing thickness.
Figure 2.1: Fracture of thermally sprayed coating

- Failure at Coating-Substrate Interface (Testing of Adhesive Strength)
- Poor Failure at the Coating-Epoxi Glue-Interface
- Poor Failure within the Epoxy Glue
- Poor failure at the Counter Part-Epoxi Glue-Interface
- Failure within the Coating (Testing of Cohesive Strength)

- Counter part of coupon
- Epoxy Glue
- Ni-Coating
- Coupon
2.3 Effect of substrate temperature on splat formation and coating adhesion

The effect of substrate preheating on the spreading and solidification of individual molten droplets in a thermal spray has been intensively investigated (e.g., Fukumoto et al. /16, 17/, Li et al./33/, Pershin et al./5,6,7,8/, Fauchais et al. /10,13,16,34,35,36,37,38,39,40,41/ and Bao et al. /20/). These studies have concluded that substrate temperature modifies the splat morphology. As the substrate temperature was increased, a transition was observed from splash splats (see Figure 2.2 a) to disk splats (Figure 2.2 b). Splashed splats are characterized by a high degree of break-up and the formation of satellite droplets /5/. Disk splats exhibit little or no fingering and all the droplet material is retained in the central splat. The transition temperature ($T_t$, see Figure 2.2 c) is defined as the substrate temperature at which only half of the splats exhibit splashing /16,17/. Fukumoto /17/ found the transition temperature for nickel particles on a stainless steel substrate was approximately 337 °C.

Experiments performed with spraying nickel particles on stainless steel at the Centre for Advanced Coating Technologies at the University of Toronto /6/ also showed changes in the particle morphology with substrate temperature (Figure 2.3). On a surface at room temperature (25 °C) the particles splashed and formed a circular ring around the central splat. Increasing the substrate temperature to 194 °C made the ring disappear, but there were still fingers
around the splat edges. At 340 °C and 640 °C the splats looked disk-shaped, with very little evidence of splashing.

Computer simulations performed by Pasandideh-Fard /9/ showed that splashing was produced by solidification. If there is sufficient heat transfer between the droplet and substrate, the edges of the droplet freeze while the droplet is still spreading. This obstructs the flow of liquid and produces an irregular splat. On the other hand, if there is low heat transfer from the droplet (as is the case when it is on a hot substrate, or if there is large thermal contact resistance between the droplet and substrate) it spreads completely before solidifying and produces a circular splat.

Sobolev et al./12/ have experimentally shown that the development of splashing splats on the substrate helps to decrease the adhesion of the coating because of voids presence at the coating-substrate interface, which results from the break up of the splats. Sakakibara et al /23/ point out that disk splats adhere well to the substrate and improve the adhesive strength of the coating. They explain the high tensile strength observed on preheated substrate as being a result of better wettability between the substrate and the droplets. They also attribute the tensile strength to the high number of disk-shaped splats due to slower solidification rate of droplets caused by preheating of the substrate.

Leger /15/ studied the adhesion strength of alumina and zirconia coatings sprayed onto a stainless steel substrate. When the substrate was preheated above its transition temperature without oxidation, the adhesion strength increased with substrate temperature. For zirconia powders sprayed on stainless
steel (304L) substrate preheated to 500 °C, the adhesion strength increased to 60 MPa, whereas it was 20 MPa on an unheated surface. However, if the substrate was allowed to oxidize during substrate preheating, the adhesion strength decreased with the substrate temperature. It is necessary to point out that the increase of the substrate temperature affects not only the splat shape, but has other effects such as oxidizing the surface thereby changing the thermal contact resistance and surface wettability. Heating the substrate also removes moisture and other volatile contaminants, producing better contact of particles to the substrate and, consequently, better coating adhesion /42-44/.

Research conducted on properties of molybdenum coatings /44/ confirmed that deposit properties are improved with an increase of deposition temperature. Splat morphology changes with the increase of substrate temperature from fragmented to more continuous shape even on roughened substrate. Hence, the wettability of preheated substrate and molten particles ensuring a better contact at the interface, the flow of molten particles enhanced by a slow solidification because of preheated substrate and the removal of substrate moisture by substrate preheating are necessary conditions which can improve the contact between substrate and particles and thus the adhesion of particles to the substrate /36/.

The high adhesion of zirconia coating on stainless steel 304L at 500 °C substrate temperature compared to that at 300 °C measured by Pech /14/ and Bianchi /36/ has then been explained as being the result of the growth of an oxide layer which produces a visible surface color change. The oxide layer
increases the thermal contact resistance of the substrate surface /45/. The splat becomes thicker with the increasing roughness of the substrate. However, adhesion can decrease if the oxide layer becomes too thick /36/.

The composition of the oxide layer on the substrate can also affect coating adhesion. Fauchais et al. /39/ studied the influence of the heating rate and preheating temperature on oxidation of a 1040 steel substrate. There were two different kinds of oxidation layers generated when a 1040 steel substrate, oxidizable steel, is preheated: a magnetite (Fe$_3$O$_4$) layer followed by a hematite layer (Fe$_2$O$_3$). A low heating rate (< 3 °C/sec) and high temperature (> 500 °C) favors the generation of an oxide layer with high hematite (Fe$_2$O$_3$) content. On the other hand, a layer with low hematite and high magnetite (Fe$_2$O$_4$) content is obtained with a high heating rate (>3 °C/sec) and low preheating temperature (<400°C). The thick hematite upper layer shows poor adhesion (34 MPa) compared to a thin hematite layer (40 MPa). When a droplet impacts on a thick hematite layer, the oxide layer is broken, but is not removed from the substrate surface. On the contrary, when a droplet impacts on a thin hematite oxide layer, the oxide layer in the centre of the splat is removed such that the substrate surface can be seen at the center and better contact with the splats is ensured /39/. 
Figure 2.2: Transition temperature results of Fukumoto/16.77/
Figure 2.3: Nickel splashing on stainless steel substrate at different substrate temperatures
CHAPTER 3

Experimental apparatus and test equipment

3.1 Design of substrate heater system

A heater system (shown in Figure 3.1) that consisted of a block heater, J-thermocouple, a temperature controller and a relay was designed to preheat the test surfaces. The test specimens were held in the copper block heater and heated while their top surface was spray-coated.

A drawing of the stainless steel test specimens is shown in Figure 3.2. They were cylindrical, 53.8 mm long and 24.7 mm in diameter. They were machined from one inch diameter bars, made of austenitic stainless steel, type 304L, which has the following chemical composition: C-0.03%, Mn-2%, P-0.045%, S-0.03%, Si-1.0%, Cr-18 to 20%, Ni-8 to 12%, N-0.1% with the remainder Fe. Inside the test specimen, an internal thread with a length of 20 mm and a diameter of 10 mm was machined. The internal thread was used to hold the specimen in the tensile test fixture.

Figure 3.3 shows the cubic-shaped copper block machined with three holes. A 150 Watt cartridge heater was inserted into each hole. To prevent oxidation, the copper block heater was nickel-plated. To reduce heat loss to the
atmosphere, the copper block was insulated with layers of 19 mm thick alumina-silica ceramic fiber insulation (Insulfrax, Unifrax Corporation, Niagara Falls, NY, USA) with a thermal conductivity of 0.1644 W/mK at 760 °C and 0.2207 W/mK at 982 °C/48/.

The copper block heater was designed to preheat two test coupons simultaneously to a maximum temperature of 750 °C and keep them at the required temperature while they were sprayed. During the spray process, the temperature of the substrates was kept constant with the aid of a temperature controller (CN77000, Omega Engineering Inc., Stamford, CT, USA). The temperature of a test coupon was monitored with a J-thermocouple attached to its periphery, 3 mm below the exposed upper surface. The temperature at the center of the test coupon was measured and found to be at most 10 °C below that at its periphery.

During heating the surface, temperature of the two substrates inserted into the heater differed by less than 5 °C. Figure 3.4 compares the temperatures of the two specimens measured at the same time during heating.
Figure 3.1: Experimental set up for substrate preheating and spraying
Figure 3.2: Cylindrical specimen for the adhesion tensile test
Figure 3.3(a): Top view of the copper block heater
Figure 3.3(b): Section view of the copper block heater
Figure 3.3(c): Section View of the copper block heater surrounded with

9 mm thick ceramic fiber insulation
Figure 3.4: Calibration curve of the specimen temperature
3.2 Tensile pull test machine

3.2.1 Standard test method for adhesive or cohesive strength of flame-sprayed coating, ASTM C633-79

The standards tensile adhesion test ASTM C 633-79 is one of the most commonly used methods for quantifying coating mechanical response. The test method determines the degree of adhesion (bonding strength) of a coating measured in tension normal to the substrate. One surface of a cylindrical specimen, which acts as the test substrate, is coated. The coating is bonded to a counter part specimen with a suitable adhesive, such as epoxy.

The glued cylinders are assembled in a self-aligning fixture which is mounted on a tensile test machine and pulled in a plane normal to that of the coating at a constant cross head speed between 0.013 mm/s (0.030 in./min) and 0.021 mm/s (0.050 in./min) until failure occurs. Once rupture occurs, the maximum load is recorded. The adhesion strength can be calculated using the following equation:

\[
\text{Adhesion strength} = \frac{\text{maximum load}}{\text{cross-sectional area of the specimen}}
\]

This tensile strength test method may be subject to errors and ambiguities. For example, results are dependent on alignment and degree of epoxy penetration into the coating. However, this test is recommended for quality
control or acceptance testing. This method is useful for comparing adhesion or cohesive strength of flame-sprayed coatings /31/.

There are some restrictions to this method /31/.

1. The bonding agent should be able to bond the coating to the loading fixture with a tensile strength that is at least as great as the minimum required adhesion strength of the coating.

2. The facing diameters of the loading and substrate fixtures should be the same, and their diameters should fall between 0.9 in (23mm) to 1.0 in (25 mm).

3. The fixtures should be made of metal.

4. Ideally, the thickness of the coating should be uniform. In practice, as long as the coating thickness does not vary more than 0.001 in. (0.025 mm), it is suitable for use in the adhesion test.

5. The test should be repeated with at least five specimens.

3.2.2 Adhesive bonding agents, fixture and oven

According to the ASTM standard C 633-79 test, an adhesive bonding agent should be used to attach the counter part to the sprayed specimen. The bonding agent should be sufficiently viscous to not penetrate through a 0.015 in (0.38 mm) coating thickness. In this study, the bonding agent used was a modified polyamide-epoxy adhesive film (FM 1000, manufactured by Cytec
Industries, West Paterson, NJ, USA), which is especially developed for bonding metals, structural plastic laminates and various composite structural plastic sandwiches /49/.

To cure this adhesive agent, an oven was preheated to 190 -200 °C. Then a 27 mm diameter disk of adhesive film was sandwiched between the sprayed coupon and the counter part which were all held in an attachment as shown in Figure 3.5 (a) & (b). Held by the fixture, the sandwiched coupon and counter part were put in the oven for 2.5 hours to cure the glue. The weight of the counter part is the force that presses the glue to the coating. After the required curing time, the glued coupons were taken from the oven and cooled to room temperature. Figure 3.6 shows a photograph of the glued specimens.

FM 1000 has a manufacturer specified tensile strength of about 90 MPa. The adhesion strength of the glue was tested to make sure that the glue had the required strength. The tensile strength of the film placed between two test coupons (with no thermal spray coating applied) was found to be approximately 83.35 MPa. The stress/strain curve of the epoxy strength test is illustrated in Figure 3.7.

3.2.3 MTS 810 machine and data acquisition software

Coating adhesion strength tests were carried out on a tensile test machine (model MTS 810, MTS System Corporation, Eden Prairie, Minnesota, USA) Tension test machines apply uni-axial loading in a uniform manner and are
generally universal in their capabilities and applications, rather than specific to one type of test or material.

Glued cylindrical specimens (Figure 3.6) were first mounted in a self-aligning fixture, which was held in tension in the MTS 810 machine, while its load and its strain were respectively measured with a load cell and an axial extensometer. A tension load cell with a maximum capacity of 100 KN was mounted on the machine.

The MTS 810 servo-hydraulic mechanical testing system was operating at room temperature with a crosshead speed of 0.0407 in/min (1.034 mm/min) that was kept constant during all the tests. On this machine, test loads were applied on the specimen through a hydraulic piston, which was attached to a self-aligning fixture through a grip. Figure 3.8 shows the complete self-aligning fixture holding the specimen and mounted on the MTS 810 machine. This fixture is made of an universal cardan, a self-aligning device (Figure 3.8), which is attached to the MTS piston by a heat treated 10 mm pin and a grip with an external thread. The other end of the self-aligning fixture is screwed to the base of the MTS machine. The inside threaded specimen and counter part are screwed to the self-aligning fixture.

Measurement of transient stress and strains in the tensile test was accomplished by using load- and strain-sensing transducers that created an electrical signal proportional to the applied stress and strain. The strain signal and load signal were recorded using an 8-bit data acquisition board (WB 800, Omega Inc, Stamford, CT, USA) in an IBM compatible computer and Labtech, a
computer based data acquisition software package. With this set-up the transient load, strain and the corresponding time during the test could be recorded until the coating or epoxy glue fractured.
Figure 3.5(a): Section side view of the glue fixture
Figure 3.5(b): Front section view of the glue fixture
Figure 3.6: Coated specimen glued with a counter part
Figure 3.7: Tensile strength versus strain of the glue film
Figure 3.8: MTS machine with a self-aligning fixture for the tensile adhesion testing (ASTM Standards C633-79)
3.3  **Particle impact conditions measurement with the DPV 2000- sensing device**

The DPV 2000 is an optical sensing device, developed by Tecnar Ltée, Montreal, Quebec, which allows on-line monitoring of individual particles in a thermal spray. The system is able to simultaneously monitor temperature, velocity and diameter of individual particles /50/. It consists of a sensing head and an optical cable connected to a central cabinet. There are three modules in the cabinet, namely the control module, the detection module, and the XY scanning unit motion controller (Figure 3.1).

The optical sensor consists of a special multi-element lens /50/. Since the sensor is placed close to the thermal spray plume, a window is installed at the end of the lens for protection. The lens is attached to a bundle of optical fibers. A two-slit photo-mask is inserted between the lens and fibers. This photomask causes radiation from a hot particle in the thermal spray to generate a two-peaked signal when it passes in front of the sensor /50/. The generated signal is collected and transmitted through the optical fiber to the detection module.

The velocity of particles is obtained by dividing the distance between the two slits by the flight time of the particles, measured from the two peaks of the signal. The temperature of particles is measured from two-wavelength pyrometry theory described in detail in Ref. /5/. Temperature is directly proportional to the ratio of signals at two different wavelengths, assuming that heated particles are
gray body emitters /50/. The particle diameter is calculated from the amplitude of the signal, assuming the particles to be spherical.

### 3.4 D.C. Plasma torch

A Miller SG-100 plasma torch from Praxair was used in the experiments. A full description of the plasma torch and its operation may be found in the operator’s manual /51/. A schematic diagram of the torch is shown in Figure 3.9. The operating principle of the torch will be briefly reviewed here.

A D. C. plasma torch includes a copper anode and a tungsten cathode. An inert gas such as argon or nitrogen is usually used as a plasma gas. The gas flows around the cathode and through the anode. A pulse of current creates an arc between the electrodes and removes some of the electrons from the inert gas. The remaining electrons and positive ions accelerate towards the cathode and the anode respectively. During acceleration, these ions collide with each other, neutral atoms and molecules in the gas, dissociating and ionizing the atoms. This cluster of ions and energetic electrons form the plasma /27/.

Collisions between electrons and positive ions convert their energy to heat and raise the temperature of the plasma gas up to 15000 °C. The copper anode and the tungsten cathode are subjected to high heat fluxes which can erode them. In order to cool the electrodes, water circulates through passages in them. A 4 ME heat exchanger from Sulzer Metco was used to provide a steady flow of coolant water.
There is a powder injection port located downstream of the anode nozzle end. Materials such as alloys, ceramics, and polymers are fed into the powder port in the form of powder, with particle size of 10-100 μm in diameter. A Sulzer Metco 60C powder feed unit was used for powder injection and the powders were injected internally and perpendicularly to the plasma flow. The powder is injected into the plasma gas and accelerated towards the substrate surface. Upon impact it cools down rapidly and forms a coating.

Figure 3.9: D.C. Plasma gun from Praxair
3.5. Microstructure analysis with scanning electron microscope and X-ray photoelectron spectrometer

3.5.1. Scanning electron microscope

The microstructure of cross-sections through the coating and substrate was analyzed with a scanning electron microscope (SEM) (model 570, Hitachi, Hitachi Ltd, Tokyo, Japan). A scanning electron microscope contains an electron source which focuses a tiny spot of electrons on the specimen. Scanning the spot across the specimen, it detects the response and transmits it to a display. The Hitachi 570 is a general purpose, 25 kV, diffusion-pumped, tungsten filament-based SEM; its maximum magnification is 300,000 with a resolution of about 4.0 nm.

Samples which are usually less than 2 cm on a side are mounted on a specimen stub with conductive paste or a metal clip. Larger pieces such as 5-10 cm wafers may be loaded with user-supplied holders. The specimen stage is non-eusentric (i.e. the focal point does not change with stage adjustments) and requires that the chamber be brought to atmospheric pressure for loading and unloading. After sample loading and evacuation, a high voltage, typically 4-25 kV, is applied. For SEM analysis, the substrates used in tests were rectangular coupons of 304L stainless steel, 3x4 mm in size and 2 mm thick.
3.5.2. **X-ray photoelectron spectrometer (XPS)**

The composition and the depth profile of the oxide layer generated during the substrate preheating were measured with X-Ray Photoelectron Spectroscopy (XPS) and argon-ion sputtering using PHI 5500 Multi-Technique System (Physical Electronics, Eden Prairie, Minnesota, USA). XPS surface analysis, also known as electron spectroscopy for chemical analysis, is an in-situ chemical technique developed in the past 20 years to determine not only the composition of a thin layer but also its chemical state.

The operation of the XPS is based on the excitation of the specimen by a source of monochromatic x-rays. In response to the excitation, electrons are ejected from the specimen. The energy of the emitted photoelectrons is analyzed by an electron spectrometer and the data presented as a graph of intensity versus electron energy. The energy of the emitted photo-electrons is generally in the range of 0 to 1000 eV /53,54/. The photoelectron energy is dependent on the precise chemical configuration of the surface atoms, and pronounced chemical shifts are reproduced in the position of the peaks in the XPS spectrum. The photoelectron spectrum will reproduce the electronic structure of an element quite accurately as all electrons with a binding energy less than the photon energy will be featured in the spectrum.

For XPS analysis, the substrates used in tests were 304L stainless steel discs 25 mm in diameter and 1.5 mm thick. The first step to be taken in characterizing the surface chemistry of the specimen under investigation is a
survey of the surface to be analyzed. Individual peaks may be identified with the aid of data in tabular or graphical format reproduced in the XPS handbook /55/.

Depth profiling of the oxide layer on surfaces was done by sputtering with an argon ion beam. Fast moving argon ions hit the surface, fracturing chemical bonds and eroding the oxide layer on the sample. Knowing the sputtering rate, the thickness of the oxide layer can be calculated from the time required to completely remove it and expose the bare metal surface. In this experiment, based on the calibration, the depth profile sputtering rate was 4 nm per minute.

3.6. **Surfometer and mercury Intrusion porosimeter**

3.6.1. Surfometer

The roughness of surface was measured with the aid of a Surfometer, (Model PDA-400 ao, Serial: 4470, Precision Devices Inc., Milan, Michigan, USA). It is a complete roughness measurement instrument consisting of an amplifier, piloter, tracer, link arm and precision reference standards. The piloter's purpose is to move the diamond tracer over a set distance in order to collect data on the return stroke and to compute the roughness. For measurements performed in this research, the stroke length and the piloter speed are respectively set up to 1.27 mm and 2.54 mm/sec. The complete roughness profile is saved in memory after a single stroke. The surfometer, model 400, measures the average
roughness ($R_a$), which is the arithmetic average of absolute values of the profile heights over the evaluation length /56/.

3.6.2 Mercury porosimeter

The porosity of nickel coatings was measured with a high pressure, mercury-intrusion porosimeter (Autopore 3, Model 9400 CE, Serial 782, Micromeritics Instruments Corporation, Norcross, Georgia, USA). Mercury is used to fill the pores of the coating. However, mercury has an exceptionally high interfacial tension so that it wets only a few materials and will not penetrate pores by capillary action. It has to be forced into the pores and high pressures are necessary to fill very small pores. The Autopore 3 has the capacity to fill pores with diameters in the range of 360 to 0.005 μm with a maximum pressure of 227.5 MPa /57,58/.

The procedure to measure the porosity is as follows: coatings are placed in a low pressure chamber, which is first evacuated and then inundated with mercury. High pressure is applied hydraulically to the mercury, and its penetration into pores can be tracked by a change in electrical capacitance of the coaxial capacitor created by the mercury within the capillary tube and the conductive cladding on its outside surface. Assuming that pores are cylindrical, pore diameters and volumes are calculated from this information. The mercury porosimeter presents results as total pore volume, pore area, and median and average pore diameters.
CHAPTER 4

Test procedure

4.1 Coating powder

The coating powder used was pure nickel powder (type 12313, Westaim Corporation, Edmonton, Canada), which was sieved to a particle size distribution of -75+63 μm. As shown in Figure 4.1, the particles were spherical in shape.

Figure 4.1: Nickel powder particle
4.2 Substrate temperatures

Tests were done at the following substrate temperatures:

1. Room Temperature (25 °C)
2. 150 °C
3. 250 °C
4. 350 °C
5. 450 °C
6. 550 °C
7. 650 °C
8. Room temperature (25 °C) after the substrate was preheated at 650°C, held at that temperature for 2 minutes and allowed to cool to room temperature.
9. 650 °C and Room temperature as in 8, but with different substrate roughness ($R_a = 0.3-0.8 \, \mu m$).

Six specimens were coated at each value of the substrate temperature and the coating adhesions strength measured for each test sample.

4.3 Torch operating parameters

The specimens were coated with an atmospheric d.c plasma spray gun operated at a power of 19.8 kW. Argon was used as plasma gas, shrouding gas and particle carrier gas. The torch operating parameters are summarized in Table 4.1.
<table>
<thead>
<tr>
<th>Arc current</th>
<th>600 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>30 V</td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>60 g/min</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>3 l/min</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>16 g/min</td>
</tr>
</tbody>
</table>

Table 4.1: Plasma gun operating parameters

4.4 Particle impact conditions

Particles impact conditions were monitored with the DPV 2000 system. Measurements of particle velocity, temperature and size were taken every five seconds. The DPV 2000 system was focused on a point 45 mm from the specimen and 55 mm from the plasma gun. Measurements were taken along the centerline of the spray plume. A typical output from the DPV-2000 is illustrated in Figure 4.2.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1570 °C</td>
<td>220 °C</td>
</tr>
<tr>
<td>Velocity</td>
<td>62 m/s</td>
<td>9 m/s</td>
</tr>
<tr>
<td>Size</td>
<td>73 μm</td>
<td>18 μm</td>
</tr>
</tbody>
</table>

Table 4.2: Particles impact conditions
Figure 4.2: Typical output of DPV 2000
4.5 **Experimental procedure**

In this study, three different kinds of experiments were conducted: first, the adhesion testing, then the SEM micro section structure analysis and finally the XPS analysis of the oxide scale.

To prepare specimens for the tensile test, they were first cleaned with alcohol and then grit blasted for 3 minutes with alumina particles, (Metcolite F (A), Sulzer Metco, Westbury, New York, USA) at a pressure of 414 KPa with the nozzle at a distance of 10 mm from the sample, producing an average surface roughness of 2 to 5 μm. Substrate conditions significantly affect the bond strength of thermal spray coatings. Dry grit blasting makes the surface of the substrate rougher and cleaner and increases adhesion strength. To remove dust from grit blasting, the specimens were blown with dry compressed air.

Specimens were inserted in the block heater, heated to the desired substrate temperature, and sprayed with the plasma gun keeping particle impact conditions (measured with the DPV 2000) within the range shown in Table 4.2. Spraying was done with a powder feed rate of 16 g/min until the coating thickness was about 0.3-0.4 mm. The powder was injected perpendicular to the plasma jet axis through a 1.8 mm I.D. injector located 3 mm upstream of the torch nozzle exit. It took approximately 2 minutes to coat the surface. After the spraying was complete, the test coupons were removed from the copper block heater and cooled with natural convection to room temperature. At room
temperature, the roughness of the coated substrate was measured with the surfometer and found to be about 7 to 10 \( \mu \text{m} \).

Sheets of FM 1000 adhesive film were cut into 27 mm diameter disks and inserted between the coating and the counter part specimen. The coated specimen, the sandwiched adhesive sheet and the counter part were mounted in a gluing fixture (Fig 3.5) which held them at an inclination of 80 degrees from the horizontal, then put into a oven for 2.5 hours to cure the glue. After 2.5 hours in the oven at 200 °C, the bonded specimens were taken out from the oven and cooled to room temperature with natural convection.

For the scanning electron microscopy (SEM) microstructure analysis of coating and substrate, rectangular specimens (3mmx4mm and 2mm thick) were prepared by the following method. The stainless steel specimens (type 304L) were first cleaned, grit blasted, blown with compressed air, and sprayed with a thin nickel coating. The substrate temperature was measured with a J-thermocouple attached at the center on the back of the substrate. The sprayed samples were cut for SEM observations. To avoid breaking of coating during cutting and to provide protection during grinding and polishing, the coated specimens were vacuum impregnated with epoxy. The specimens were placed in a vacuum impregnation system and the chamber was evacuated with aid of a pump to 660 mm Hg (26 inches Hg) for 5-10 minutes in order to fill the pores of coating with the liquid epoxy. Then, they were cut with a diamond-cutting wheel (Accutom-2 cutting machine, Struers Company, Rodovre, Denmark) at a speed of 2800 rpm. The specimen was first planar ground with a fixed 45 \( \mu \text{m} \) diamond
grinding disc turning at 300 rpm, then polished with a semi-fixed polycrystalline (PC) diamond suspension (9 μm) on a hard polyester cloth at 200 rpm. Fine scratches left by the ultra fine abrasive paper and semi-fixed polycrystalline diamond were removed by using a Texmet 1000 cloth charged with 3 μm polycrystalline diamond suspension. In the final polishing stage, very fine abrasives (sub-micron) were used to produce at 120 rpm a very clean and undistorted microstructure without causing relief or edge rounding. The specimens were then examined using an SEM.

For the XPS analysis of oxide layer, the specimens were 25 mm diameter disc shaped and 1.5 mm thick. Surface preparation was the same as in the previous experiments; only instead of spraying the samples, they were only preheated to different set substrate temperatures, held for 2 minutes at that temperature, then cooled to room temperature. The composition and the thickness of the oxide layer formed during heating were measured using the XPS and the argon ion sputtering system.
CHAPTER 5

Results and discussion

5.1 Adhesion strength

Coated specimens were glued using epoxy to a matching test coupon, placed in a tensile-testing machine, and pulled until the two parts separated. Only coating applied on specimens (Ra = 0.3-0.8 µm) sprayed at 650°C and room temperature after substrate preheating at 650°C (Chapter 4.2, substrate temperature 9) could not adhere to the substrate and so, the adhesion strength could not be measured.

Failure occurred generally at the substrate coating interface, as illustrated in Figure 5.1(a). Figure 5.1(b) shows the corresponding tensile stress-strain curve. The failure of the coatings was brittle, as seen from the linear relation between the stress and strain. However, sometimes the fracture did not occur only at the substrate/coating interface. A small portion of the glue/coating interface also failed as shown in Figure 5.2(a). In such a case the stress-strain curve is not fully linear but shows some ductile behavior (Figure 5.2(b)). Finally, in a few cases, there was cohesive fracture (Figure 5.3(a)), where a small portion of the coating itself failed. In these cases the stress-strain curve also showed some non-linear behavior (Figure 5.3(b)).
The maximum stress measured in all these cases was recorded as the adhesive/cohesive strength of the coatings. Figure 5.4 shows the variation of coating strength with substrate temperature. Each point in the graph represents a different specimen. Fracture modes of specimens are detailed in Appendix C. The coating strength is seen to increase with substrate temperature. The tensile strength increase is small from room temperature to a substrate temperature of 250 °C ranging from an average of 10.13 MPa at room temperature to 17.15 MPa at 250 °C; then after 250 °C, the tensile strength increases significantly from 30.44 MPa at 350 °C to 73.60 MPa at 650 °C.

Heating the substrate can have the following effects:

a) Reduce the cooling rate of particles impinging on the surface, giving them more time to flow into the surface roughness and form stronger bonds.

b) Form an oxide layer on the surface. This will increase the contact resistance between the droplet and substrate, thereby reducing the droplet solidification rate. The oxide layer can also change the wettability of the surface.

c) Evaporate moisture and other volatile contaminants on the surface, allowing better contact between impacting particles and the substrate.

The increase in adhesion strength when the substrate temperature was raised above 300 °C corresponded to the change in splat morphology previously seen when nickel particles were sprayed on a stainless steel surface /6,7/. Particles deposited on a surface below 300 °C were irregular in shape, whereas those deposited on a hotter surface were disk shaped. Disk splats provided
better contact with the substrate and therefore greater adhesion strength. Computer simulations /9/ showed that the most important reason for the change in splat shape was the increase in thermal contact resistance and the reduced rate of solidification because of the oxide layer.

To separate the effects of the oxide layer and substrate temperature, a set of specimens were preheated to 650 °C, held for two minutes at 650 °C, then cooled down. The temperature variation during heating and cooling are shown in Figure 5.5 and 5.6 respectively. After they had cooled, the specimens were coated and the adhesion strength of the coating measured. The tensile strength of the coatings on preheated and cooled specimens is shown in figure 5.7, where it is compared with that of specimens that were sprayed without preheating and therefore had no oxide layer. Heating the specimens produced no measurable change in surface roughness, though it did create an oxide layer. It can be seen that the oxidized surfaces had an average adhesion strength of 13.53 MPa, which was 24 % higher that of the non-oxidized surfaces (average 10.13 MPa). Therefore, the large increase in adhesion strength with surface temperature does not seem to be due to the increased thermal contact resistance alone.

Oxidation of the surface depends on the heating time. Table 5.1 shows the time taken to heat the surface to each of the temperatures used in experiments, and the corresponding heating rate. The average heating rate was 0.36 °C/sec, which was much lower than the heating rate of 2 to 5 °C/sec used by Fauchais et al /39/ for experiments done in the same temperature range. However, in spite
of the slower heating, and possibly greater oxidation, the adhesion strength continued to increase with temperature.

![Figure 5.1(a)](image1)

Figure 5.1(a): Fracture surface of specimen preheated to 650 °C at the coating/substrate interface

![Figure 5.1(b)](image2)

Figure 5.1(b): Tensile strength/strain curve of coating/substrate fracture with substrate sprayed at 650 °C
Figure 5.2(a): Fracture surface of specimen preheated to 250 °C at the coating/substrate interface

Figure 5.2 (b): Tensile strength/strain curve of coating/substrate fracture with substrate sprayed at 250 °C
Figure 5.3(a): Fracture surface of specimen preheated to 25 °C at the coating/substrate interface

Figure 5.3 (b): Tensile strength/strain curve of coating/substrate fracture with substrate sprayed at 25 °C
Figure 5.4: Tensile strength of preheated substrates
Figure 5.5: Specimen (304L) preheating curve to 650 °C

Figure 5.6: Specimen (304L) cooling from 650 °C to 25 °C by natural convection
Table 5.1: Preheating time of specimens at different temperatures

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>Preheating time (min)</th>
<th>Heating rate (°C/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C</td>
<td>8</td>
<td>0.31</td>
</tr>
<tr>
<td>250 °C</td>
<td>14</td>
<td>0.29</td>
</tr>
<tr>
<td>350 °C</td>
<td>18</td>
<td>0.32</td>
</tr>
<tr>
<td>450 °C</td>
<td>20</td>
<td>0.38</td>
</tr>
<tr>
<td>550 °C</td>
<td>22</td>
<td>0.42</td>
</tr>
<tr>
<td>650 °C</td>
<td>25</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 5.7: Effect of the oxidation on the adhesion

Heated up to 650 °C and cooled down to 25 °C, Cycle time: 25 min.  
Non oxidized substrates at 25 °C
5.2 **Porosity of the coating**

The porosity of the coating measured using the mercury porosimeter at room temperature, 250 °C, 450 °C and at 650 °C is presented in the figure 5.8. The porosity of the coating decreased with the increase of substrate temperature, diminishing from 16.4 % at room temperature to 13.6 % at 650 °C. This tendency has previously been observed by other researchers /10,11,24/. Microstructure analysis using a scanning electron microscope (SEM) confirmed this reduction in porosity. Figure 5.9 shows SEM images cross-sections through the coating and substrate for coatings made on substrates at a) 25 °C, b) 350 °C, c) 450 °C and d) 650°C. From the images, it can be seen that the coating on a substrate at 25 °C has the greatest porosity. There also appears to be a visible gap at the coating-substrate interface, which is not seen at the higher temperatures.

![Figure 5.8: Porosity of the coating on preheated substrate](image_url)
Figure 5.9: Microstructures of coating/substrate interface
5.3 Oxide layer thickness and composition

As described in chapter 4.1, the specimens used in this project are made of stainless steel, type 304L, containing mainly iron, chromium and nickel. Heating the surfaces produced a visible change in their colour because of oxidation. Analysis of heated specimens showed that the oxide layer on their surface consisted of two distinct layers. As illustrated in Figure 5.9 uppermost was a layer of iron oxide, consisting mostly of hematite, (Fe$_2$O$_3$). Below this was a chromium oxide layer (Cr$_2$O$_3$). The oxidation of pure iron involves the formation of a scale composed of three oxides: wustite (FeO), which oxidizes to magnetite (Fe$_3$O$_4$), which finally oxidizes to the most stable state, hematite (Fe$_2$O$_3$). Chromium undergoes internal oxidation and therefore chromium oxide (Cr$_2$O$_3$) was observed between the steel substrate and the hematite layer.

The thickness of the oxide layer increased with the substrate preheating temperature. Figure 5-11 shows the thickness of the oxide layer measured by argon ion sputtering for specimens sprayed at 150 °C, 350 °C and 650 °C. The corresponding oxide layer thickness was respectively 60 nm, 180 and 288 nm.
Figure 5.10: Oxide composition on a Stainless steel substrate 304L

Figure 5.11: Thickness of oxide layers at different substrate temperatures
Chapter 6

Conclusions and recommendations

6.1. Conclusions

A system has been built to preheat cylindrical test specimens to a required temperature and to coat their ends using a D.C. plasma torch. Particle impact conditions (temperature, velocity, and size) were monitored using a DPV 2000 system and held constant during spraying. Substrate temperature was varied from 25 °C to 650 °C. The adhesion strength of the coatings was measured using a standard ASTM C 633-79 test.

The adhesion strength of the coating increased from 10 MPa to 75 MPa when substrate temperature was raised from 25 °C to 650 °C. Heating a substrate to 650 °C, cooling it to 25 °C, and then spraying it produced a 24% increase in adhesion strength. For specimen with a roughness of 0.3-0.8μm, there was no adhesion of the coating to the substrate. Heating the substrate removes moisture and other volatile contaminants, slows the solidification rate of impinging particles allowing them to make better contact with the substrate, and produces an oxide layer on the surface which can change its thermal contact
resistance and wettability. All of these effects may be significant in the experiments.

Increasing substrate temperature reduced the porosity of the coating as measured by a mercury intrusion porosimeter. Coating cross-sections examined under an SEM also showed a reduction in porosity.

The oxide layer generated by specimen heating was analyzed using XPS and argon ion sputtering method. The results showed the presence of a dual oxide layer made of a thicker chromium oxide (Cr₂O₃) on the steel substrate followed by a thinner hematite (Fe₂O₃) layer. The oxide layer thickness increased with substrate temperature.

6.2. Recommendations

Substrate preheating as a means of improving coating quality is not widely used in industry and deserves further investigation. It has generally been assumed that preheating will produce an oxide layer on the substrate, resulting in poor adhesion of the coating. However, the results of this project show that this is not always the case: preheating may actually increase adhesion strength.

The reasons for the increase in adhesion strength are not absolutely clear. It is likely that they are related to the change in splat morphology that has been observed on a heated substrate, where splashing is seen on a cold surface and disk splats are formed on a hot surface. Further work is therefore needed to understand the effect that the oxide layer has on thermal contact resistance and wettability of the surface, and how this affects coating build-up.
References


Appendix A

Energy spectrum of Chromium

XPS and Ion Sputtering curves
Energy spectrum of Iron

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>2p\textsubscript{3/2} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>708</td>
</tr>
<tr>
<td>FeS</td>
<td>706</td>
</tr>
<tr>
<td>Fe\textsubscript{2}S (marcasite, pyr)</td>
<td>707</td>
</tr>
<tr>
<td>FeCl\textsubscript{3}</td>
<td>708</td>
</tr>
<tr>
<td>FeCl\textsubscript{2}</td>
<td>709</td>
</tr>
<tr>
<td>FeO</td>
<td>709</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>710</td>
</tr>
<tr>
<td>Fe(CO\textsubscript{2})</td>
<td>711</td>
</tr>
<tr>
<td>FeSO\textsubscript{4}</td>
<td>712</td>
</tr>
<tr>
<td>K\textsubscript{2}Fe(CN)\textsubscript{6}</td>
<td>713</td>
</tr>
<tr>
<td>KFe(CN)\textsubscript{6}</td>
<td>714</td>
</tr>
</tbody>
</table>

\[ 2p_{3/2} = 710.9 \text{ eV} \]
\[ \Delta = 136 \text{ eV} \]
Iron oxide scale analysis at 350 °C

[Graph showing iron oxide scale analysis with peaks labeled Fe and Fe$_2$O$_3$.]
A.4 Sputtering of substrate (Substrate temp. 150 °C) for Iron
A.5 Sputtering of substrate (Substrate temp. 350 °C) for Iron
Sputtering of substrate (Substrate temp. 150 °C) for Chromium
Sputtering of substrate (Substrate temp. 350°C) for Chromium
A.9 Sputtering of substrate (Substrate temp. 650 °C) for Chromium
APPENDIX B

Porosity result data from the mercury intrusion porosimetry
Sample: NIROOM
Operator: Mundel
Submitter: File: C:\WIN9420\DATA\NIROOM.SMP

LP Analysis Time: 24/10/00 14:19:15  Sample Weight: 5.2135 g
HP Analysis Time: 24/10/00 15:02:37  Correction Type: None
Report Time: 25/10/00 11:14:47  Show Neg. Int: No

Summary Report

Penetrometer: 0860-(13) 3 Bulb, 0.412 Stem, Solid

Pen. Constant: 10.790 µL/pF  Adv. Contact Angle: 130.000 degrees
Pen. Weight: 61.8973 g  Rec. Contact Angle: 130.000 degrees
Stem Volume: 0.4120 mL  Hg Surface Tension: 485.000 dynes/cm
Max. Head Pressure: 4.6800 psia  Hg Density: 13.5335 g/mL
Pen. Volume: 3.5207 mL  Sample Weight: 5.2135 g
Assembly Weight: 104.7467 g

Low Pressure:
Evacuation Pressure: 50.000 µmHg
Evacuation Time: 5 mins
Mercury Filling Pressure: 0.61 psia
Equilibration Time: 5 secs
Maximum Intrusion Volume: 100.000 mL/g

High Pressure:
Equilibration Time: 5 secs
Maximum Intrusion Volume: 100.000 mL/g

No Blank Correction

Intrusion Data Summary

Total Intrusion Volume = 0.0233 mL/g
Total Pore Area = 0.205 m²/g
Median Pore Diameter (Volume) = 2.7217 µm
Median Pore Diameter (Area) = 0.0523 µm
Average Pore Diameter (4V/A) = 0.4536 µm
Bulk Density = 7.0476 g/mL
Apparent (skeletal) Density = 8.4315 g/mL
Porosity = 16.4137 %
Stem Volume Used = 29 %

B.1 Porosity measurement data (substrate temp. 25 °C)
Sample: NI250  
Operator: Mundel  
Submitter:  
File: C:\WIN9420\DATA\NI250.SMP  
LP Analysis Time: 15/09/00 16:38:37  
Sample Weight: 2.8065 g  
HF Analysis Time: 15/09/00 17:51:12  
Correction Type: None  
Report Time: 25/10/00 11:07:04  
Show Neg. Int: No

Summary Report

Penetrometer: #s/n - 9-99 3 Bulb, 0.412 Stem, Solid
Pen. Constant: 10.790 μL/pF  Adv. Contact Angle: 130.000 degrees
Pen. Weight: 61.7466 g  Rec. Contact Angle: 130.000 degrees
Stem Volume: 0.4120 mL  Hg Surface Tension: 485.000 dynes/cm
Max. Head Pressure: 4.6800 psia  Hg Density: 13.5335 g/mL
Pen. Volume: 3.5207 mL  Sample Weight: 2.8065 g
Assembly Weight: 106.6925 g

Low Pressure:
Evacuation Pressure: 50.000 μmHg
Evacuation Time: 5 mins
Mercury Filling Pressure: 0.64 psia
Equilibration Time: 10 secs
Maximum Intrusion Volume: 100.000 mL/g

High Pressure:
Equilibration Time: 10 secs
Maximum Intrusion Volume: 100.000 mL/g

No Blank Correction

Intrusion Data Summary

Total Intrusion Volume = 0.0184 mL/g
Total Pore Area = 0.443 m²/g
Median Pore Diameter (Volume) = 5.2633 μm
Median Pore Diameter (Area) = 0.0106 μm
Average Pore Diameter (4V/A) = 0.1665 μm
Bulk Density = 6.8958 g/mL
Apparent (skeletal) Density = 7.8990 g/mL
Porosity = 12.7012 %
Stem Volume Used = 13 % ****

B.2 Porosity measurement data (substrate temp. 250 °C)

87
Sample: NI450
Operator: Mundel
Submitter:
File: C:\WIN9420\DATA\NI450.SMP

LP Analysis Time: 16/09/00 14:52:35
Sample Weight: 2.724 g

HP Analysis Time: 20/09/00 15:33:08
Correction Type: None

Report Time: 25/10/00 11:01:46
Show Neg. Int: No

Summary Report

Penetrometer: #s/n - 9-99 3 Bulb, 0.412 Stem, Solid
Pen. Constant: 10.790 μL/pF  Adv. Contact Angle: 130.000 degrees
Pen. Weight: 61.7466 g  Rec. Contact Angle: 130.000 degrees
Stem Volume: 0.4120 mL  Hg Surface Tension: 485.000 dynes/cm
Max. Head Pressure: 4.6800 psia  Hg Density: 13.5335 g/mL
Pen. Volume: 3.5207 mL  Sample Weight: 2.7240 g

Low Pressure:
Evacuation Pressure: 50.000 μmHg
Evacuation Time: 5 mins
Mercury Filling Pressure: 0.54 psia
Equilibration Time: 5 secs
Maximum Intrusion Volume: 100.000 mL/g

High Pressure:
Equilibration Time: 5 secs
Maximum Intrusion Volume: 100.000 mL/g

No Blank Correction

Intrusion Data Summary

Total Intrusion Volume = 0.0179 mL/g
Total Pore Area = 0.337 m²/g
Median Pore Diameter (Volume) = 2.7032 μm
Median Pore Diameter (Area) = 0.0123 μm
Average Pore Diameter (4V/A) = 0.2124 μm
Bulk Density = 7.9833 g/mL
Apparent (skeletal) Density = 9.3116 g/mL
Porosity = 14.2645 %
Stem Volume Used = 12 %

B.3 Porosity measurement data (substrate temp. 450 °C)
Sample: NI650  
Operator: Mundel  
Submitter:  
File: C:\WIN9420\DATA\NI650.SMP

<table>
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<tr>
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<th>Sample Weight</th>
<th>Correction Type</th>
<th>Show Neg. Int.</th>
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<td>HP Analysis</td>
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<td>Report Time</td>
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Summary Report

Penetrometer: #s/n - 9-99 3 Bulb, 0.412 Stem, Solid

- Pen. Constant: 10.790 μL/pF  
- Pen. Weight: 61.7466 g  
- Stem Volume: 0.4120 mL  
- Max. Head Pressure: 4.6800 psia  
- Pen. Volume: 3.5207 mL

Low Pressure:
- Evacuation Pressure: 50.000 μmHg  
- Evacuation Time: 3 mins  
- Mercury Filling Pressure: 0.60 psia  
- Equilibration Time: 5 secs  
- Maximum Intrusion Volume: 100.000 mL/g

High Pressure:
- Equilibration Time: 5 secs  
- Maximum Intrusion Volume: 100.000 mL/g

No Blank Correction

Intrusion Data Summary

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<tr>
<th>Parameter</th>
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<tr>
<td>Total Intrusion Volume</td>
<td>0.0183 mL/g</td>
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<tr>
<td>Total Pore Area</td>
<td>0.275 m²/g</td>
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<tr>
<td>Median Pore Diameter (Volume)</td>
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<tr>
<td>Median Pore Diameter (Area)</td>
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<tr>
<td>Average Pore Diameter (4V/A)</td>
<td>0.2664 μm</td>
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<tr>
<td>Bulk Density</td>
<td>7.4208 g/mL</td>
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<td>Apparent (skeletal) Density</td>
<td>8.5904 g/mL</td>
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<td>Porosity</td>
<td>13.6147 %</td>
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<tr>
<td>Stem Volume Used</td>
<td>15 % **</td>
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B.4 Porosity measurement data (substrate temp. 650 °C)
APPENDIX C

Fracture modes of specimens

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>Fracture mode</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>70 % adhesive</td>
<td>9.73</td>
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<tr>
<td></td>
<td>30 % cohesive</td>
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<tr>
<td>21</td>
<td>90 % adhesive</td>
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<td></td>
<td>10 % cohesive</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>90 % adhesive</td>
<td>10.7</td>
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<tr>
<td></td>
<td>10 % cohesive</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>60% adhesive</td>
<td>12.1</td>
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<tr>
<td></td>
<td>40 % cohesive</td>
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</tr>
<tr>
<td>24</td>
<td>100 % adhesive</td>
<td>10.4</td>
</tr>
<tr>
<td>25</td>
<td>90 % adhesive</td>
<td>7.38</td>
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<tr>
<td></td>
<td>10 % coating/glue</td>
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<table>
<thead>
<tr>
<th>Specimen #</th>
<th>Fracture mode</th>
<th>Tensile strength (MPa)</th>
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<tbody>
<tr>
<td>33</td>
<td>90 % adhesive</td>
<td>18.6</td>
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<tr>
<td></td>
<td>10 % coating/glue</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>90 % adhesive</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>10 % cohesive</td>
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</tr>
<tr>
<td>35</td>
<td>100 % adhesive</td>
<td>13.7</td>
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<tr>
<td>36</td>
<td>100 % adhesive</td>
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<td>19</td>
<td>100 % adhesive</td>
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<td>37</td>
<td>100 % adhesive</td>
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<td>Substrate temp. 250 °C, Exp.3</td>
<td>Fracture mode</td>
<td>Tensile strength (MPa)</td>
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<tr>
<td>Specimen #</td>
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<tr>
<td>1</td>
<td>95% adhesive 5 % coating/glue</td>
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<td>2</td>
<td>90% adhesive 10 % coating/glue</td>
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<td>3</td>
<td>90% adhesive 10 % coating/glue</td>
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<td>4</td>
<td>100% adhesive</td>
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<td>5</td>
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<td>6</td>
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<table>
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<td>Specimen #</td>
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<tr>
<td>7</td>
<td>100% adhesive</td>
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<td>12</td>
<td>90% adhesive 10 % coating/glue</td>
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<table>
<thead>
<tr>
<th>Substrate temp. 450 °C, Exp.3</th>
<th>Fracture mode</th>
<th>Tensile strength (MPa)</th>
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</thead>
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<td>Specimen #</td>
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<tr>
<td>13</td>
<td>100% adhesive</td>
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<td>15</td>
<td>95% adhesive 5 % coating/glue</td>
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<td>95% adhesive 5 % coating/glue</td>
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<tr>
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<td>100% adhesive</td>
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<td>95% adhesive 5 % coating/glue</td>
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<td>Specimen #</td>
<td>Fracture mode</td>
<td>Tensile strength (MPa)</td>
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<td>Oxidized substrates, sprayed at 25°C, Exp.5</td>
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