

The effect of particle impact temperature on the deposit efficiency and cutting wear rate of 88/12 WC/Ni coatings sprayed with the TOP GUN HVOF thermal spray system

by

Hendrik Oliver Lambrecht

An 18 point research project submitted to the faculty of Engineering, University of the Witwatersrand, Johannesburg, in the partial fulfilment of the requirement for the degree of Masters of Science in Engineering

Johannesburg, April 1997

Declaration

I declare that this dissertation is my own unaided work, except where due reference is made to others. This dissertation is being submitted for the degree of Masters of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination at any other University.



Hendrik Oliver Lambrecht

21 April 1997

Acknowledgements

I would like to thank United Thermal Technologies (Pty) Ltd. for offering their spray and laboratory facilities.

I would like to thank and acknowledge my supervisor, Mr M.W. Seitz whose support made this dissertation possible.

I would like to thank my wife, L. McLelland, for her moral support.

Abstract

A relatively new thermal spray system, the TOP GUN High Velocity Oxy Fuel (HVOF) system, has been developed which is able to deposit coatings of high quality. The supplier's parameters, however, do not always obtain the quality that the system is supposed to achieve. This has led into an investigation of the effect of spray parameters on the quality and properties of the coating.

The investigation assesses that the coating quality and properties are influenced by the coating particle impact temperature. The gun parameters which affect the particle impact temperature are spray distance, volume flow rate, oxygen fuel ratio and the combustion chamber size. Samples sets with varying spray distances were sprayed with 88/12 tungsten carbide / nickel (WC/Ni) powder onto 15 mm diameter copper tubing. In each set one of the gun parameters which affect the particle impact temperature was changed. The samples were then analysed with respect to deposit efficiency, wear resistance, hardness and microstructure.

The results show that the deposit efficiency is directly proportional to the wear resistance. The hardness as well as the porosity level of the coating are not related to the wear resistance of the coating.

It appears that the deposit efficiency and wear resistance of a coating is related to the bonding of the coating particles to one another. If the coating particle remains bonded during the wear process the material loss is limited to the wear of the WC in the coating particles. If the coating particle is disbonded during the wear process the material loss is directly proportional to the bond strength of the particles.

The mechanisms which affect the wear resistance of a coating are not the same as those which affect the hardness. The hardness trends are thus not related to the wear resistance trends. Since the coating consists of a composite of WC and Ni it is the concentration of the WC which determines the hardness of the coating. If the Ni content in a coating particle becomes liquid due to overheating, it will flatten severely on impact allowing some of the WC to be repelled and be lost to the coating. This loss in WC results in a reduction of hardness.

Table of Contents

DECLARATION	I
ACKNOWLEDGEMENTS.....	II
ABSTRACT	III
1. INTRODUCTION.....	1
2. LITERATURE SURVEY.....	3
2.1. The Thermal Spray Process	3
2.2. Coating Quality	5
2.2.1. Porosity	5
2.2.2. Bond Strength.....	6
2.2.3. Homogeneity.....	7
2.3. Thermal Spray Systems	8
2.3.1. The Flame Spray System	8
2.3.2. The Arc Spray System	9
2.3.3. Plasma Spray System	10
2.3.4. The Detonation System.....	12
2.3.5. The HVOF System.....	13
2.3.6. TOP GUN HVOF System	13
2.4. TOP GUN Parameters which affect coating quality.....	14
2.4.1. Parameters which affect the particle temperature.....	15
2.5. The effect of grain size distribution on particle temperature and velocity	18
2.6. Mechanisms of wear.....	18
3. EXPERIMENTAL.....	19
3.1. Spraying.....	19
3.1.1. Gun Parameter Settings and Limits	20
3.2. Measuring	21
3.3. Abrasion Resistance	21
3.4. Metallographic Preparation and Examination	22
3.5. Data Manipulation.....	22
3.5. Statistical Evaluation.....	24
4. RESULTS AND DISCUSSION.....	26
4.1. The influence of spray distance on the particle temperature and deposit efficiency	26
4.2. The influence of spray distance on the cutting abrasion resistance of the coating.....	29
4.3. Comparison between the wear resistance and deposit efficiency data.....	33
4.4. The effect of particle impact temperature on porosity	33
4.5. The effect of particle impact temperature on hardness	35
4.6. The effect of combustion temperature on the coating properties.....	39
4.7. The effect of combustion chamber size on the coating properties	42
4.8. The effect of volume gas flow rate on the deposit efficiency	45
5. SUMMARY OF CONCLUSION	48
6. REFERENCES	50
7. APPENDIX A - SAMPLE CALCULATION FOR STATISTICAL EVALUATION.....	I
8. APPENDIX B - SUMMARY TABLES OF STATISTICAL CALCULATIONS.....	IV

Table of Figures

Figure 2.1-Schematic presentation of the formation of a thermally sprayed coating ¹	3
Figure 2.2-Schematic model of the flattening of a particle on impact onto the substrate ³	4
Figure 2.3-Schematic representation of the flame spray system ¹	8
Figure 2.4-Schematic representation of the arc spray system ¹	9
Figure 2.5-Schematic drawing of the plasma spray system ¹	11
Figure 2.6-Schematic model of the detonation spray system ³	12
Figure 2.7-Schematic representation of the HVOF spray system ³	13
Figure 2.8-Variation of theoretical flame temperature with oxygen-fuel ratio ³	15
Figure 2.9-Effect of barrel length on exit particle temperature ³	16
Figure 2.10-Variation of theoretical flame and particle temperature with barrel length and spray distance ³	17
Figure 4.1 - The schematic trend of flame temperature and velocity on the particle temperature and velocity.....	26
Figure 4.2 -The effect of deposit efficiency against spray distance sprayed with the following parameters, propane with a 19 mm nozzle, propane with a 12 mm nozzle, ethylene with a 19 mm nozzle and ethylene with a 12 mm nozzle.....	27
Figure 4.3 -The effect of spray distance on the wear rate of coatings sprayed with the following parameters: propane with a 19 mm nozzle, propane with a 12 mm nozzle, ethylene with a 19 mm nozzle and ethylene with a 12 mm nozzle.....	30
Figure 4.4 -Schematic representation of the wear mechanisms experienced in thermally sprayed coatings.	32
Figure 4.5 -Micrograph of coating sprayed at 200 mm spray distance.....	34
Figure 4.6 -Micrograph of coating sprayed at 300 mm spray distance.....	34
Figure 4.7 -Micrograph of coating sprayed at 400 mm spray distance.....	34
Figure 4.8 -Micrograph of coating sprayed at 500 mm spray distance.....	34
Figure 4.9 -Micrograph of coating sprayed at 600 mm spray distance.....	34
Figure 4.10 -Micrograph of coating sprayed at 700 mm spray distance.	34
Figure 4.11 -The effect of spray distance on coating hardness with change in the following parameters: propane with 19 mm nozzle, propane with 12 mm nozzle, ethylene with 19 mm nozzle and ethylene with 12 mm nozzle.	37
Figure 4.12 -The effect of propane and ethylene on the deposit efficiency and wear resistance using the 19 mm combustion chamber.	40
Figure 4.13 -The effect of propane and ethylene on the coating deposit efficiency and wear resistance using the 12 mm combustion chamber.	41
Figure 4.14 -The effect of the 19mm Nozzle and the 12 mm Nozzle on the coating deposit efficiency and wear resistance using propane fuel gas.....	43
Figure 4.15 -The effect of the 19 mm nozzle and the 12 mm nozzle on the coating deposit efficiency and wear resistance using ethylene fuel gas.	44
Figure 4.16 -The effect of stoichiometric volume gas flow on the deposit efficiency.	46
Figure 4.17 -The effect of stoichiometric volume gas flow on the peak deposit efficiency as obtained from Figure 4.16.	47

1. Introduction

Thermal spray techniques have been used for more than eight decades¹. During this time, a number of different thermal spray processes have been developed^{2,3}. The improvement of these processes has brought with it the increase in applications and of spray materials¹. Thermally sprayed coatings enhance the protection of components which are exposed to severe environments. Problems relating to abrasion, erosion, corrosion, oxidation and overheating can be solved by applying the correct coating material. Furthermore, thermally sprayed coatings are often used to build up undersized components. Coatings from a wide range of materials are suitable for spraying. These include various metals, ceramics, composites and even some plastics¹.

Thermally sprayed coatings have frequently not been considered for application due to their weak bond strengths of typically 10 MPa and high porosity levels lying between 5 and 10 per cent³. Research has therefore been targeted towards increased bond strengths, reduced porosity and increased coating life³.

A new thermal spray process, known as the high velocity oxygen-fuel (HVOF) process, has been developed in the last decade. This process passes hot combustion gases through a diverging supersonic nozzle to accelerate the coating particles to high velocities of the order of 900 m/s, before they impact onto the component³.

One of these commercially available HVOF systems is known as the TOP GUN HVOF system. This system is capable of producing coatings of a high density of less than 0.1 per cent porosity³. The parameters supplied by the manufacturers of the TOP GUN are, however, often not optimised and are limited to the coating powders which they supply. This has led to an investigation of the variables which affect the coating properties.

During the thermal spray process particles are heated and accelerated through a gas stream to flatten and bond onto a substrate. The manner in which the particles flatten affects the metallographic properties as well as the wear, corrosion and heat resistant properties of the coatings^{1,3}. The flattening of the particles onto the substrate is dependent mainly on the particle

impact velocity and temperature^{1,2,3}. Nakagawa⁴ *et al*, however, have shown that the flattening of a molten impacting particle does not improve significantly above particle impact velocities of 50 m/s when sprayed with the arc spray system. The impact velocities of the coatings sprayed with the TOP GUN system are of the order of 900 m/s³. Changes in particle velocities are thus unlikely to have an effect on the coating properties.

The particle impact temperature is thus the prime parameter to affect the properties of the coating. The particle impact temperature is dependent on the flame temperature and dwell time in the flame^{3,5}. The flame temperature, in turn, is dependent on the fuel type and oxygen-fuel ratio, whilst the dwell time is dependent on the combustion chamber size and spray distance^{4,5}.

This project intends to investigate the effect of spray parameters on the properties of 88/12 WC/Ni coatings sprayed with the TOP GUN thermal spray system. By choosing a range of the above mentioned parameters and analysing the effect of the parameters on the coating properties, a process can be developed which optimises the properties of the coating.

In order to fully optimise the process a full range of tests would have to be run on a matrix basis. Due to limited equipment time and budget only a slice of the parameters could be sprayed for testing. Therefore the emphasis of this dissertation is focused around the trends and qualitative analysis of the trends.

By running through these processes a cheap, quick and easy methodology of evaluating coatings will be established.

2. Literature Survey

2.1. The Thermal Spray Process

Thermal spraying is a coating process whereby molten or semi-molten particles of either metal, carbide, ceramic or plastic are accelerated through a gas stream onto a prepared substrate¹. The coating material is available in either powder or wire form. The thermal spray systems use either electric current or combustion to heat the material to a molten or semi-molten state. The high pressure gases emitted by the thermal spray gun accelerate the particles to the substrate where they impact and flatten to form a coating. As the particles flatten they take on the shape of the substrate and adhere via an interference fit^{1,6,7}. In some cases a certain amount of metallurgical fusion or diffusion may also take place to enhance bonding^{1,6,7}. As the particles continue to impinge onto the substrate the flattened particles bond to one another forming a coating. A schematic representation of the coating process is shown in Figure 2.1.

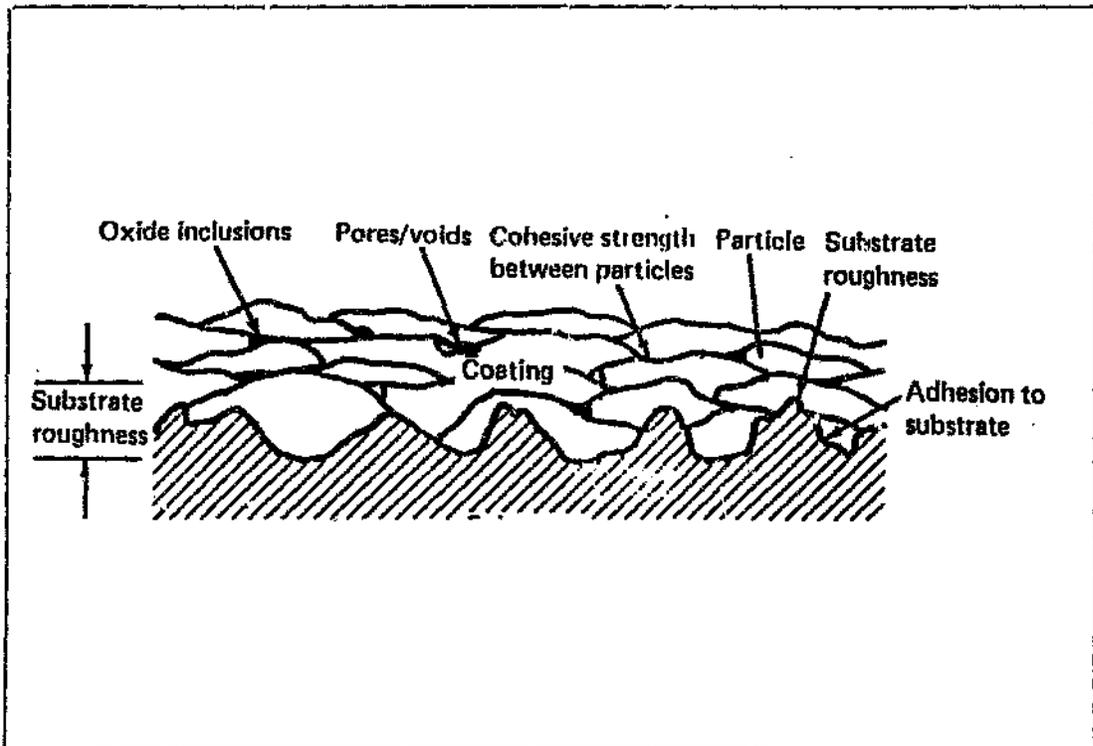


Figure 2.1-Schematic presentation of the formation of a thermally sprayed coating¹.

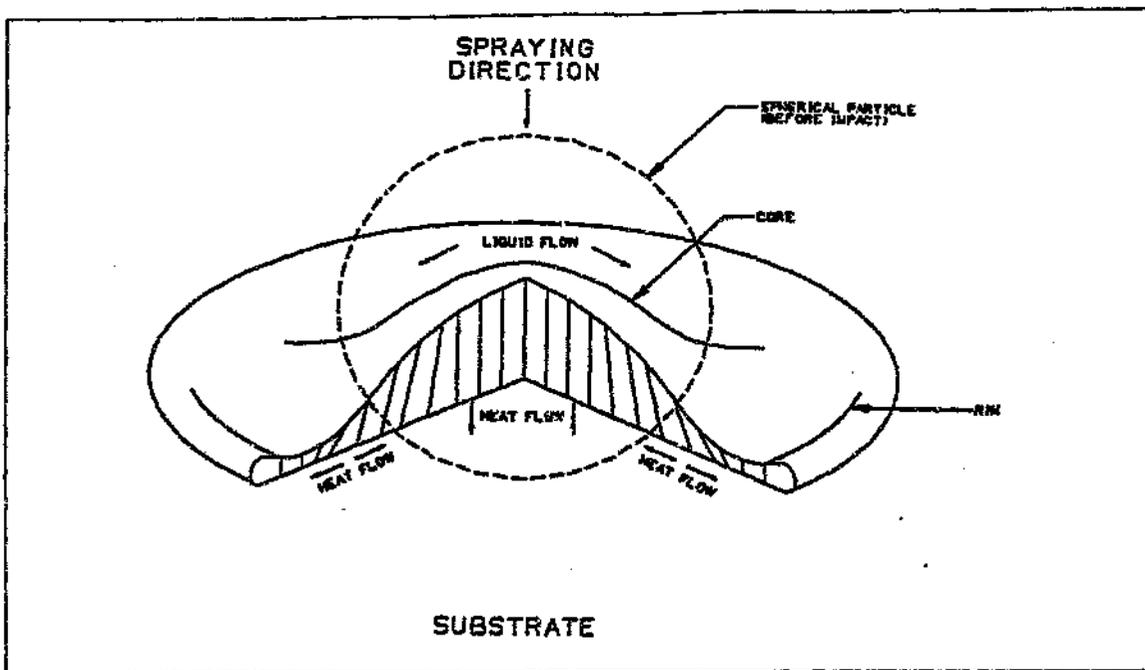


Figure 2.2-Schematic model of the flattening of a particle on impact onto the substrate⁵

In order to understand the theory surrounding thermal spray coatings one needs to investigate the coating as well as the coating process. The characteristics of a coating as well as some of the properties can become apparent when viewed under a microscope^{8,9}. A schematic model of the formation and solidification of a single flattened particle is shown in Figure 2.2. The melt-flow characteristics of the particle on impact is dependent on the particle temperature, melting point, superheat, viscosity, velocity and interaction with the substrate.³⁻⁶

In order for the particle to flatten uniformly it is important that the particle is heated evenly throughout its mass and that it is in a semi-molten state. Solid particles will tend to rebound off the substrate³, while liquid particles will tend to splash, forming peripheral, spherical droplets. These droplets tend to show poor quality bonding which may result in porosity^{1,3,5}.

If the substrate is angular and rough, the particles are able to attach themselves onto the substrate via an interference fit. If the underlying substrate is smooth, the particles are unable to interlock with the substrate.

All coatings shrink during cooling causing tensile stresses to form in a coating. If the tensile stresses of a coating are too high the coating may crack and disbond. Thus for a coating to bond, the adhesion forces have to be stronger than the contraction forces¹⁰⁻¹².

If a coating is sprayed too thick, the coating may crack. This occurs when the contraction forces (between 200 and 600 MPa, depending on material) exceed the tensile strength of the coating¹². The thermally sprayed coating is therefore limited in thickness. This thickness limit is material and process dependent and is usually of the order of 200 μm - 800 μm ^{11,12}.

2.2. Coating Quality

The thermal spraying process may introduce many defects to a coating which affect the characteristics and therefore the quality of the coating. Traditionally, the quality of a coating is generally defined by three parameters¹ which all require destructive testing for evaluation:

- Porosity
- Bond Strength
- Homogeneity

If these parameters show good integrity then the physical properties of the coating, i.e. mechanical strength, wear, corrosion and heat resistance should be of the correct quality.

2.2.1. Porosity

The porosity of a coating is defined in terms of the percentage of microvoids per unit volume of coating. In order to determine the porosity levels of a coating a cross-sectional micrograph of the coating is examined under a microscope⁸. The percentage porosity is calculated with the aid of an image analyser⁹.

The presence of porosity is believed to be due to insufficient impact deformation of the particle^{6,7}. Porosity can be decreased by increasing the amount of deformation or flattening of the particle on impact with the substrate. Particle flattening is a function of the impact temperature and velocity^{1,5,7}.

Particle Temperature - Particle temperature is determined by the temperature of the flame and the particle dwell time in the flame^{1,5,7}. Heating occurs inside the nozzle as well as in the exiting flame. With spray distance, however, the flame temperature drops due to the increasing air entrainment in the flame. As a result the coating particle is also cooled. The temperature of the coating particle thus reaches a peak, after which it reduces with spray distance. The optimum particle impact temperature is the temperature at which the particle is in a semi-molten state.

Particle Velocity - When the combustion gases are passed through the gun nozzle, the flame velocity may reach a peak of over 1200 m/s⁽³⁾. The particles are accelerated in the gas stream. The particle velocity is thus directly related to the gas velocity as well as the dwell time in the gas stream. Adjustment of the flow of exiting gases as well as the spray distance would, therefore, affect the velocity of the particle^{1,3,5,6}.

2.2.2. Bond Strength

The bond strength of a coating is the sum of the adherence bond strength, or interlocking bond strength, and the metallurgical bond strength and/or chemical bond strength between the coating particle and the underlying substrate^{3,4,5,7}.

Adherence Bonding - The degree of adherence depends largely on how many interlocking points a flattened particle will be in contact with, which is highly dependent on the underlying surface. The probability, however, of increasing the number of interlocking points is directly proportional to the area to which the particle is exposed to³. The particle bonding is increased by increasing the amount of flattening and angular roughness of the substrate.

Metallurgical Bonding - The metallurgical and or chemical bond between the coating particle and the underlying surface is dependent on the degree of diffusion, adsorption and chemical reaction that the particle undergoes. These processes are vastly enhanced when the substrate surface is clean and oxide free and when the particle and substrate temperatures are increased^{1,10-12}.

2.2.3. Homogeneity

The homogeneity of a coating is a qualitative measure which is generally defined with respect to the following:

Phase Distribution - The finer and more even the phase distribution within the coating, the more even the properties of the coating. The coating quality, therefore, improves with increasing homogeneity in phase distribution.

Oxide Content - If the particles are exposed to oxygen while in their semi-molten or molten stage they may be, depending on their chemical composition, highly susceptible to oxidation. Oxide formation on the particle will be transmitted onto the coating. The oxide content will change the chemical composition, structure of the coating as well as the physical properties of the coating with respect to wear and corrosion resistance.

Unmolten Particles - Unmolten particles can be imbedded into the coating due to the particles not being sufficiently heated or particles being over-cooled. Unmolten particles are distinctly round in appearance. Unmolten particles due to their low surface area to volume ratio and low wettability show poor bonding characteristics. The coating quality could, therefore, be affected by the amount and size of unmolten particles present in a coating.

Interparticle Bonding - Interparticle bonding can be analysed to a limited extent. Defects between particles can often be observed. The quality of the coating improves with the reduction of interparticle defects.

2.3. Thermal Spray Systems

There are five different thermal spray systems available to industry. These are the flame spray, the arc spray, the plasma, the detonation and the high velocity oxygen-fuel (HVOF) systems^{1,3}.

2.3.1. The Flame Spray System

The flame spray system uses powder that is gravity fed into the centre of an oxygen-acetylene flame. The powder is subsequently heated and accelerated by the flame where it bonds with the substrate to form a coating. A schematic representation of the flame spray system is shown in Figure 2.3.

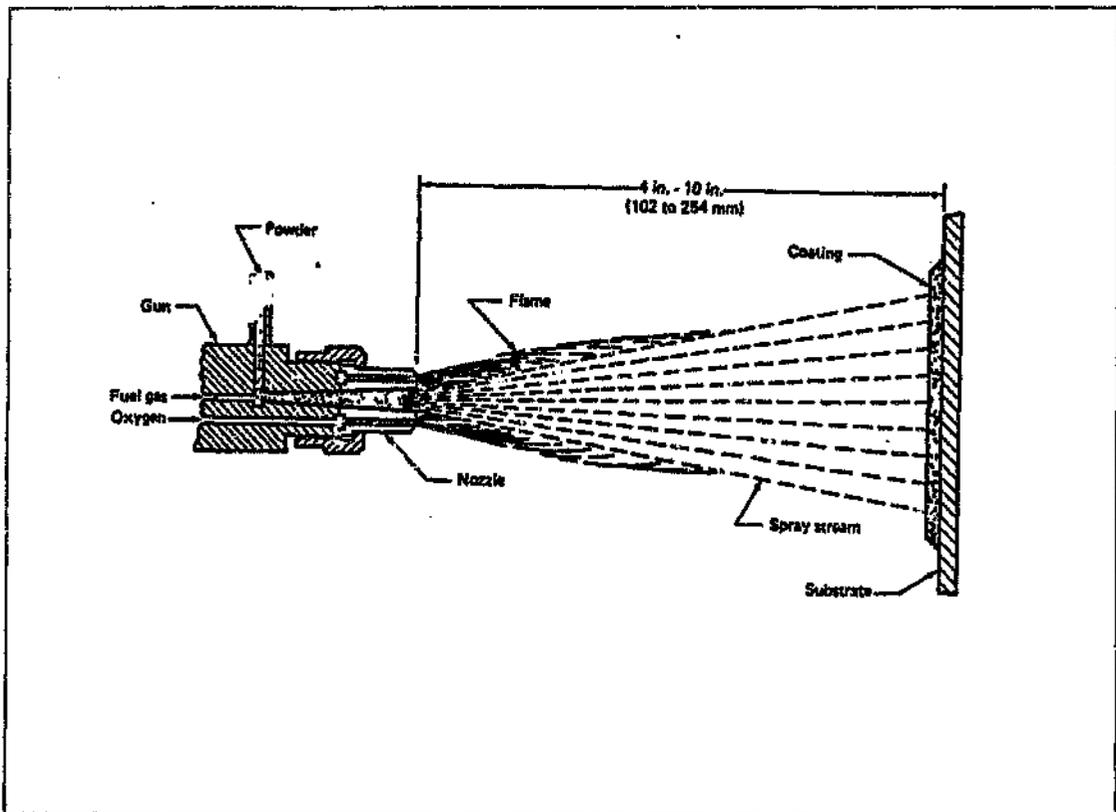


Figure 2.3-Schematic representation of the flame spray system¹.

The flame spray system is portable. Due to the high temperature of the oxygen-acetylene flame (2300 °C) the range of materials that can be sprayed include plastics, metals, carbides and some ceramics¹. The particle impact velocities is relatively low when using this system. The coating properties tend to be inferior, in particular with respect to bond strength and coating porosity .

2.3.2. The Arc Spray System

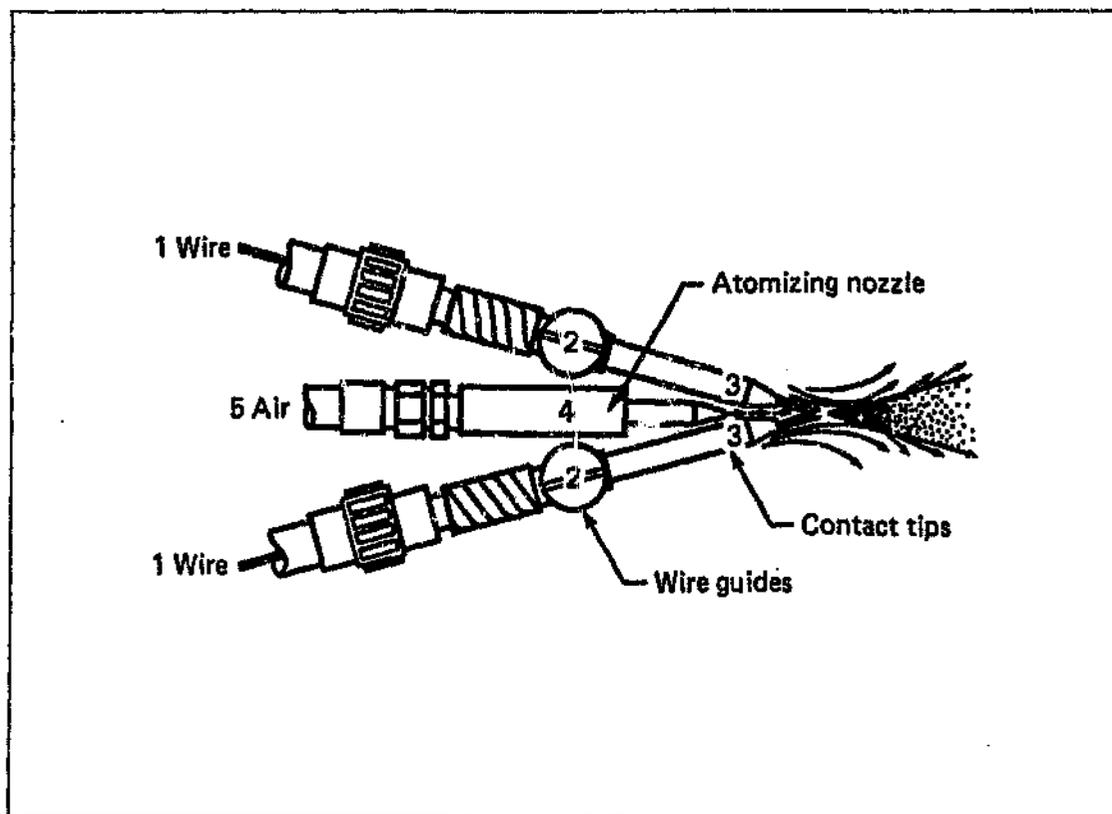


Figure 2.4-Schematic representation of the arc spray system¹.

The arc spray system uses two consumable wire electrodes which are guided to a common point by a wire feeder. An electrical potential difference is placed between the wire electrodes, resulting in an arc forming at the junction point. The two wires melt and compressed air is forced through the molten pool, atomising the molten metal into fine particles and accelerating them onto the substrate¹. Figure 2.4 shows the schematic representation of the arc spray system.

This process shows improved coating quality compared to the flame spray system. This is largely due to the considerably higher particle velocity of the arc spray system. This system is also portable. Since the particles are accelerated by air there is a high tendency for oxide formation. Due to the nature of the system, only conductive material, in wire form, can be used. This includes wires with powder cores¹.

2.3.3. Plasma Spray System

A schematic drawing of the plasma spray system is shown in Figure 2.5. The plasma spray system uses a plasma flame to heat and accelerate powder particles onto a substrate. The plasma gun consists of a positive potential electrode and a negative anode nozzle. Inert gas is fed between the electrode and the anode. A plasma flame is formed, which can exceed 10 000 °C, and is passed through the anode nozzle¹. The powder is then fed tangentially into the flame, and is heated and accelerated onto the substrate to form a coating.

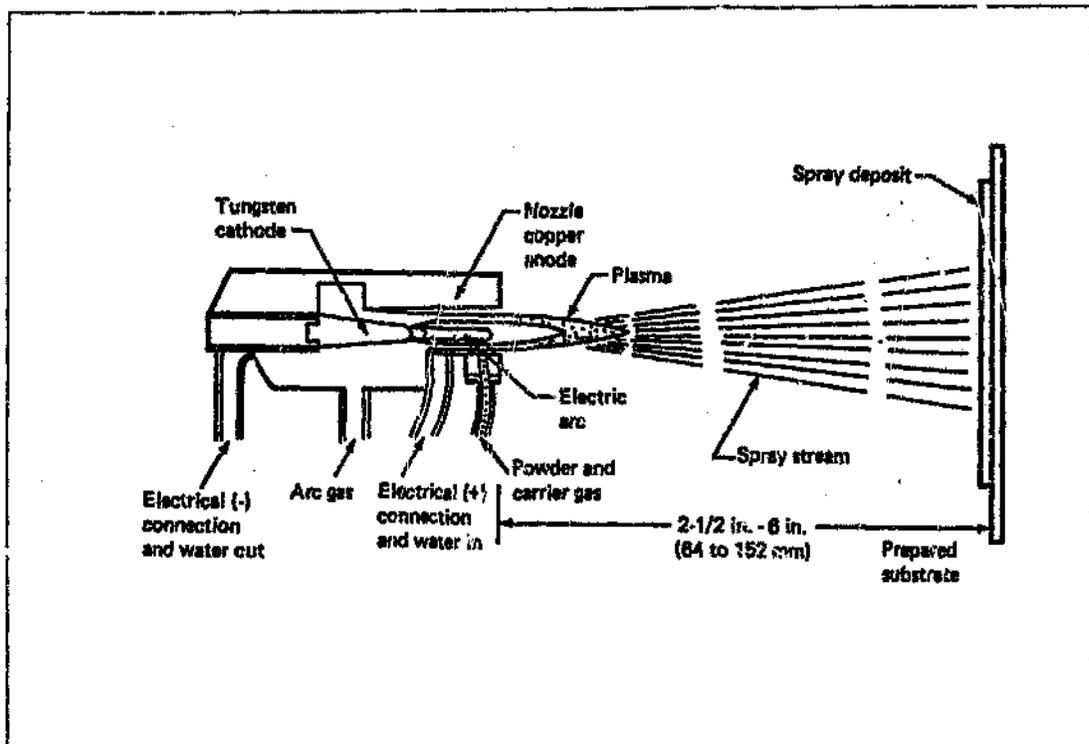


Figure 2.5-Schematic drawing of the plasma spray system¹.

The plasma flame system, due to its high temperature, has the ability to spray high melting point materials. It is thus the only system which can successfully spray ceramics such as Zirconia¹. Some materials, such as Tungsten Carbide, are volatile at high temperatures and run the risk of changing their chemical composition whilst being sprayed. Different coating properties might therefore be obtained. Very dense and high quality coatings can be obtained with the plasma system.

The main disadvantage of the plasma system is the lack of portability and high running and equipment costs.

2.3.4. The Detonation System

The detonation system uses the detonation of an oxygen-acetylene gas mixture to accelerate the powder onto the substrate. The system uses a long barrel into which the oxygen-fuel gases and the powder are fed. The mixture is ignited by a spark which results in a detonation front. This detonation front can accelerate particles up to a velocity of 760 m/s¹. Multiple detonations are made every second resulting in a build up of a coating. The excellent particle flattening characteristics, when using this system, gives the coating a superior coating quality with extremely high bond strengths and low porosity levels¹. A schematic representation of the detonation system is shown in Figure 2.6.

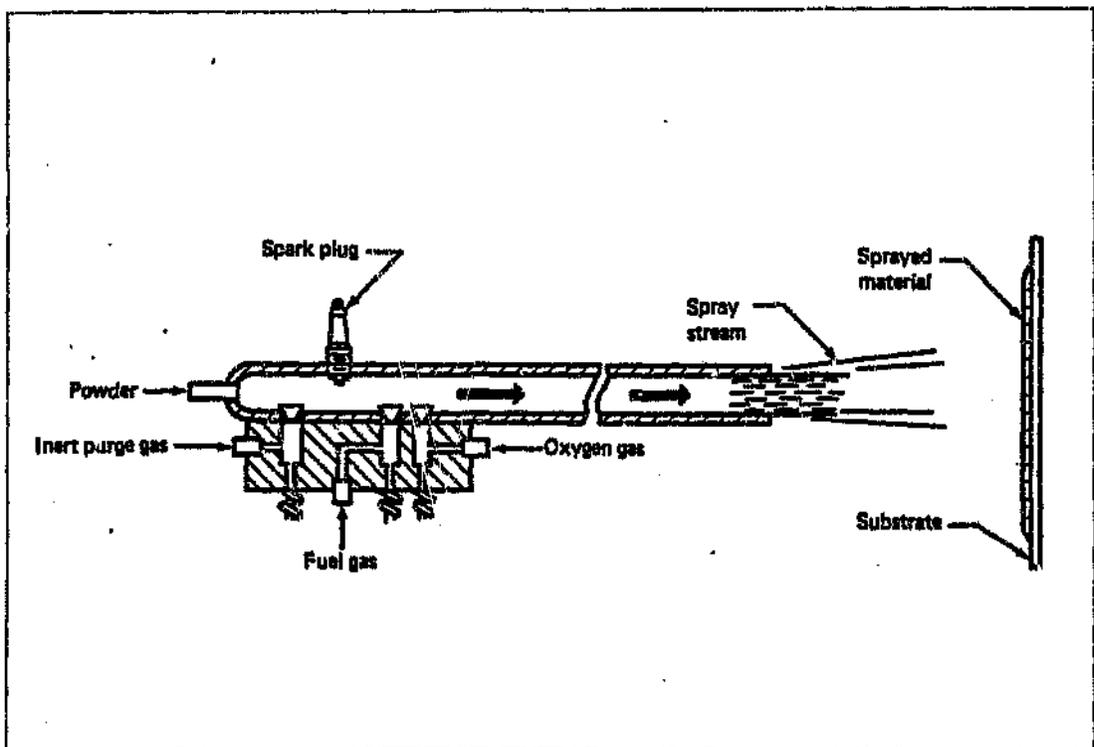


Figure 2.6-Schematic model of the detonation spray system³.

The detonation system needs to be placed in a sound proof spray booth, since it results in high noise levels¹ in excess of 150 dB. For most applications the operations are automated. Thus, this system does not lend itself to portability.

2.3.5. The HVOF System

The HVOF system uses an oxygen-fuel mixture in combination with a jet nozzle to accelerate the exit gases to supersonic velocities. Relative gas velocities of up to 2000 m/s are obtained³. These high velocity gases in turn accelerate the powder particles to supersonic velocities of the order of 700 m/s³. The high particle velocities allows for excellent flattening of the particles to take place, resulting in superior bond strengths and porosity levels of below 1 per cent³. In the past, these systems have not been portable. The latest available HVOF systems have been designed to overcome this disadvantage.

2.3.6. TOP GUN HVOF System

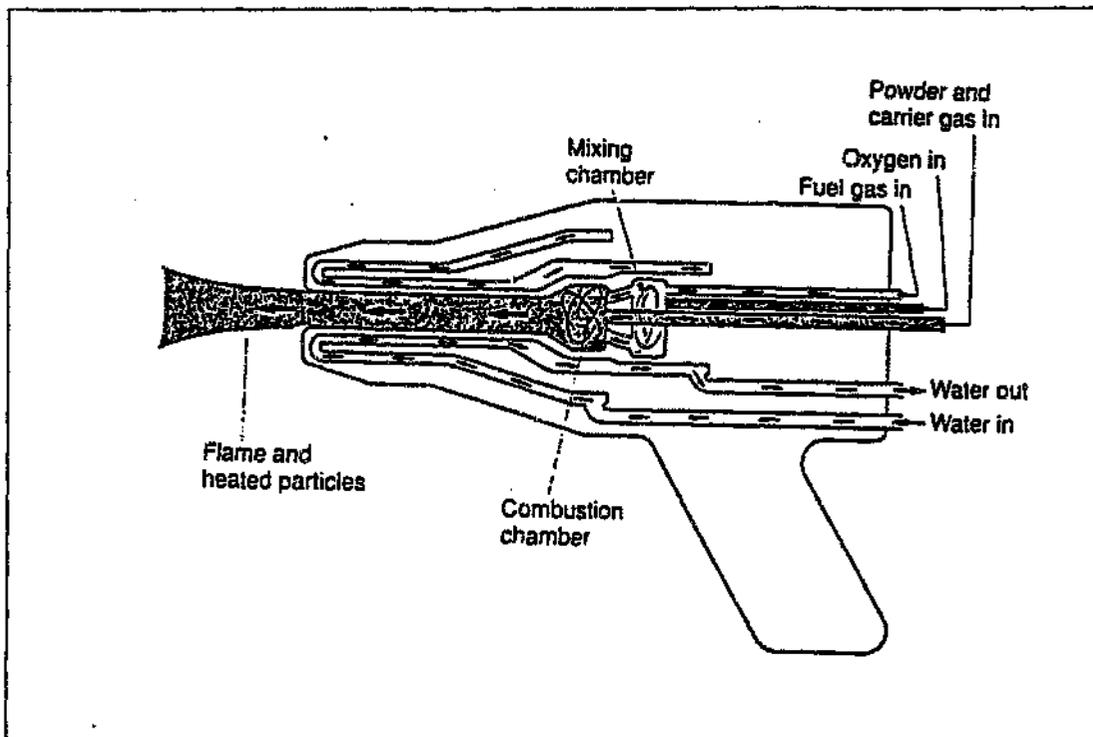


Figure 2.7-Schematic representation of the HVOF spray system².

The TOP GUN HVOF system was designed in the mid to late 1980's. The TOP GUN system consists of four units: the control unit, the water cooling unit, the powder feeder and the spray gun (Figure 2.7). The gun runs on an oxygen-fuel mixture where the fuel may consist of either hydrogen, propane,

propylene, acetylene or ethylene. The coating powder is fed from the powder feeder to the gun with either argon or nitrogen. In the gun the gases are mixed in a mixing block and then fed into a combustion chamber where they ignite. The gases expand through the nozzle and reach sonic conditions on exiting the gun. Gas velocities of up to 2000 m/s are reached³. The coating powder is fed axially into the combustion chamber and is heated and accelerated through the nozzle by the hot gases. On exiting the gun the powder particles reach velocities³ of up to 900 m/s.

2.4. TOP GUN Parameters which affect coating quality

Coating quality is determined by the impact temperature and velocity of a coating particle^{1,3}. The temperature of the gas that passes through a supersonic nozzle has a direct influence on the exit velocity of that gas. Thus, the parameters which affect the particle temperature have a direct influence on the particle velocity.

Nakagawa⁴ *et al* have shown that there seems to be a limiting velocity above which the flattening characteristic of the particle does not improve significantly. They have shown that this limiting velocity, when using an arc spray system, is of the order of 50 m/s. Although the particles that are sprayed with the TOP GUN HVOF system are probably not quite liquid and are different in composition to the particles of the arc spray system it seems reasonable that the particles of the HVOF system will follow a similar trend to that of the arc spray system. This suggests that the limiting flattening velocity of these particles is significantly lower than the actual particle velocity of approximately 900 m/s. Variations in particle impact velocity due to changes in parameters are therefore unlikely to affect the quality of the coating .

2.4.1. Parameters which affect the particle temperature

Combustion Chamber Size - The temperature of the particle is dependent on its dwell time in the flame. Thus, an increase in the barrel length or combustion chamber size will increase the particle temperature³. Figure 2.8 shows the effect of barrel length on the exit particle temperature for various grades of powder.

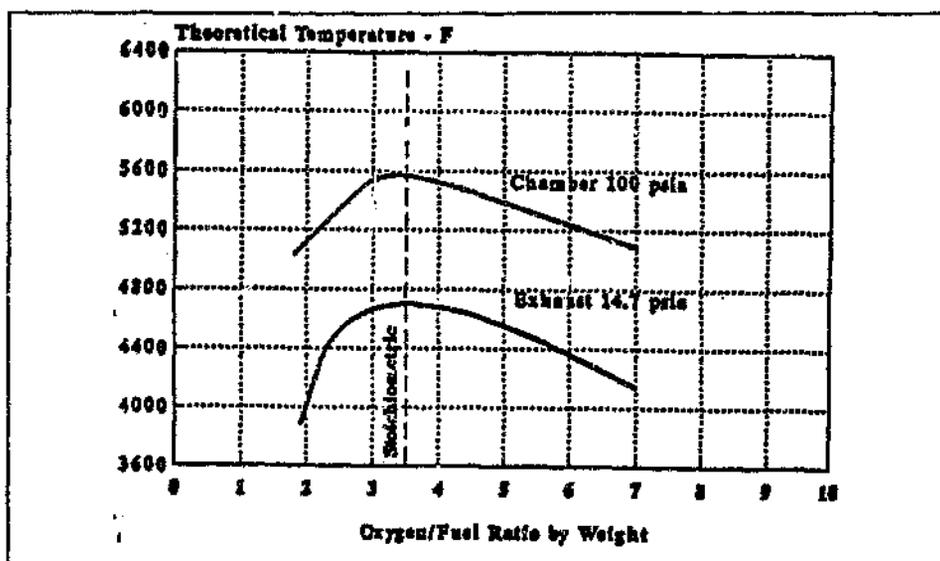


Figure 2.8-Variation of theoretical flame temperature with oxygen-fuel ratio³.

Oxygen Fuel Ratio - The oxygen-fuel ratio affects the temperature of the flame. Gas mixtures which are not stoichiometric have gases which do not combust, resulting in a cooling of the flame. The gas mixtures which allow for complete combustion to take place render the highest temperature flames. Since complete combustion does not always take place in the barrel of the HVOF gun it has been found that a maximum flame temperature can be obtained from a slightly oxidising flame as shown in Figure 2.9³.

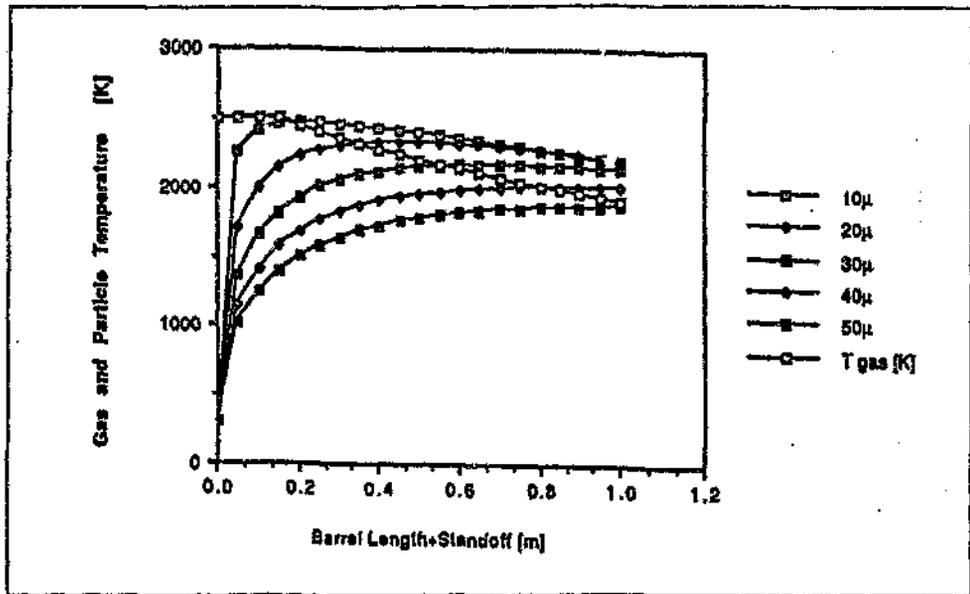


Figure 2.9-Effect of barrel length on exit particle temperature³.

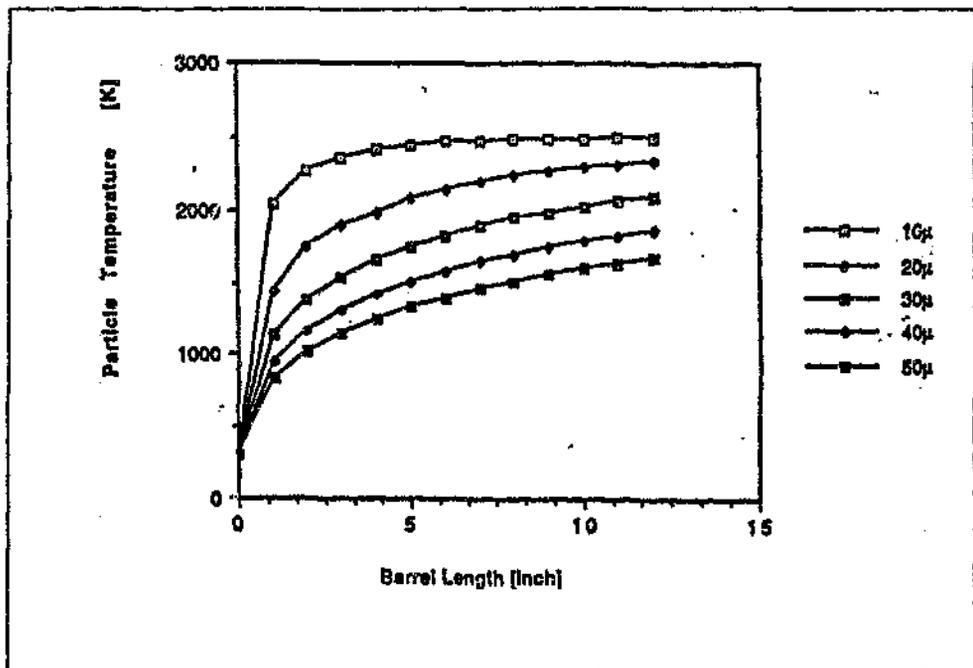


Figure 2.10-Variation of theoretical flame and particle temperature with barrel length and spray distance³.

Spray Distance - The supersonic flame gases are cooled when exiting the gun by the entrainment of the surrounding air. As the spray distance increases the flame and hot gases are cooled more severely. The particle temperature, therefore, reaches a maximum at a critical distance from the gun. This critical distance is material and gun parameter dependent^{1,3}. The effect of the entraining air on the flame and particle temperature is shown in Figure 2.10.

Gas volume flow - Some combustion of the fuel gases takes place outside of the nozzle, keeping the surrounding gases hot. An increase in gas volume flow will lengthen the flame front due to added combustion taking place. The extra length of the flame allows for an extended dwell time and can thus increase the particle impact temperature³. The lengthened flame front, however, also allows for added acceleration of the coating particle and results in higher particle velocities. The higher particle velocities reduce the dwell time and thus the particle impact temperature.

2.5. The effect of grain size distribution on particle temperature and velocity

The particle size distribution has a significant effect on particle temperature and velocity. Due to their higher area to volume ratio, smaller particles heat faster than larger particles. Smaller particles exhibit a more uniform temperature distribution throughout the particle. Smaller particles have less mass than larger particles and will therefore accelerate faster. Particle size can, therefore, make a significant impact on the coating quality. A large range of particle sizes will result in a large range of particle impact velocities and temperatures and therefore uneven spray conditions^{1,3}. This could result in reduced coating quality.

2.6. Mechanisms of wear

WC coatings are applied to components to protect them from wear. Wear is the displacement and detachment of particles from a surface caused by contact and shear movement of the surface of another body. Adhesive and abrasive wear is the movement of liquids or gases in contact with the surface of the body¹³.

The wear of each surface is affected by a variety of conditions, including environment, type of loading, relative speeds of mating surfaces, lubricant, hardness, surface finish, presence of foreign particles, and composition and compatibility of mating surfaces¹³.

In adhesive wear the two mating surfaces interlock resulting in tearing free of material due to relative motion. In abrasive wear the harder surface penetrates the softer surface, which results in gouging and removal of material from the softer surface when moved relative to each other. In erosion the removal of material is similar to abrasion except that material is removed on a micro scale due to tiny particles, which are suspended in the gas or liquid stream, impacting onto the surface¹³.

3. Experimental

The experimental work that was carried out for this dissertation can be divided into the following sections:

- Spraying samples with various parameters.

These include:

- The change in combustion gases with change in spray distance.
- The change in combustion chamber size with change in spray distance.
- The change in volume gas flow rate with change in spray distance.

- Data measurement, manipulation and evaluation

These include:

- The measurement of coating thickness.
- The measurement of the cutting time of the coating.
- The measurement of the hardness of the coating.
- Metallographic analysis of the coating.
- Standardisation of data
- Correlation evaluation
- Significance testing using the paired t-test evaluation method
- Point of inflection

3.1. Spraying

Copper pipes, 300 mm in length and 15 mm in diameter, were used as substrate. All sample pipes were shot blasted with grade 24 alumina grit at 4 bar air pressure. The sample pipes were mounted onto a turning device and rotated at approximately 250 rpm. The gun was mounted on a traverse unit and moved sideways to the rotating pipe at 1.1 m/minute in each direction. A total of thirty traverses were sprayed onto each pipe.

3.1.1. Gun Parameter Settings and Limits

Spray Distance - The spray distance is the coating parameter which is believed to have the most profound effect on the coating properties. The entrainment of the surrounding air has a significant effect on the flame and particle temperature as spray distance increases. The spray distance used for the samples varied between 200 mm and 700 mm. This is the maximum range for the spray distance for which a coating can be sprayed, since the sample would overheat and melt at shorter spray distances than 200 mm and not deposit at all at a spray distance greater than 700 mm.

Combustion Temperature - In order to investigate the effect of the combustion temperature on the properties of the coating, the two fuel gases, which were suitable for spraying with the TOP GUN HVOF system were selected, i.e. propane and ethylene. Propane has a combustion temperature of 2825°C and ethylene 2940°C. A stoichiometric oxygen-fuel ratio was selected for both the fuel gases. The oxygen flow rate remained the same for both the test sets.

Combustion Chamber Size - The TOP GUN has the option of using either a 12 mm combustion chamber or a 19 mm combustion chamber. The powder is fed into the combustion chamber at a relatively low velocity and is heated. It then enters the nozzle, where it is accelerated. The size of the combustion chamber determines the dwell time of the powder particle in the chamber and thus the amount of heat input into the particle.

Gas Volume Flow - The investigation on the effect of gas volume flow with spray distance on the coating properties was carried out by changing the gas volume flow from 70% to 110 % of that recommended by the manufacturer of the TOP GUN system, keeping the gas mixture stoichiometric. This is the maximum range over which the flame was stable.

3.2. Measuring

The coating thickness was measured with the aid of a micrometer. The diameter of the pipe was measured with the micrometer before and after coating was applied. In order to compare the coatings to each other the coating thickness is expressed in terms of a percentage, where 100% represents the coating with the highest deposit efficiency.

3.3. Abrasion Resistance

The abrasion resistance was determined by placing the coated copper pipes on a slow turning abrasive diamond wheel and measuring the time taken for the diamond wheel to cut through the diameter of the pipe. The reason for using thin copper tubes was to ensure that the base material has a minimal effect on the wear process. The standard laboratory cutting machine uses a 200 mm diameter circular diamond impregnated cutting disk. The sample is clamped onto a weighted lever arm and rests on top of the cutting disk. As the disk rotates at about 120 rpm the sample is lubricated and cut. The abrasion resistance was determined by dividing the time required to cut the coated pipe with the thickness of the coating and expressing it in units of seconds per micrometer (s/ μm).

There was a concern that the copper from the specimen could smear onto the cutting disk and subsequently clog it. On investigation of the cutting of the specimen it was noted that the main wear on the disk was coating. The first and last few seconds of the cut of a sample are coating only. The coating is very hard and brittle compared to the soft copper base resulting in automatic dressing of the cutting disk. The cutting disk is also wafer thin and turns relatively slowly. This makes the smearing of the copper onto the disk almost impossible.

For consistency in the data it is assumed that the force acting on the cutting disk, the diameter of the cutting disk and the rotational speed of the cutting disk remain constant throughout the experiment. To reduce the effect of the pipe material on the cutting time, thin walled copper pipe was used, which is significantly softer than steel or even Tungsten Carbide. Two cuts were taken per sample to indicate repeatability.

In order to compare the coatings to each other the abrasion resistance is expressed in terms of a percentage, where 100% represents the coating with the highest abrasion resistance.

3.4. Metallographic Preparation and Examination

The cut samples were mounted in resin using a standard metallographic mounting press. The samples were successively sanded for 20 seconds with emery paper ranging from grade 200, 400, 800 and 1200. They were then polished using a 6 μm and 1 μm polishing paste successively. The samples were then cleaned with alcohol.

The coatings were examined using a standard metallographic microscope where magnifications of up to 800 could be obtained. The hardness of the coating was measured using a standard Vickers micro hardness machine with a 300 g weight.

3.5. Data Manipulation

The raw data that is received from the experimentation is in the form of coating hardness, coating thickness and cutting time against spray distance.

Hardness: No manipulation was done on the hardness data.

Converting Coating Thickness to Deposit Efficiency: The coating thickness is directly proportional to the deposit efficiency. Of all the samples sprayed, the sample with the thickest coating was deemed to have the highest deposit efficiency. In order to allow for ease of comparison, all deposit efficiency data was standardised against the maximum deposit efficiency. The coating with the maximum deposit efficiency is therefore standardised to the value of 100. All the other data points are adjusted proportionally to give a total range between 0 and 100. This does not mean, however, that the coating with the highest deposit efficiency has a physical deposit efficiency of 100 %, since there will always be some off-spray during the spray process.

Converting Cutting Time to Wear Resistance: Because the coating thickness of the sprayed samples varied significantly the cutting time in itself showed little relevance to the abrasion properties of the coating. The abrasion properties of the coatings can, however, be expressed in time per unit thickness or seconds per micrometer (s/ μm). Again, in order to allow for ease of comparison, all abrasion resistance data is standardised against the maximum data point found for the wear resistance. This data point is given the value of 100 and all the other data are adjusted proportionally.

Standardisation of deposit efficiency data to wear resistance data:

Standardisation is a scaling technique used to compare the trends and behaviour of two or more sets of data. In this case the wear resistance data is to be compared to the deposit efficiency data. The aim is to ascertain whether the wear resistance and deposit efficiency of the coatings follow the same trend and behaviour.

The standardisation technique requires that a reference data point in each set of data is selected. These are usually maximum or a minimum data points or data points with a fixed x value. The ratio of the reference points are then used to scale one of the data sets. Once the new standardised data set is determined, the data sets can be compared and evaluated to one another.

3.5. Statistical Evaluation

The aim of the statistical evaluation is to determine how well each set of data compares to a trend, how data sets relate to one another and whether there is a significant difference between the sets of data.

Curve Fitting:

When plotting the data sets against spray distance it became obvious that the data was related to the spray distance. An attempt was made to fit polynomial functions onto the data sets using Newton's Interpolary Divided Difference Method¹⁴.

Correlation:

To ensure that the fitted curve correlated with the actual data the correlation coefficient of the actual data against the function data is determined using the following equation¹⁵:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}}$$

Where \bar{x} represents the mean of the actual data point, x_i the actual data value, \bar{y} the mean of the corresponding data function value, y_i the corresponding data function value and n the number of data points.

If the correlation coefficient is greater than 0.90 the correlation is considered to be acceptable, indicating that the derived function is likely to be a fair representation of the trend observed by the data sets.

The correlation coefficient can be used to evaluate the behaviour between two data sets or a data set and its fitted function. A sample of the workings is shown in Appendix A.

Significance testing using the paired t-test method:

The paired t-test method is an evaluation technique used to determine whether there is a significant difference between the two data sets. The paired t-test methodology sets two hypothesis:

$$H_0: \mu_d = 0$$

$$H_1: \mu_d \neq 0$$

Where d is the difference of the corresponding data between two data sets and μ_d is the mean of the population from which d is drawn. The standard deviation s_d of the population of d is determined by:

$$s_d = \sqrt{\frac{\sum (d - \mu_d)^2}{n}}$$

from which t_{n-1} is then calculated for n number of data points.

$$t_{(n-1)} = \frac{-\mu_d}{\left(\frac{s_d}{\sqrt{(n-1)}} \right)}$$

The t_{n-1} is then compared to the t-distribution which shows that for ν degrees of freedom there is a P % probability that $|t|$ will exceed the tabulated value.

A probability level of 5% has been set as being significantly low enough to show that there is no difference between the corresponding data of two data sets. Therefore, if the absolute t_{n-1} value is less than the t-distribution at the 5% probability level, then H_0 is retained and there is no significant difference between the data sets. If the absolute t_{n-1} value is greater than the t-distribution at the 5% probability level, then H_1 is retained and a significant difference is said to exist between the data sets. A sample of the working is shown in Appendix A.

4. Results and Discussion

The changes in the parameter settings of the TOP GUN HVOF system affect the particle impact temperature and velocity. The particle impact temperature in turn affects the properties of the coating. The manner in which these coating properties manifest themselves and their mechanisms will be discussed in the results section.

4.1. The influence of spray distance on the particle temperature and deposit efficiency

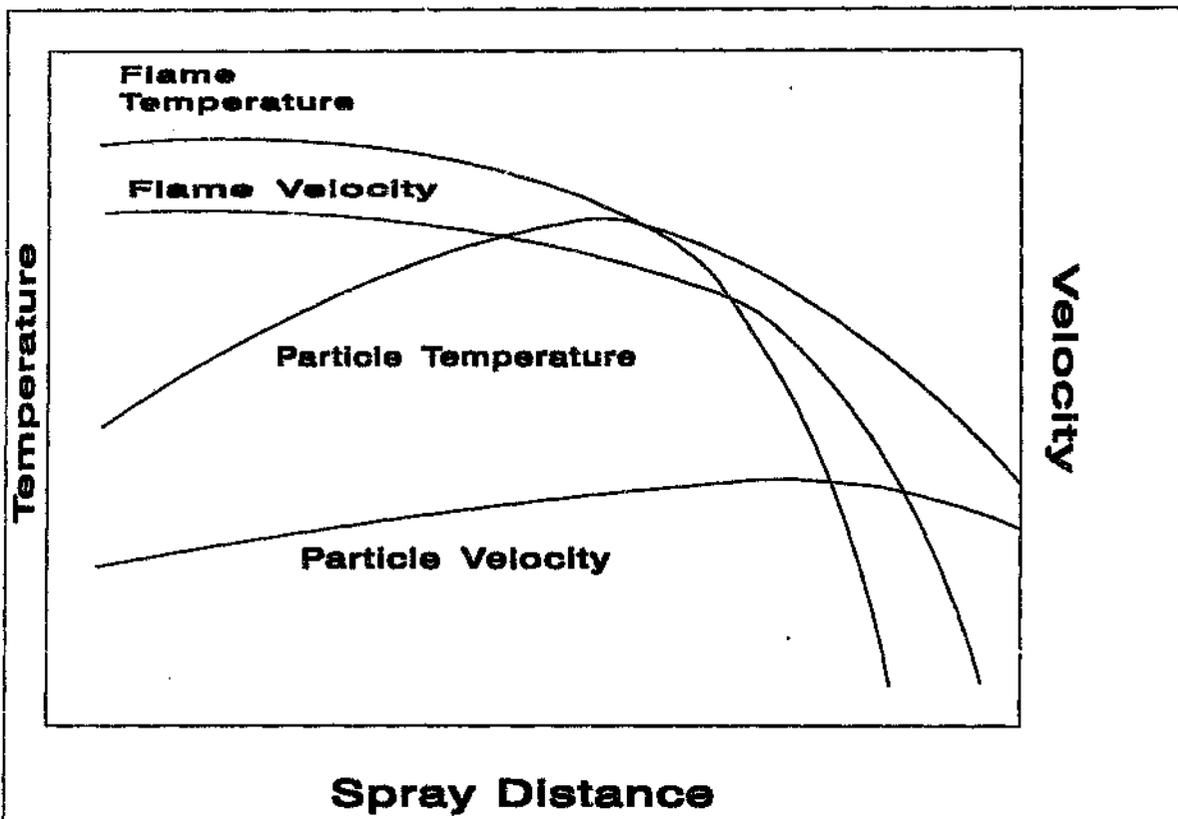


Figure 4.1 - The schematic trend of flame temperature and velocity on the particle temperature and velocity.

The coating particle is injected into the combustion chamber with the aid of the nitrogen carrier gas. It passes through the combustion chamber and is heated by the surrounding combusting gases. The particle is then accelerated through the nozzle. The surrounding combustion gases at this point take on supersonic velocities of up to 2000 m/s. The particle temperature and velocity continue to increase.

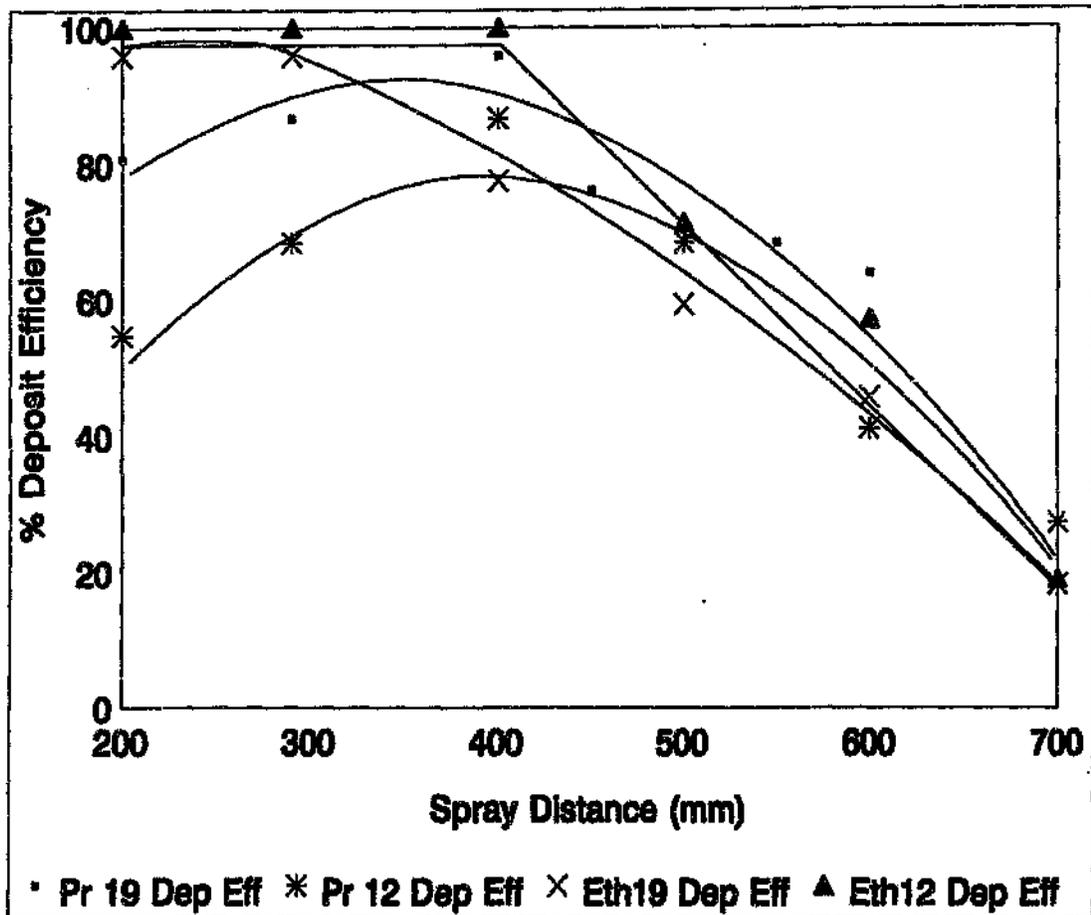


Figure 4.2 -The effect of deposit efficiency against spray distance sprayed with the following parameters, propane with a 19 mm nozzle, propane with a 12 mm nozzle, ethylene with a 19 mm nozzle and ethylene with a 12 mm nozzle.

On exiting the nozzle the flame is exposed to the cool stationary surrounding air. The surrounding air starts to entrain into the flame due to turbulence. This entrainment of the air increases with spray distance and results in rapid cooling and deceleration of the flame. The particle temperature and velocity thus also reduce due to air entrainment. The typical behaviour of the flame and particle velocity is portrayed in Figure 4.1.. As can be seen in Figure 4.1, the slopes of the increasing particle temperature is not the same as the slope of

the decreasing particle temperature. Such a curve can be described by a cubic polynomial function. It is clear from Figure 4.2 and Table 4.1 that the cubic function fitted to the data sets correlates well with the actual data, with correlation coefficients greater than 0.90.

Parameter	Spray Distance for max data	Spray Distance for max f(x)	Correlation Coefficient
Propane 19 mm Nozzle	400	352	0.96
Propane 12 mm Nozzle	400	360	0.91
Ethylene 19 mm Nozzle	290	285	1.00
Ethylene 12 mm Nozzle	400	380	1.00

Table 4.1 - The correlation coefficient of the deposit efficiency data with corresponding data of the fitted function as well as spray distance for which the data and the function of the data are at a maximum (Appendix B).

Figure 4.2 shows that a maximum deposit efficiency is reached at spray distance between 290 mm and 400 mm. This trend of increasing and decreasing deposit efficiency seems to correlate well with the particle temperature behaviour shown in Figure 4.1., indicating that the particle impact temperature and deposit efficiency behave in a similar fashion.

When the coating particle temperature rises to above the ideal temperature for bonding, the deposit efficiency remains constant. This is shown by the parameter set sprayed with ethylene and the 12mm nozzle in Figure 4.2. The deposit efficiency is not changed between spray distances of 200 and 400 mm. This is the region where the particle impact temperature is above its optimum level. Only once the particle impact temperature drops to below its optimum level, i.e. at spray distances above 400 mm, does the deposit efficiency drop.

Table 4.1. shows that the peak maximum data varies between a spray distance of 290 mm and 400 mm, whereas the maximum function value ranges between a spray distance of 285mm and 380 mm. The difference between data maximum and the function maximum varies between 5 mm and 48 mm. This is a relative short range, keeping in mind that the coating properties do not change significantly within a range of 48 mm, especially when in the range of peak deposit efficiency. The paired t-test between the function maximum and actual maximum confirms that there is no significant difference between the spray distance for the four sets of data. The summary calculations of the statistical evaluations are shown in Appendix B.

4.2. The influence of spray distance on the cutting abrasion resistance of the coating

Figure 4.3 displays that the trend of abrasion resistance of the coatings against spray distance is similar to the trend of the particle impact temperature against spray distance. From Figure 4.3 and Table 4.2 it is clear that the cubic functions fitted to the data sets correlate well with the actual data with correlation coefficients of greater than 0.91.

Parameter	Spray Distance for max data	Spray Distance for max $f(x)$	Correlation Coefficient
Propane 19 mm Nozzle	400	345	0.92
Propane 12 mm Nozzle	400	367	0.97
Ethylene 19 mm Nozzle	290	295	0.98
Ethylene 12 mm Nozzle	290	304	1.00

Table 4.2. - The correlation coefficient of the abrasion resistance data with the corresponding data of the fitted function as well as spray distance for which the data and the function of the data is at a maximum (Appendix B).

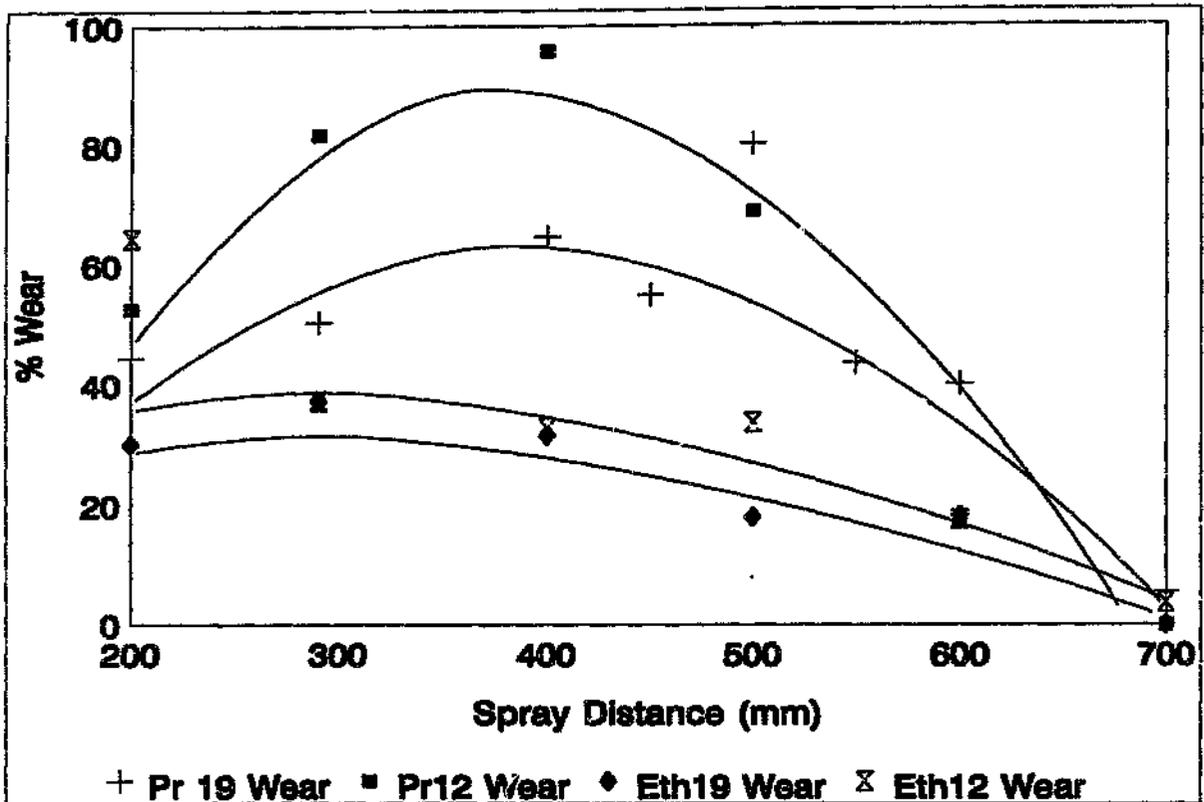


Figure 4.3 -The effect of spray distance on the wear rate of coatings sprayed with the following parameters: propane with a 19 mm nozzle, propane with a 12 mm nozzle, ethylene with a 19 mm nozzle and ethylene with a 12 mm nozzle.

Table 4.2. shows that the peaks of the points of the data sets range between a spray distance of 290 mm and 400 mm, whereas the maximum function values ranges between a spray distance of 304 mm and 367 mm. The difference between actual maximum and function maximum varies between 5 mm and 55 mm. The difference between the observed maximum and calculated maximum value could be attributed to the limited range of data samples available compared to the endless range available to the function. This difference in range is a relatively short, keeping in mind that the coating properties do not change significantly within a range of 55 mm, especially when in the range of peak deposit efficiency. The paired t-test between the function maximum and actual maximum confirms that there is no significant difference between the spray distance for the four sets of data. The summary calculations of the statistical evaluations are shown in Appendix B.

The abrasion resistance of a coating is dependent on its ability to withstand the mass removal of coating due to abrasion or erosion. In a sintered WC material, where the particles are fused to each other via the matrix, the abrasion mechanism is based solely on the synergistic effect of a cement. In a WC cement the tough matrix holds the hard carbide particles and prevents them from being broken away, whilst the hard carbide particle offers a high abrasion resistance and reduces the abrasion of the matrix material.

The WC coating powder used for spraying is sieved to a size fraction of between 5 μm and 45 μm . This powder consists of fine WC particle, approximately 2 μm in diameter sintered with Ni in a 88%/12% WC/Ni by mass ratio, to form the larger particles of up to 45 μm in diameter. In a WC coating, the coating particles, which consist of sintered WC and matrix material, are packed together very tightly and bond via an interference fit. The bond strength of these particles, often not as good as that of the parent sintered material, depends on the particle impact temperature and velocity.

When the coating is exposed to abrasion or erosion, two wear mechanisms operate simultaneously. This is shown schematically in Figure 4.4. The individual flattened coating particles consist of fine WC particles, typically 2 μm in size, which are sintered with Ni. The wear mechanism is focused on the rip out of these fine WC, which are very hard (2300 HV₃₀₀) and totally embedded by the matrix material. The rate of mass removal is solely dependent on the rate of removal of these fine WC particles.

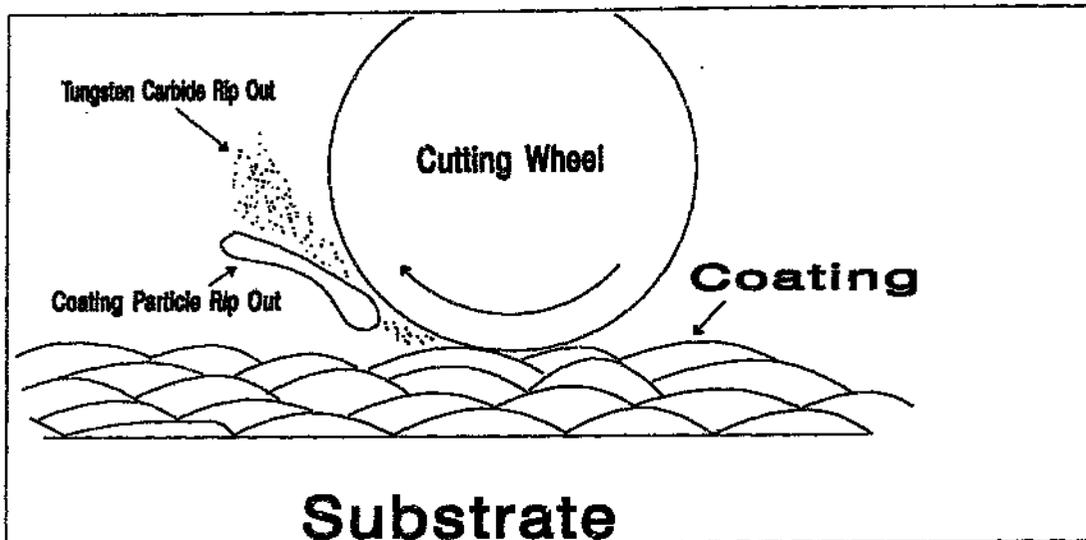


Figure 4.4 -Schematic representation of the wear mechanisms experienced in thermally sprayed coatings.

If, however, the bonding of the flattened coating particles is poor, the shear forces of the wear mechanism will exceed the bonding forces and the flattened coating particle will tend to break free. The resistance to break free depends primarily on the bond strength of the coating particle. If the wear mechanism succeeds in overcoming the bond strength of the coating particle the mass loss rate of the coating due to abrasion is directly dependent on the bond strength of the coating.

The coating particles impact at great velocities onto the surface. On impact, the coating particle transforms some of its kinetic energy into flattening. The rest of the kinetic energy is passed onto the substrate and reflected via a shock wave. In an impacting coating particle where the Ni is in its plastic state, the particle is partially flattened and the fine WC particles are held by the Ni matrix as the repelling shock wave passes through the coating.

It should be noted that the abrasion resistance of the coatings sprayed with ethylene is lower than that of the coatings sprayed with propane. This is due to the overheating of the coating particle and liquefaction of the Ni matrix. When the Ni matrix is liquid it flattens out very thinly on impact. The fine WC particles do not hold firmly in the Ni matrix any longer and may be repelled by the reflecting shock wave. The loss of WC content in the coating will reduce the abrasion resistance.

4.3. Comparison between the wear resistance and deposit efficiency data

The comparison between the standardised deposit efficiency data and the wear resistance data shows that the wear resistance and deposit efficiency behave in a similar fashion. Table 4.4. statistically compares the standardised deposit efficiency with the wear resistance data and shows that the correlation between the data sets are relatively high with a minimum of 0.84 and an maximum of 0.98. From the paired t-test, calculations show that no significant difference could be found between the data sets. Furthermore, the difference between the maximum point of inflection between the two data sets ranged from 6 mm to 43 mm. This is a relatively insignificant difference, since changes in coating properties can hardly be detected when sprayed at a 50 mm different spray distance.

The comparison measures between the standardised deposit efficiency and the wear resistance thus seem to indicate that these properties follow a similar trend and supports the notion that the deposit efficiency and wear resistance are related to the particle impact temperature as discussed in Sections 4.1 and 4.2.

Parameter	Correlation	Significant difference between data	Difference in spray Distance between Max data points (mm)
Eth 19	0.98	no	30
Eth 12	0.86	no	43
Prop 19	0.88	no	6
Prop 12	0.84	no	3

Table 4.4 - Statistical comparison between the standardised deposit efficiency and wear resistance data for various parameters (Appendix B)

4.4. The effect of particle impact temperature on porosity

One of the traditional ways of measuring coating quality is by measuring the coating porosity, where the lowest coating porosity indicates the highest quality of the coating. With the introduction of superior spray equipment, however, the difference in the measurement

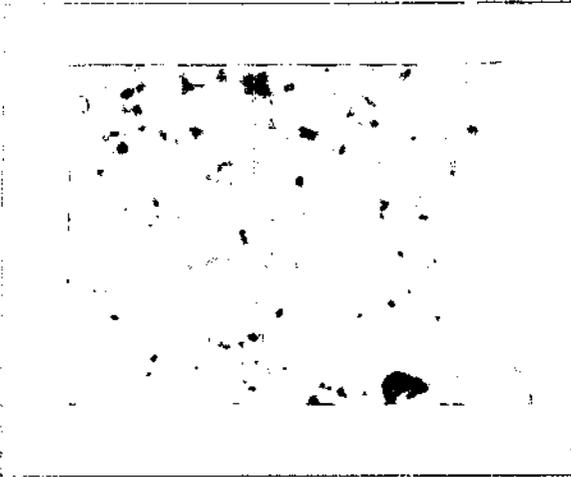


Figure 4.5 -Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 200 mm. (x 200)

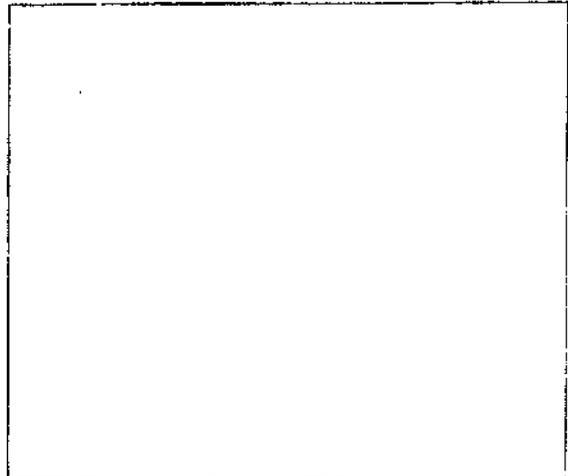


Figure 4.6 - Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 290 mm. (x 200).

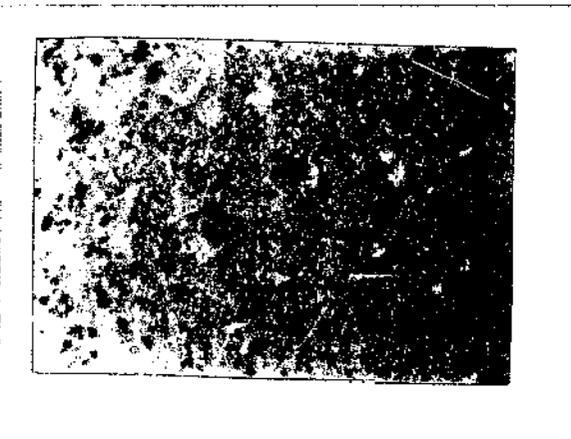


Figure 4.7 - Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 400 mm. (x 200).

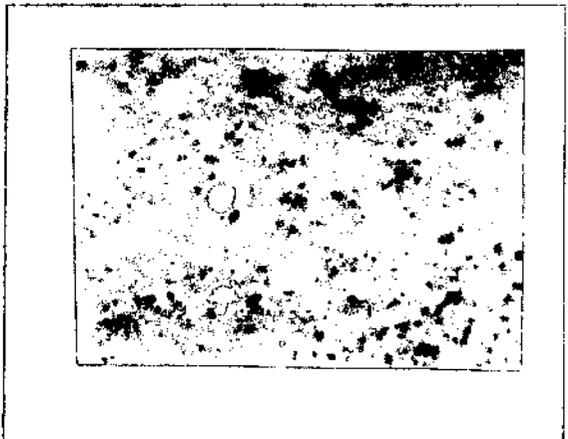


Figure 4.8 - Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 500 mm. (x 200).

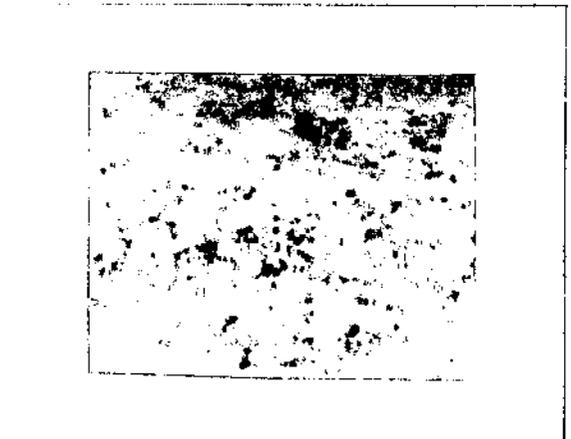


Figure 4.9 - Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 600 mm. (x 200)

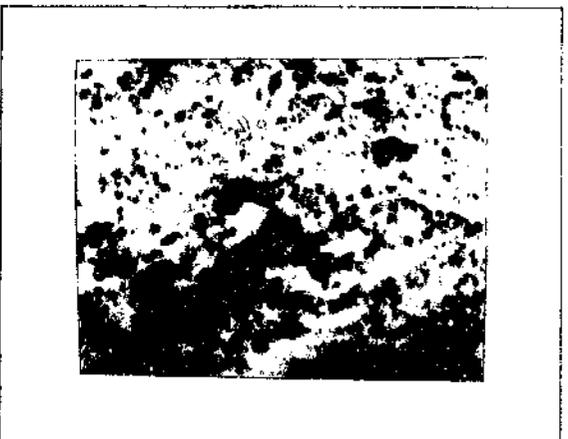


Figure 4.10 - Micrograph of a coating sprayed with propane and a 12 mm nozzle, at a spray distance of 700 mm. (x 200).

of the coating porosity is very difficult to distinguish, since the variance of porosity within the coatings often matches the porosity variance between the coatings. Porosity measurements have thus not become the appropriate measuring tool to determine the quality of coatings sprayed the HVOF systems.

The metallographic analysis of the coatings shows no clear distinction or trends between the various coatings. Although a few small differences in porosity can be found, the variance within the coating often matches the variance between the coatings and is too small to make a sound judgement on any trends that might be present. Figure 4.5 to 4.10 show the micrographs of a typical group of coatings, sprayed with Propane and a 12 mm nozzle, which were sprayed at spray distances between 200 mm and 700 mm.

The only conclusion the metallographic analysis can make is that the coatings, which were sprayed beyond 600 mm, have high porosity levels. This is due to the particles being sprayed too cold. At 600 mm spray distance the air has cooled the flame and coating particle to such an extent that the particle does not deform sufficiently on impact. This causes the particles to partially deposit or wedge themselves into the coating or even be repelled on impact. This in turn results in a high porosity level.

4.5. The effect of particle impact temperature on hardness

One of the traditional methods of measuring coating quality was to measure the hardness of the coating. Since an increase in porosity results in a decrease in coating hardness, this methods was a sound measuring tool for coating quality. With the introduction of HVOF spray equipment, however, the porosity level of the coating remains less than 1 %, whereas the wear resistance of the coating can vary significantly. This method of measuring coating quality has therefore become invalid for coatings sprayed with HVOF spray systems.

In many materials the wear resistance is often directly related to the hardness of the material. A coating, however, being a composite of particles is far more dependant on the bonding of the particles for wear resistance than the hardness of the coating. From Figure

4.11 and Figure 4.3. it is obvious that the hardness data does not correlate well with the wear resistance data. Table 4.5. shows a correlation between 0.62 and 0.95, which varies from poor to good correlation. The paired t-test between the data revealed that there was a significant difference between all the sets of wear resistance and hardness data.

Parameter	Correlation	Significant difference between data
Eth 19	0.89	Yes
Eth 12	0.94	Yes
Prop 19	0.62	Yes
Prop 12	0.87	Yes

Table 4.5. - The correlation coefficient and paired t-test for significant difference between the hardness sets of data. (Appendix B)

During the hardness measurements it was noticed that the measurements within a coating varied in range between 200 HV and 300 HV. The mean of three readings on each coating is used to determine the data points shown in Figure 4.11. From Figure 4.11 it is evident that the hardness of the coating decreases with spray distance and slopes down significantly at spray distances above 500 mm.

At spray distances beyond 500 mm the coatings show high porosity levels and poor particle adhesion. It is thus not surprising that these coatings display relatively poor hardness results.

The mechanism causing the hardness to decrease with spray distance is not clear. The hardness measurement in a WC/Ni coating is directly proportional to the WC content in the coating. A possible cause to the decrease in the hardness of the coating could be the loss of the fine WC particles to the coating. This occurs when the Ni in the coating particle softens or liquefies when impacting onto the substrate. The loss of the WC to the coating depends on how soft the Ni becomes on impact. The softer the Ni becomes on impact, the more it will flatten, allowing more of the fine solid WC particles to be repelled and be lost to the coating. This in turn reduces the overall hardness of the coating.

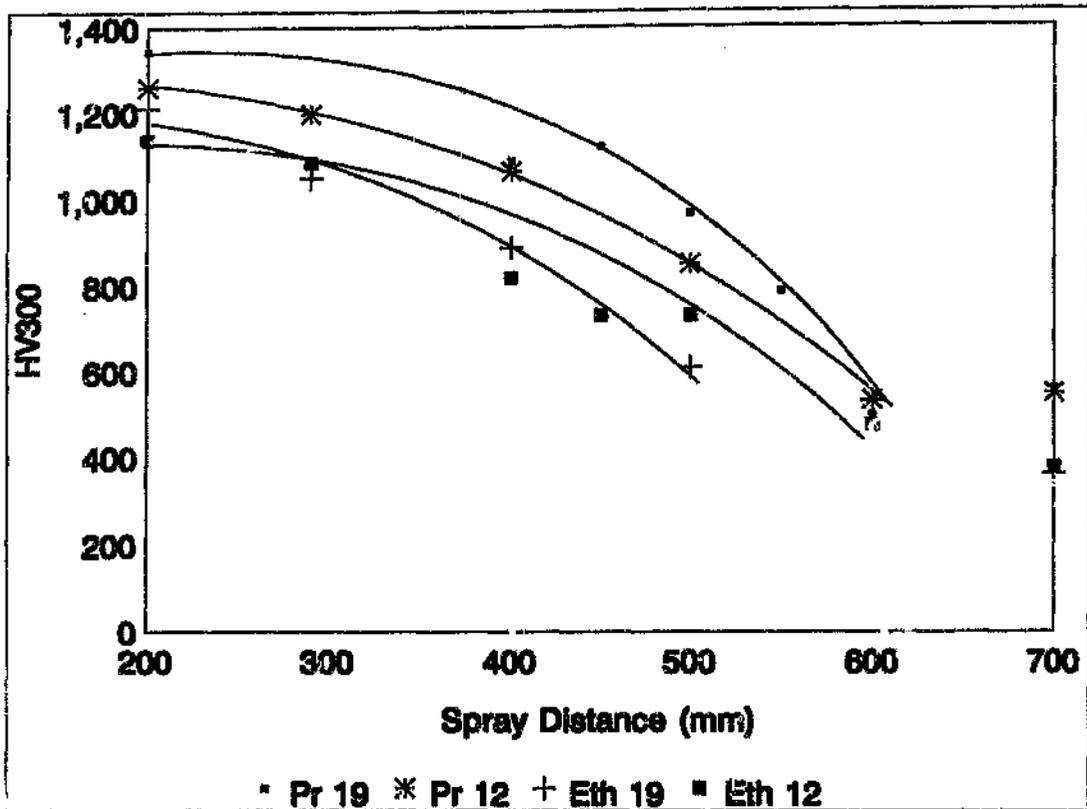


Figure 4.11 -The effect of spray distance on coating hardness with change in the following parameters: propane with 19 mm nozzle, propane with 12 mm nozzle, ethylene with 19 mm nozzle and ethylene with 12 mm nozzle.

The loss of the WC particles in the coating results in a rapid loss in overall coating hardness. At spray distances of more than 600 mm the coatings show increasing porosity levels with spray distance which adds another variable to the hardness measurement of the coatings. A linear trend would thus not be appropriate. The function of coating hardness against spray distance would thus better be defined by a quadratic polynomial. Figure 4.11 and Table 4.6 show that the quadratic function fitted to the data sets correlates well with the actual data with correlation coefficients of more than 0.95.

Parameter	Correlation coefficient of data against the function
Propane 19 mm Nozzle	0.95
Propane 12 mm Nozzle	0.98
Ethylene 19 mm Nozzle	0.95
Ethylene 12 mm Nozzle	0.97

Table 4.6. - The correlation coefficient of the hardness data with the corresponding data of the fitted function. (Appendix B)

Figure 4.11. shows that the coatings sprayed with propane are harder than those sprayed with ethylene. Table 4.7 confirms this by showing that there is a significant difference between the data sets of Propane12 and Ethylene12 and the data sets of Ethylene19 and Propane19. This difference could be due to the fact that ethylene flame burns at a higher temperature than that of propane. The increased flame temperature could lead to overheating and liquafaction of the particle and subsequent increased loss of WC particles on impact. This would in turn result in a lower WC content in the coating and thus an overall reduction in the hardness of the coating.

Parameters	Correlation	Significant Difference
Eth12 -Eth19	0.97	No
Eth12-Prop12	0.85	Yes
Prop12-Prop19	0.99	No
Prop19-Eth19	0.93	Yes

Table 4.7. - The correlation coefficient and paired t-test for significant difference between the hardness sets of data

4.6. The effect of combustion temperature on the coating properties

The difference in flame temperature between propane and ethylene is relatively small. Ethylene burns at 2940°C and propane at 2825°C. The flames, however, seem to be very different in nature. The ethylene flame is shorter, better defined and with a darker flame colour than that of propane. This seems to suggest that ethylene has a faster combustion flame with a shorter high level heat input than propane.

Figure 4.12 and Figure 4.13 indicate that the deposit efficiency trends between propane and ethylene are not the same. The deposit efficiency of propane peaks at a spray distance of 400 mm and appears to fit in well with the trend discussed in Figure 4.1. The deposit efficiency increases steadily until a peak is reached after which it drops off due to entraining air.

The deposit efficiency of the coating, when sprayed with ethylene is already at a peak at 200 mm and begins to drop only at a spray distance of between 300 mm and 400 mm. This corresponds with a shorter and better defined flame which was observed during spraying. This observation together with the trends shown in Figure 4.12 and Figure 4.13 suggests that the particles were heated faster and to a higher level. The deposit efficiencies between a spray distance of 200 mm and 300 mm remains constant, which indicates that the Ni in the particles was heated to beyond its melting point.

It should be noted that the abrasion resistance follows the trend of the coating deposit efficiency. This supports the notion that the two properties are related to the bond strength of the coating particle. The abrasion resistance trends of the ethylene coatings were 30% to 50% lower than the coatings sprayed with propane. This could be due to the overheating of the coating particles when sprayed with the hotter ethylene. When the Ni in the particles liquefies, they run the risk of losing some of their fine WC particles on impact due to repulsion.

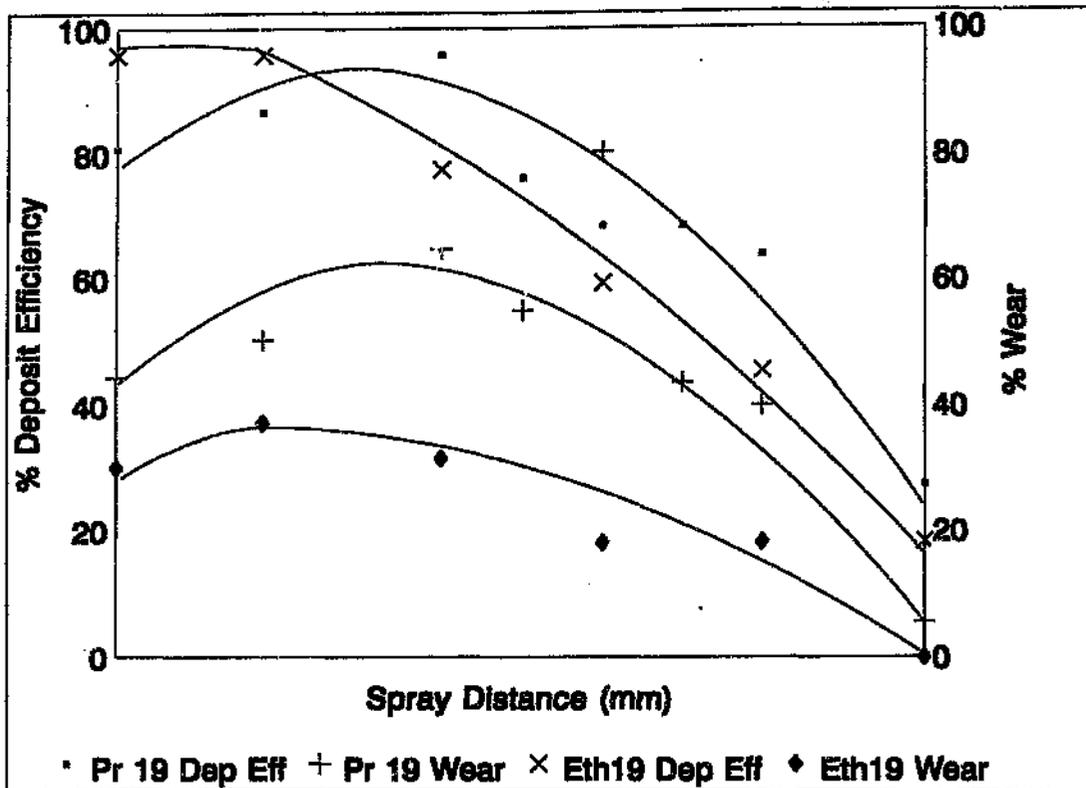


Figure 4.12 -The effect of propane and ethylene on the deposit efficiency and wear resistance using the 19 mm combustion chamber.

At greater spray distances the Ni in the coating particles cools down to below its liquidus level, forming a hard exterior shell, which will break open on impact onto the substrate. This does not lend itself particularly well to bonding and thus also to the abrasion resistance.

Table 4.8. shows that the correlation coefficient between the sets of data ranges between 0.73 and 0.85. This shows that the data sets for the different parameters do not correlate well. The wear data of the Ethylene 19 and Propane 19 sets and the Ethylene 12 and Propane 12 show a significant difference based on the paired t-test whereas the deposit efficiency of the same sets show no significant difference. This is also seen in Figure 4.12 and Figure 4.13. It seems that the deposit efficiencies of the data sets are both relatively high, whereas the wear resistance of the coatings sprayed with the ethylene flame is significantly lower than the equivalent coatings sprayed with propane. This could be due to overheating of the particles sprayed with ethylene, which subsequently lose a significant amount WC particles on impact with the substrate but still retains the bulk of volume which consists of the Nickel matrix.

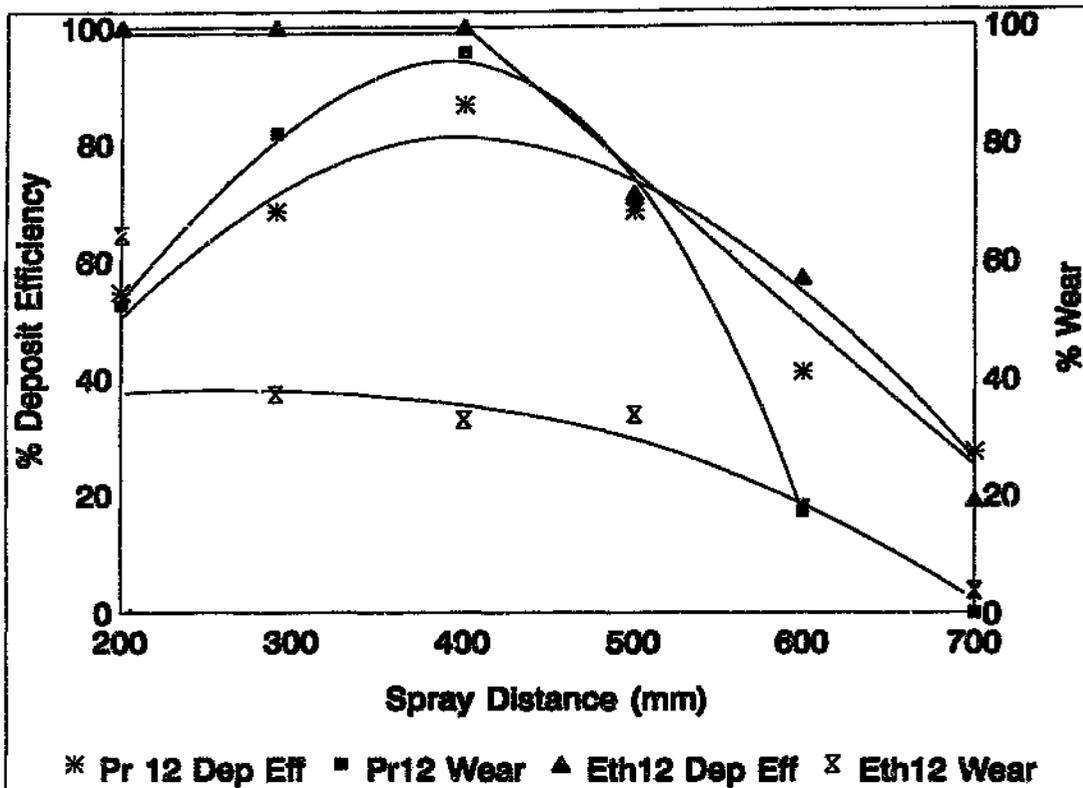


Figure 4.13 -The effect of propane and ethylene on the coating deposit efficiency and wear resistance using the 12 mm combustion chamber.

Parameters	Correlation	Significant Difference	Spray Distance at point of inflection
Deposit Efficiency (Prop 19 - Eth 19)	0.85	No	121
Deposit Efficiency (Eth 12 - Prop 12)	0.82	No	80
Wear Resistance (Prop 19 - Eth 19)	0.85	Yes	97
Wear Resistance (Eth 12 - Prop 12)	0.73	Yes	39

Table 4.8. - The correlation coefficient, paired t-test for significant and the difference between the spray distance of point of inflection between data sets

4.7. The effect of combustion chamber size on the coating properties

In Figure 4.14, where the coating was sprayed using propane, the deposit efficiency peak for the 19 mm combustion chamber is at a slightly shorter spray distance than for the 12 mm combustion chamber. The deposit efficiency trends have different slopes. The trend of the 12mm combustion chamber shows a much steeper curve than that of the 19 mm combustion chamber. This corresponds to the expected behaviour of the coating when changing the combustion chamber.

It takes longer for the coating particle to pass through a larger combustion chamber than through a smaller combustion chamber. The larger combustion chamber size should thus allow the coating particle to heat to a higher temperature before it is accelerated through the nozzle. It therefore seems plausible that the coating properties should peak at a shorter spray distance if a larger combustion chamber is used. The shorter combustion chamber allows for less heating and thus lower coating particle temperature on exiting the gun. As the particles travel through the flame they are heated further until they are cooled by the entraining air.

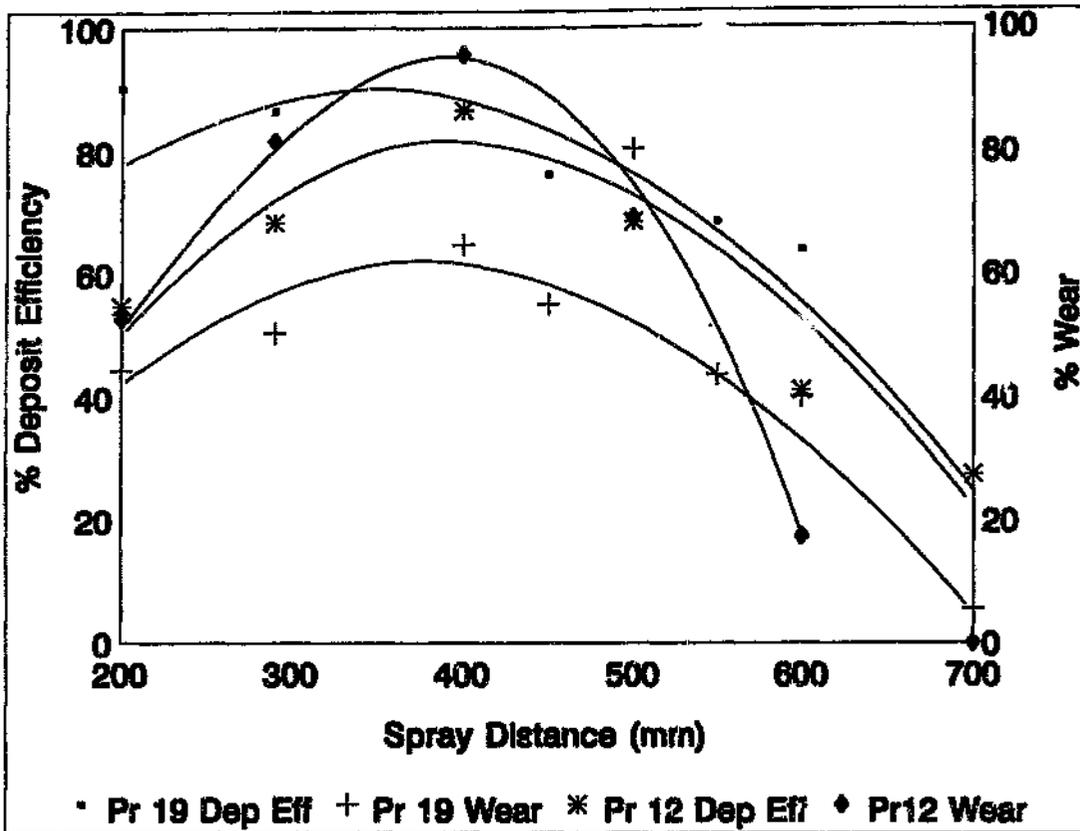


Figure 4.14 -The effect of the 19mm Nozzle and the 12 mm Nozzle on the coating deposit efficiency and wear resistance using propane fuel gas.

If the particles are heated to a higher temperature in the gun the peak will be less defined. There is a possibility that the Ni in the coating particles was overheated and liquefied when the coatings were sprayed with the 19 mm combustion chamber. This is evident from the lower abrasion resistance trend of the 19 mm combustion chamber compared to the abrasion resistance trend of the coatings sprayed with the 12 mm combustion chamber.

In Figure 4.15, where the coatings were sprayed with ethylene, the coating properties of the specimens sprayed with the 19 mm and the 12 mm combustion chambers are almost that same. At spray distances between 200 mm and 300 mm the deposit efficiency seems to be at its maximum throughout this range with both combustion chamber sizes. This indicates that the particles in the combustion chambers are molten at a spray distance before 200 mm.

Since the cooling effect of the entraining gases are similar for both combustion chamber sizes it seems reasonable that the trend of coating properties with spray distance should be similar. The abrasion resistance trend is again very similar to the deposit efficiency trend for the coatings sprayed with ethylene. There is no significant difference in abrasion resistance when changing the combustion chamber size. From the deposit efficiency trends of the coatings sprayed with the 19mm and the 12 mm combustion chamber it is evident the Ni in the coating has liquefied. It is therefore reasonable to expect that the coatings would have lost some of their WC when impacting onto the substrate. The abrasion resistance of the coating is thus expected to be relatively low.

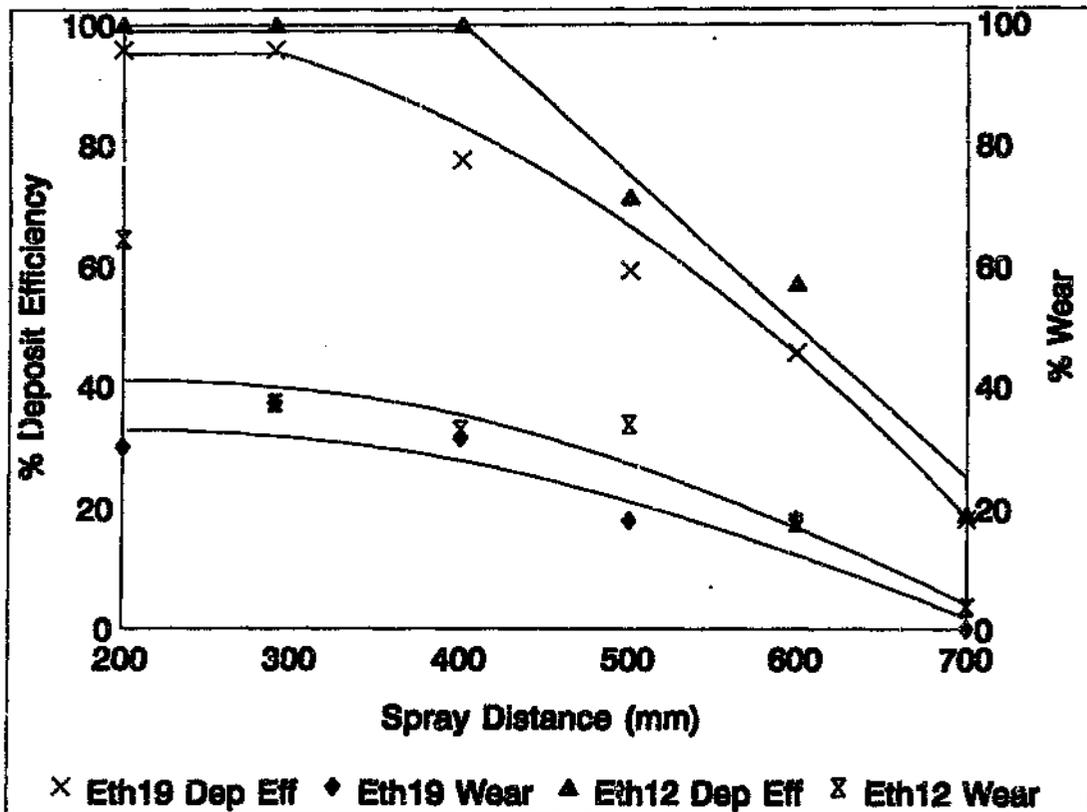


Figure 4.15 -The effect of the 19 mm nozzle and the 12 mm nozzle on the coating deposit efficiency and wear resistance using ethylene fuel gas.

Table 4.9. shows that the correlation coefficient between the sets of data ranges between 0.75 and 0.87. The correlation is not particularly good, but it should be noted that no significant difference could be found between the Propane 12 and Propane 19 data sets for the deposit efficiency as well as wear resistance. Furthermore, the spray distance for peak

deposit efficiency and wear resistance between these sets is not more than 25 mm. This is a small difference in spray distance and may be attributed to the difference in spray nozzles.

Parameters	Correlation	Significant Difference	Spray Distance at point of inflection
Deposit Efficiency (Prop 19 - Prop 12)	0.85	No	16
Deposit Efficiency (Eth 19 - Eth 12)	0.87	No	25
Wear Resistance (Prop 19 - Prop 12)	0.78	No	20
Wear Resistance (Eth 19 - Eth 12)	0.75	No	38

Table 4.9. - The correlation coefficient, paired t-test for significant and the difference between the spray distance of point of inflection between data sets

Again no significant difference could be found between the Ethylene 12 and Ethylene 19 data sets for the deposit efficiency as well as wear resistance. The spray distance for peak deposit efficiency and wear resistance between these sets is not more than 38 mm. This difference in spray distance could be attributed to the difference in spray nozzles.

4.8. The effect of volume gas flow rate on the deposit efficiency

For the stoichiometric volume gas flow rate the 100% level represents the suggested level by the suppliers of the equipment. The deposit efficiency was measured for stoichiometric volume gas flow rates ranging from 70% to 110%. These are the levels between which the flame is stable and the maximum output capability of the spray equipment is reached.

Fig 4.16 clearly indicates that the deposit efficiency shows a peak with a change in spray distance for each volume gas flow rate setting. The peak deposit efficiency value and position with respect to spray distance changes with volume gas flow rate. Figure 4.17 shows how the trend of the deposit efficiency peaks vary with change in volume gas flow rate.

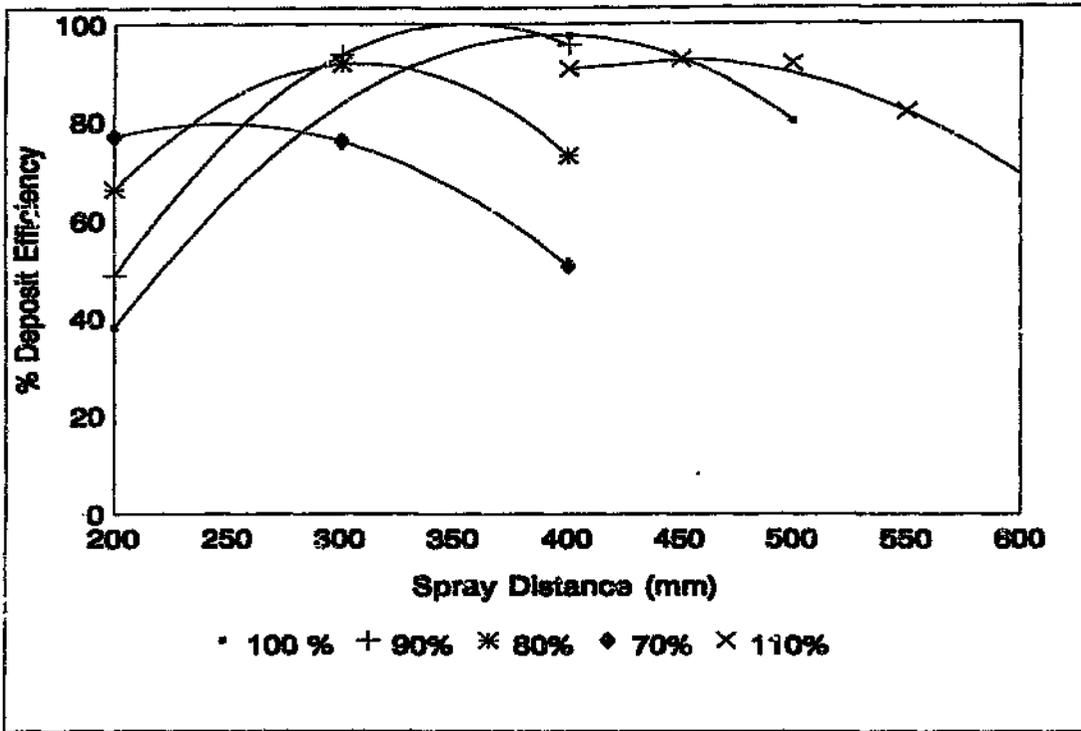


Figure 4.16 -The effect of stoichiometric volume gas flow on the deposit efficiency.

With the increase in volume gas flow rate, the length of the flame is increased. This causes the cooling of the entraining gas to affect the flame at a longer spray distance. The coating particle is thus exposed to the flame for a longer time reaching higher impact temperatures. The increase of the volume gas flow rate also increases the thrust of the flame and effectively the acceleration of the particle. The increase of the particle acceleration and velocity results in a shorter dwell time in the flame and thus a lower particle impact temperature. The effect of these two influences is clearly evident in Figure 4.16 and Figure 4.17 where the 70% to 90% curves show an increase in deposit efficiency whilst the 100% and 110% curves show that the deposit efficiency decreases with increases with volume gas flow rate.

Since the data sets for the volume flow rate only had three points the highest polynomial function that can be fitted is a quadratic curve which has to be a perfect fit and will thus have a correlation coefficient of 1. If more data were available a cubic polynomial could have been fitted, with probably a lower correlation coefficient.

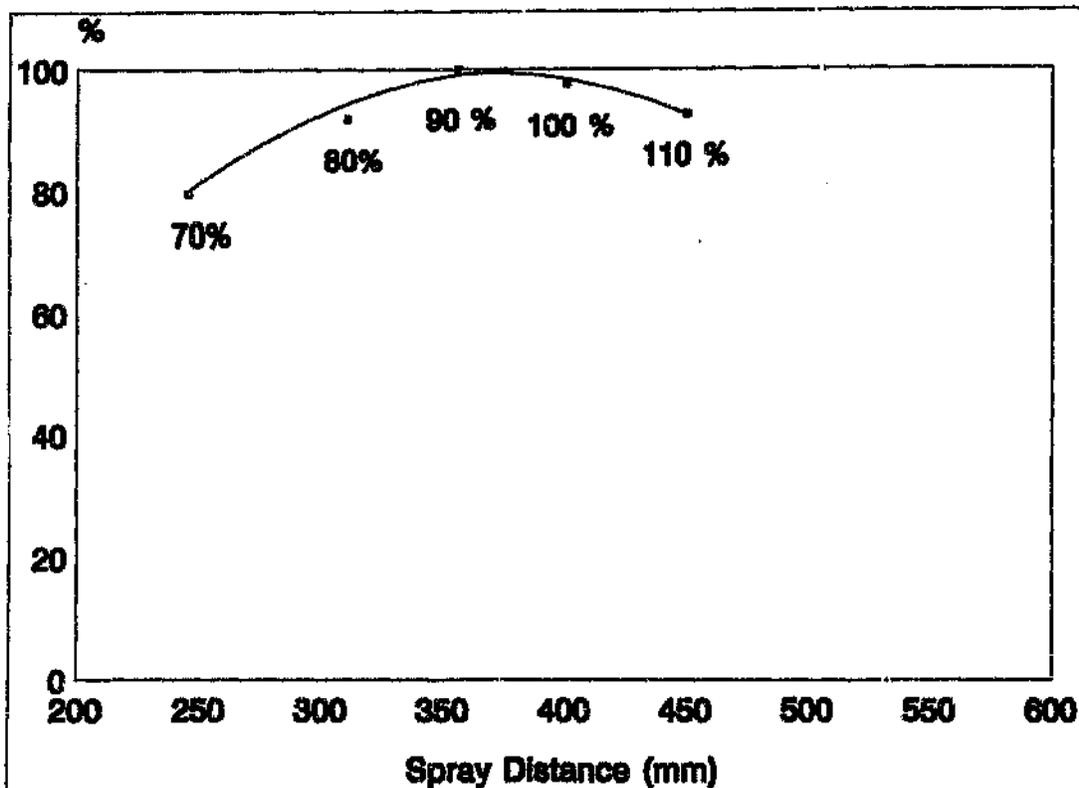


Figure 4.17 -The effect of stoichiometric volume gas flow on the peak deposit efficiency as obtained from Figure 4.16.

5. Summary of Conclusion

The primary objectives of this project were to investigate and analyse the effect of spray parameters on the properties of 88/12 WC/Ni coatings sprayed with the TOP GUN thermal spray system.

These objectives were achieved by:

- 1 - Identifying the relevant spray parameters affecting the properties of the coatings.
- 2 - Spraying coatings with various parameters.
- 3 - Measuring the properties of the coatings.
- 4 - Analysing the effect of the spray parameters on the coating properties.
- 5 - Deducing the mechanisms which govern the properties of the coatings.

From the work performed in this project the following conclusions can be made:

- 1 - With the change in spray parameters the hardness shows a tendency to decrease with spray distance, while the abrasion resistance and deposit efficiency increases, peaks and decreases with change in spray distance. The hardness data can best be approximated by fitting a linear or cubic curve. It was shown that there is a significant difference between the standardised hardness data and the wear resistance data. Porosity levels do not change significantly with spray distance except at spray distances above 600 mm where abrasion resistance and deposit efficiency is poor. The traditional methods of measuring the hardness and coating porosity to determine the quality of the coatings therefore do not apply to coatings sprayed with a HVOF thermal spray system.
- 2 - The deposit efficiency and abrasion resistance show related trends to that of the particle impact temperature, with a change in spray distance. This trend behaviour can best be approximated by fitting a cubic polynomial to the data. The wear mechanism is shown to be related to the resistance of the coating particle to be ripped out of the coating during abrasion. This resistance to rip out is related to the bond strength of the particle to the coating, which in turn is related to the particle impact temperature. The deposit

efficiency is also related to how well a particle will bond to the coating. Thus, by measuring the deposit efficiency of a coating one can determine whether the abrasion properties are at an optimum.

- 3 - Changes in fuel gas does not seem to affect the abrasion resistance significantly. This is, however not the case for the deposit efficiency. The coating particles sprayed with ethylene reach a higher temperature at shorter spray distances than the coating particles sprayed with propane. The deposit efficiency data showed no significant difference between the coatings sprayed with ethylene and those sprayed with propane. The wear resistance data, however, was significantly lower for coatings sprayed with ethylene than those sprayed with propane.
- 4 - The change in combustion chamber size changes the particle temperature with spray distance. The deposit efficiency and abrasion resistance trends thus shift with spray distance respectively. No significant difference could be found between the wear resistance and deposit efficiency data for the coatings sprayed with the 19 mm nozzle and the coatings sprayed with the 12 mm nozzle. The only difference depicted is that the spray distance of the peak values for the wear resistance and the deposit efficiency was slightly higher for the coatings sprayed with the 19 mm nozzle than those sprayed with the 12 mm nozzle.
- 5 - The change in volume gas flow rate shifts the deposit efficiency peak with spray distance. As the volume gas flow rate increases the peak deposit efficiency increases, levels off and decreases again. This is due to the dynamics of the change in thrust of the flame, the acceleration of the particle and the entrainment of the surrounding air.

The fact that the deposit efficiency of a coating relates to the wear resistance of a coating has significant implications in the improving the ease and decreasing the cost of determining the peak wear resistance of coatings sprayed with a HVOF thermal spray system.

6. References

- 1 Thorne, M.L., Peake, T.A. Jr and Meyer, W.B., 1985: *Thermal Spraying: Practice, Theory, and Application*, American Welding Society, Miami.
- 2 Sturgeon, A., 1992: Ceramic coatings - a growing technology, *Welding Journal, Bulletin 2*, p. 31-35.
- 3 Thorpe, M.L. and Richter, H.J., 1992: A pragmatic analysis and comparison of HVOF processes, *Journal of Thermal Spray Technology*, Vol. 1 No. 2, p. 161-170.
- 4 Nakagawa, M., Shimoda, K., Tomoda, T., Koyama, M. Ishikawa, Y and Nakajima, T., 1990: Development of mass production technology of arc spraying for automotive engine aluminium alloy valve lifters, Proceedings of the 3rd National Thermal Spray Conference, Long Beach, California, 20-25 May, pp. 457-464.
- 5 Fauchais, P., Coudert, J.F., Vardelle, M., Vardelle, A. and Denoirjean, A., 1992: Diagnostics of thermal spray plasma jets, *Journal of Thermal Spray Technology*, Vol. 1 No. 2, p. 117-128.
- 6 Berndt, C.C., 1992: Current problems in plasma spray processing, *Journal of Thermal Spray Technology*, Vol. 1 No. 4, p. 341-356.
- 7 Fukunuma, H., 1994: A Porosity and Flattening Model of an Impinging Molten Particle in Thermal Spray Coatings, *Journal of Thermal Spray Technology*, Vol. 3 No. 1, pp. 33-44.
- 8 Blann, G.A., Diaz, D.J. and Nelson, J.A., 1989: Raising the standards for coating analysis, *Advanced Materials and Processes*, December, pp.62-65.

- 9 Fowler, D.B., Riggs, W. and Russ, J.C., 1990: Image Analysis Applied to Thermal Sprayed Coatings, Proceedings of the 3rd National Thermal Spray Conference, Long Beach, California, 20-25 May, pp. 303-320.
- 10 Lin, C.K. and Berndt, C.C., 1994: Measurement and analysis of adhesion strength for thermally sprayed coatings, *Journal of Thermal Spray Technology*, Vol. 3 No. 1, p. 75-104.
- 11 Kuroda, S., Fukushima, T. and Kitahara, S., 1992: Significance of quenching stress in the cohesion and adhesion of thermally sprayed coatings, *Journal of Thermal Spray Technology*, Vol. 1 No. 4, p. 325-332.
- 12 Gudge, M., Rickerby, D. S. and Kingswell, R., 1990: Residual Stresses in Plasma Metallic and Ceramic Coatings, Proceedings of the 3rd National Thermal Spray Conference, Long Beach, California, 20-25 May, pp. 331-338
- 13 Avner, S.H., *Introduction to Metallurgy*, 2nd ed., Mc Graw-Hill Book Company
- 14 Burden, R.L., and Faires, J.D., *Numerical Analysis*, 3rd ed. Boston: Prindle, Weber & Schmidt, 1985.
- 15 Guttman, I., Wilks, S.S., and Hunter S. J., *Introductory Engineering Statistics*, John Wiley & Sons, 1982.

7. Appendix A – Sample calculation for statistical evaluation

Sample Data - Properties of Coatings Sprayed with Propane and a 19 mm Nozzel

Spray Distance	Deposit Efficiency %	Wear Resistance %	Standardized Dep Efficiency against Wear Resistance	(Wear - St Dep Eff) d	(Wear - St Dep Eff) ² d ²
200	91	46.60	62.73	16.13	260.21
290	98	50.94	67.95	17.01	289.46
400	99	68.57	68.61	0.04	0.00
450	75	58.24	52.27	-5.97	35.61
500	74	51.66	50.96	-0.70	0.49
550	71	46.20	49.00	2.80	7.86
600	66	42.39	45.74	3.35	11.23
700	28	5.77	19.60	13.83	191.31
Sum	601.88	370.37	416.88	46.51	796.17
Mean (μ)	75.24	46.30	52.11	5.81	99.52
St dev	22.79	18.31	15.79	8.67	125.54
n				8	

Table 7.1. - Data used to determine the significant difference of the standardised deposit efficiency and the wear resistance of the coatings sprayed with propane and a 19 mm nozzle for the coating

Standardisation

The maximum value for the wear resistance is 68.57 %. The maximum Value for the Deposit efficiency is 99 %. To standardise the deposit efficiency values against the wear resistance values the deposit every deposit efficiency value needs to be divided by 99 and multiplied by 68.57.

Significance evaluation using the paired t-test

The paired t-test methodology sets two hypothesis:

$$H_0: \mu_d = 0$$

$$H_0: \mu_d \neq 0$$

Where d is the difference of the corresponding data between two data sets and μ_d is the mean of the population from which d is drawn. The standard deviation s_d of the population of d is determined by:

$$s_d = \sqrt{\frac{\sum (d - \mu_d)^2}{n}}$$

Thus, based on the data in Table 7.1,

$$s_d = 8.67$$

From the mean and the standard deviation of the difference of the two data sets in Table 7.1.,

$$t_{(n-1)} = \frac{-\mu_d}{\left(\frac{s_d}{\sqrt{(n-1)}} \right)}$$

$$t_{(8-1)} = \frac{-5.81}{\left(\frac{8.67}{\sqrt{(8-1)}} \right)} = -1.77$$

calculated for 8 number of data points.

The t_7 is then compared to the t-distribution table¹⁵ which shows that for 7 degrees of freedom there is a 5 % probability that $|t|$ will exceed the tabulated value.

$$v = 2.36$$

Since

$$T_7 < 2.36$$

H_0 is retained. Thus, there is no significant difference between the two sets of data.

Correlation

Spray Distance	Deposit Efficiency %	Wear Resistance %	(Wear - μ)	(Wear - μ) ²	Dep Efficiency Standardized %	(St. Dep. Eff - μ)	(Wear - μ) ²	(Wear - μ) [*] (St. Dep - μ)
200	91	46.60	0.30	0.09	62.73	10.62	112.81	3.23
290	98	50.94	4.64	21.56	67.95	15.84	251.03	73.57
400	99	68.57	22.27	496.12	68.61	16.50	272.31	367.56
450	75	58.24	11.94	142.65	52.27	0.16	0.03	1.94
500	74	51.66	5.36	28.77	50.96	-1.15	1.31	-6.15
550	71	46.20	-0.10	0.01	49.00	-3.11	9.65	0.30
600	66	42.39	-3.91	15.26	45.74	-6.37	40.56	24.88
700	28	5.77	-40.53	1642.38	19.60	-32.51	1056.80	1317.44
Σ	601.88	370.37		2346.84	416.88		1744.50	1782.77
μ	75.24	46.30			52.11			

Table 7.2. - Data used to determine the correlation coefficient of the standardised deposit efficiency and the wear resistance of the coatings sprayed with propane and a 19 mm nozzle for the coating

The Correlation between the data sets of the wear resistance and the standardised deposit efficiency is

$$r^2 = \frac{1782.77}{\sqrt{2346.84 * 1744.50}} = 0.88$$

8. Appendix B – Summary Tables of Statistical calculations

Comparison between the Standardised Dep Eff and Wear Resistance data					
	Corr	Std Dev	Paired t	t-value	d (SD) of max f(x)
Eth 19	0.98	3.98	0.77	3.18	30
Eth 12	0.86	10.55	2.40	2.57	43
Prop 19	0.91	8.11	1.89	2.36	6
Prop 12	0.84	21.93	0.21	2.78	3

Comparison between Deposit Efficiency Data Sets					
	Corr	Std Dev	Paired t	t-value	d (SD) of max f(x)
Eth19 - Eth12	0.87	20.45	2.17	2.57	25
Prop 19 - Prop12	0.85	29.59	-1.22	2.78	16
Eth 12 - Prop 12	0.82	15.97	0.87	2.78	80
Prop19 - Eth 19	28.30	24.31	-2.11	2.57	121

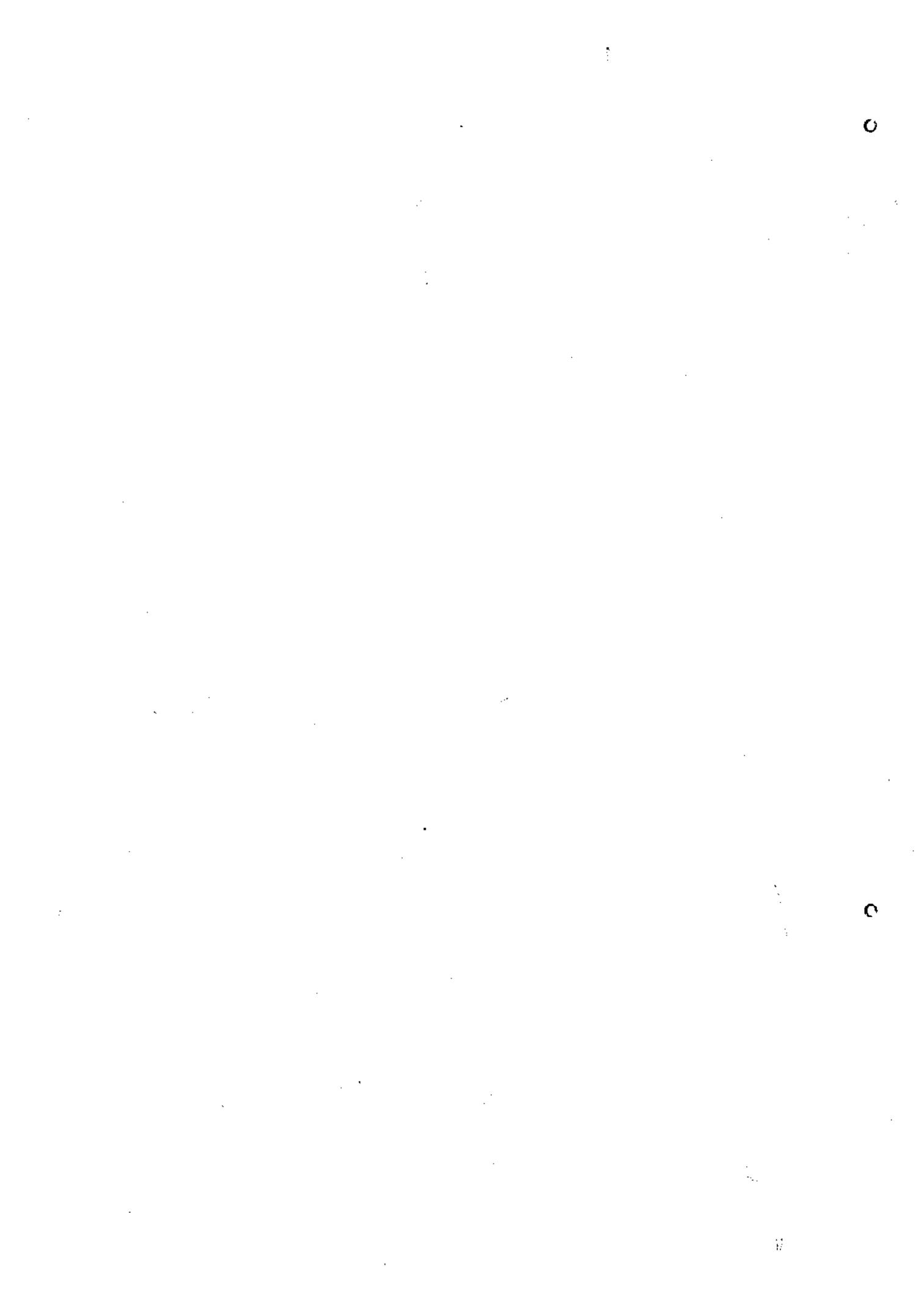
Comparison between Wear Resistance Data Sets					
	Corr	Std Dev	Paired t	t-value	d (SD) of max f(x)
Eth19 - Eth12	0.75	11.88	2.53	2.57	38
Prop 19 - Prop12	0.78	29.02	0.13	2.78	20
Eth 12 - Prop 12	0.73	22.11	-1.90	2.78	39
Prop19 - Eth 19	0.85	23.12	-2.77	2.57	97

Comparison between Hardness Data Sets					
	Corr	Std Dev	Paired t	t-value	
Eth19 - Eth12	0.97	70.26	-0.15	2.57	
Prop 19 - Prop12	0.99	187.39	-0.41	2.78	
Eth 12 - Prop 12	0.85	63.50	-4.45	2.78	
Prop19 - Eth 19	0.93	115.14	-3.27	2.57	

Comparison between standardised Hardness and Wear Resistance Data Sets					
	Corr	Std Dev	Paired t	t-value	
Eth 19	0.89	11.32	-5.86	3.18	
Eth 12	0.94	7.85	-6.59	3.18	
Prop 19	0.62	17.17	-3.71	2.36	
Prop 12	0.87	13.36	-2.86	2.78	

Comparison of Data and Best Fit Function

	Wear Eth 19	Dep Eth 19	HV Eth 19	Wear Eth 12	Dep Eth 12	HV Eth 12	Wear Prop 19	Dep Prop 19	HV Prop 19	Wear Prop 12	Dep Prop 12	HV Prop 12
Spray Distance=200	33.26	100.00	1213	39.39	100.00	1138	46.60	90.57	1345	58.20	57	1261.00
Spray Distance=290	41.24	100.00	1216	41.24	100.00	1085	50.94	98.11	1203	90.45	71	1198.00
Spray Distance=400	34.91	80.19	1050	36.41	100.00	820	68.57	99.06	1089	61.71	90	1065.00
Spray Distance=450							58.24	75.47	1120			
Spray Distance=500	8.22	73.00	850	37.33	70.75	732	81.77	73.58	968	76.40	71	851.00
Spray Distance=550							46.20	70.75	790			
Spray Distance=600	6.76	9.43	530	19.55	56.60	476	42.39	66.04	498	19.22	42	533.00
Spray Distance=700	0.00	4.72	361	8.11	9.43	375	5.77	28.30	560	0.00	28	548.00
Coefficient a	3.27E-06	3.44E-06	-4.63E-03	-3.38E-06	-3.00E-07	-4.64E-03	-8.94E-07	-9.30E-08	-1.10E-02	-8.38E-07	1.51E-06	-4.64E-03
Coefficient b	-4.21E-03	-4.67E-03	1.92E+00	4.19E-03	-1.00E-04	1.92E+00	5.56E-04	-2.96E-04	6.83E+00	-9.70E-06	-2.63E-03	1.92E+00
Coefficient c	1.60E+00	1.71E+00	1.05E+03	-1.71E+00	1.26E-01	1.05E+03	2.19E-02	1.91E-01	3.55E+02	3.37E-01	1.30E+00	1.05E+03
Coefficient d	-1.46E+02	-8.48E+01		2.66E+02	8.16E+01		2.45E+01	9.40E+01		1.06E+00	-1.15E+02	
Corr of data vs. f(x)	0.98	0.99	0.94	1.00	0.99	0.97	0.92	0.96	0.94	0.97	0.91	0.94
Number of Data Points	4	4	4	6	6	6	7	7	7	6	6	6
Spr. Dist. for max. data	290	290		290	290		400	400		400	400	
Spr. Dist. for max. f(x)	285	255		223	280		382	376		362	360	



Author: Lambrecht Hendrik Oliver.

Name of thesis: The effect of particle impact temperature on the deposit efficiency and cutting wear rate of 88/12 WC/Ni coatings sprayed with the TOP GUN HVOF thermal spray system.

PUBLISHER:

**University of the Witwatersrand, Johannesburg
©2015**

LEGALNOTICES:

Copyright Notice: All materials on the University of the Witwatersrand, Johannesburg Library website are protected by South African copyright law and may not be distributed, transmitted, displayed or otherwise published in any format, without the prior written permission of the copyright owner.

Disclaimer and Terms of Use: Provided that you maintain all copyright and other notices contained therein, you may download material (one machine readable copy and one print copy per page) for your personal and/or educational non-commercial use only.

The University of the Witwatersrand, Johannesburg, is not responsible for any errors or omissions and excludes any and all liability for any errors in or omissions from the information on the Library website.