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*Review paper*

# Erosion - Corrosion of Cermet Coating

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Cermet-based coatings are being increasingly used to combat erosion-corrosion in oil and gas industries such that occurring in offshore piping, production systems and machinery involving fluid and/or slurry flowing corrosive media which often contain solid particles such as sand. This leads to material/ substrate damage caused by the combined surface degradation mechanisms of erosion and corrosion. This review assesses the erosion-corrosion resistance and performance of cermet coatings applied by different thermal spraying methods. Electrochemical measurements, which monitor the erosion-corrosion mechanisms and coating integrity by themselves and when both erosion and corrosion act simultaneously are considered. In addition, surface characterization, and the extent of weight loss that covered through different combinations of cermet were reviewed. This paper also discusses different types of substrates as well as the thermal spray coating processes that appeared in the majority of publications such as atmospheric plasma spraying (APS) and electric arc spray (EArc) with special emphasis on high velocity oxy-fuel (HVOF) with regard to cermets applied to enhance erosion and corrosion resistance of the substrate. Electrochemical polarization measurements and salt spray test to evaluate the erosion-corrosion mechanisms and coating integrity are used to quantify the synergistic effects present when both erosion and corrosion acting simultaneously.

**Keywords:** HVOF; Corrosion; Erosion; Cermet coating

## 1. INTRODUCTION

Offshore oil and gas production environments represent aggressive conditions in terms of erosion and corrosion. Consequently, materials selection must be given a detailed attention at every stage of the design, construction and operation of systems and equipments including piping systems and their accessories, such as bends, elbows, tees, and valves. They also include devices that impart movement to fluid such as pumps, impellers, propellers, and blowers, which are exposed to or transport particle-laden fluids such as seawater. Therefore, full attention should be given to general erosion and corrosion resistances, in order to minimize premature failures, which lead to loss of production due to total shut downs and severe economic losses because of the inflating maintenance costs. Even more important is the need to maintain offshore safety. Thus the specification and the use of materials which combine erosion and corrosion resistances with high mechanical strength is a fundamental requirement in industrial applications leading to be the focus of interest in numerous researches. The electrochemical attack is caused by the surface condition and inherent nature of the bare metal and the corrosive fluid. The protective film on the metal surface is swept away by rapid movement of the processing fluid. [1, 2]. This review summarizes the various thermal spray coating processes such as high velocity oxy fuel (HVOF), electric arc spray (EArc) and atmospheric plasma spraying (APS) processes that are usually used in coating components subject to combined erosion-corrosion during service. Work in progress is reviewed to illustrate attempts being made to understand the interaction between erosion and corrosion with the aim to allow robust surface selection for fluid machinery and handling equipment, [3-5, 6-17]. Such coatings are applied by thermal spray technologies. The microstructure of a thermally sprayed coating is usually inhomogeneous. Discontinuities, such as pores, oxide lamellas or incomplete molten spray particles are typically present in the sprayed materials. The deposition methods for the wear protective coatings are (APS) and (HVOF) processes. Both of these methods have their own characteristics such as particle velocity and flame temperature, which results a coating layer that has different microstructure and properties, [3, 18].

The second purpose of this paper is to review: (a) the processing and characterization of various thermal spray coating materials; (b) erosion properties and resistance of cermet composite coatings; and (c) corrosion properties of the sprayed coatings strongly affect the materials loss rate under wear corrosion conditions.

## 2. EROSION, CORROSION AND THEIR INTERACTION

Actually, both erosion and corrosion processes assist each other to bring about larger amount of damage than the simple sum of the damage caused by each process separately [7]. The general area of material selection for erosion-corrosion service therefore poses a complex problem and the potential solutions offered in most literature are often reached by consideration of the independent erosion and corrosion behavior [8]. By definition, erosion-corrosion is the acceleration in the rate of deterioration of metal caused by the combined action of mechanical erosion and electrochemical attack. This combined effect, often termed synergy, can lead to greater damage and higher metal loss rate beyond that due to either erosion or corrosion alone and as a result can considerably shortens the service life of components [9]. In addition, the erosion in specific not only affects the protective coatings itself but may also damage the substrate, thus increasing the likelihood of substrate corrosion. This type of attack is known as erosion-corrosion [11, 14, 19]. The component of material loss under erosion-corrosion (T) is often represented by equation (1).

$$T = E + C + S \quad (1)$$

Where E is the material loss by pure mechanical erosion processes, C is the material loss by electrochemical corrosion processes and S, the synergy, is the combined interaction between the two processes. Thus, synergy is defined as "the difference between erosion-corrosion and the summation of its two parts" and can be expressed by equations (2) and (3).

$$S = T - (E + C) \quad (2)$$

Synergy can be broken down into two components, $\Delta E$ and $\Delta C$, where $\Delta E$ is the corrosion-enhanced erosion (sometimes called enhanced erosion loss due to corrosion: $\Delta E_C$ [18] and $\Delta C$ is the erosion-enhanced corrosion (sometimes called enhanced corrosion loss due to erosion: $\Delta C_E$ [18], as in equation (3).

$$S = \Delta E + \Delta C. \quad (3)$$

Erosion can mechanically strip the protective corrosion film creating fresh reactive corrosion sites, i.e., producing $\Delta C$, which depends on the integrity of the film formed. In reference to earlier publications, Wharton et al [14] have summarized the possible erosion-enhanced corrosion mechanisms which include: (i) increased mass transport by high turbulence levels; (ii) lowering of fatigue strength by corrosion; and (iii) surface roughening of the specimen during particle impact causing enhanced mass transfer effects and increased corrosion rate. In addition Corrosion-enhanced erosion mechanisms ($\Delta E$) are also possible, including: (iv) the removal of work hardened surfaces by corrosion processes which expose the underlying base metal to erosion mechanisms; (v) preferential corrosive attack at grain boundaries resulting in grain loosening and eventual removal. Most of the above mechanisms, if dominant, would be expected to lead to positive synergy but in some instances negative synergy can occur.

## 3. SUBSTRATES

The study of erosion-corrosion properties of materials in corrosive environments has been the object of great attention in recent years [6]. Several work investigating erosion-corrosion rates [20] and mechanisms has been focused towards metallic materials, ranging from cast iron [21], carbon steels [6] to the higher grades of austenitic [6, 7], super duplex stainless steels [8, 9], cast nickel- aluminum-bronze (NAB) [11, 14] high-grade nickel-base [20] and cobalt-base Stellite-6 alloys [8]. It is acknowledged that corrosion resistant alloys generally do not resist erosion well and the interactions (synergy effects) that exist between corrosion and erosion are not comprehensively covered. This presents a problem when erosion–corrosion resistant surface are being selected.

## 4. CERMET COATINGS

### *4.1 Definition, types and function of cermet coatings*

On account of the vulnerability of metallic materials in aggressive erosion-corrosion conditions, there is a strong incentive for alternative surface engineering options to be developed and implemented to more efficiently resist damage by this cause. Ceramic- metallic "Cermets" materials are often considered in service involving high erosion and corrosion conditions and there has been extensive consideration of thermal-sprayed cermets as surface coatings on conventional metallic materials [20]. The ceramic particles provide a high erosion resistance. The metallic binder phase makes the coating more ductile than a pure ceramic coating. The success of applying thermal spray coatings for improvement of wear resistance has been well documented [5, 13, 22, 23]. Examples of applications where both erosion and corrosion properties are involved is in the offshore structures and components. Valve components and certain parts of pipes like contractions, bends, T-connections etc. may be exposed to erosion and corrosion. In extreme cases, valves have been severely eroded within hours of service. Increasing the life times for these components by improving both the erosion and corrosion resistances, will improve the safety conditions, fewer shut-downs and large reductions in maintenance costs [24].

There are various types of cermet and also many different grades within the different types. Although cermet coatings have been around since the mid 1960’s, the coatings have evolved greatly over the past 15 years. Today’s coatings are superior in all aspects including cost, bond strength, reduced friction as well as corrosion and erosion resistance, [25]. Protection of the metallic components by cermet is an effective method to reduce erosion and corrosion, however, it has been stated [3] that cermet carbide coating; $Cr_3C_2$-NiCr, is an excellent replacement to hard oxide; $Cr_2O_3$. Generally the cermet coatings consist of WC or Cr C particles embedded in a metal binder, which can be a pure metal or a mixture consisting of Ni, Cr and Co. WC-Co and CrC-NiCr systems constitute two main carbide materials used in thermal spraying processes in order to improve the erosion/wear resistance and decrease the friction coefficient between various sliding components. Coatings of the WC-Co system generally have a higher hardness and wear resistance than CrC-NiCr coatings [26], however, the decarburization of WC into $W_2C$, $W_3C$ and even metallic W phase leads to the degradation of coating properties and limit the application of these coatings as well as due to the dissolution of Co phase leading to low corrosion resistance [18]. Such coatings are applied by thermal spray technologies. The microstructure of a thermally sprayed coating is usually inhomogeneous and contains discontinuities, such as pores, oxide lamellas or incompletely molten spray particles all of which may be present in the sprayed coating materials [3].

### *4.2 Performance of cermet coatings in erosive-corrosive environments*

The CrC-NiCr system coatings are widely used in high temperature-wear resistance and corrosion-resistant applications in aggressive environments such as oil and gas, aerospace and power generating industries. The CrC-NiCr coatings can be used in corrosive environments at service temperatures up to 800 to 900 $^{o}$C. The main shortcoming of CrC-NiCr coatings is a lower hardness than WC-Co system coatings. At low erosive conditions the erosion–corrosion and corrosion resistance of WC-Co-Cr coatings increase when increasing the Cr content in the metallic binder from 5 to 8.5 w t.% [12]. At high erosive conditions an increase of Cr content in the metallic binder from 5 t o 8.5 wt.% did not give any increase of the erosion- corrosion and corrosion resistance of WC- Co- Cr coatings. A reduction of the heat input during spraying reduced the degree of WC decomposition and improved the coating properties when the spray powder contained a large fraction of small grains.

De Souza et al [27] have focused on understanding the synergy effect (defined as the enhancement of erosion due to corrosion effects) on material loss of WC- Co- Cr thermally sprayed coating when two different microstructures are formed and also the influence of chemical composition of the coating. These microstructures resulted from the application of two thermal spraying techniques; namely, HVOF and Super Detonation-Gun (D-gun) process. Experiments showed that HVOF coatings have a slightly lower corrosion resistance than the (D-Gun) coatings but higher overall erosion–corrosion resistance. They concluded that different microstructures of thermal spray coatings lead to different erosion-corrosion resistances; hence the degradation rates and mechanisms are also different. The synergy of erosion-corrosion behavior of the coatings can change depending on the environment (sand loading), composition and microstructure. The formation of different tungsten carbides and a higher Cr amount can reduce the toughness of WC-Co-Cr coatings and reduce the corrosion rates under erosion–corrosion.

In other work [28], the authors have isolated the electrochemical and mechanical factors which affect the material degradation under erosion-corrosion environments as a means of understanding the degradation mechanisms and therefore moving towards coating improvement. The coating was WC-Co-Cr thermally sprayed using HVOF which was compared to austenitic and super duplex stainless steels. In this work it was demonstrated that the benefits of this type of coatings is dependant on environment severity and can provide good protection against erosion and corrosion in liquid–solid impingement when compared with stainless steels [28, 29]. The role of corrosion and synergy in the total damage on WC-Co-Cr- HVOF coating is more crucial than on the super duplex stainless steel. It was also found that the corrosion of small hard phase particles WC can accelerate the material loss under erosion–corrosion environments and is one important feature of the synergy effect. Results have shown that the damage of WC-Co-Cr- HVOF coating moves towards and falls into the corrosion-dominated regime meaning that there is an obvious potential benefit to be exploited if the corrosion component of damage, and in turn the synergy can be reduced [28]. De Souza et al [29], on the other hand, have concluded that the mechanisms of damage are dominated by erosion processes but corrosion is affected by erosion processes and is more important at the lower solid levels.

R. Wood [18] has reviewed some practical concerns when using WC- Co- Cr - HVOF coatings such as the level of porosity within the coatings which can accelerate crack propagation and coating removal under erosion and also can be interconnected such that electrolyte can permeate into the coating/substrate interface accelerating corrosion and corrosion driven coating-substrate de-bonding. An additional concern with multiphase coatings (carbide/metal matrix) is the potential for de-bonding between hard phase and softer matrix that can accelerate surface degradation. The role of corrosion and synergy in the erosion-corrosion degradation of WC-Co-Cr- HVOF thermally sprayed coatings have been studied [28] using electrochemical polarization techniques in saline solutions (3.5% NaCl) at varying temperatures. It was reported that corrosion proceeds, in the first instance, primarily by dissolution of the Co phase, depending on the integrity and thickness of the passive film on the binder phase ($Cr_2O_3$). Similar observations are reported for other compositions of thermally sprayed cermet coatings (WC-CrNi and WC/CrC- CoCr) [20]. The dissolution of the binder matrix phase at the hard phase/matrix interface is known mechanisms for synergy contributing to $\Delta E$. The action of erosion is also likely to weaken the hard phase/matrix interface and after cyclic loading from repeated solid particle impacts could lead to crack initiation at the interface. Permeation of electrolyte into these cracks could induce localized environments which are dramatically different (i.e low pH) from the bulk conditions and induce crevice corrosion which in turn contributes to increased $\Delta C$ levels.

Improvements in coating durability for erosion-corrosion applications are therefore more likely if the corrosion resistance can be enhanced. This can be achieved, as proposed [28], by improving the binder integrity by alloying, improving the hard phase stability and improving the integrity of the hard phase/binder interface. Coating $Cr_3C_2$-NiCr thermal spray coating using HVOF appear to be a better alternative to WC- Co-Cr in most cases mainly when better erosion or corrosion is required and therefore this type of coating was the focus of interest of some publications. N. Espallargas et al. [30] have compared two HVOF thermal spray coatings ($Cr_3C_2$-NiCr and WC-Ni) with the conventional hard chromium coatings. The coatings compositions were 80 $Cr_3C_2$-20 NiCr and 88 WC-12 Ni respectively. Both of these coatings were found to be promising alternatives to hard chromium from the point of view of erosion-corrosion resistance. At high erosive conditions, the coating structure and hardness play an important role in the erosion-corrosion mechanisms. The anisotropic behavior of the materials led to a higher material loss for lamellar structure; resulting from layer by layer deposition parallel to the substrate, than for the columnar one; resulting from Cr growth perpendicular to the substrate, when comparing hard chromium coatings and $Cr_3C_2$-NiCr coatings. WC-Ni coatings gave the lowest material loss due to its high hardness. It was also found that at high erosive conditions, the microstructure of WC coatings was responsible of its high erosion-corrosion resistance compared with $Cr_3C_2$ and hard chromium coatings. The reason is due to the fine and well distributed WC particles in the Ni binder. Electrochemical measurements, however, showed that $Cr_3C_2$-NiCr coatings were superior with respect to corrosion resistance compared to WC-Ni under both erosive conditions.

The effect of coating thickness on the corrosion behavior of thermally sprayed $Cr_3C_2$-NiCr HVOF coatings has been studied [15]. Thicker coatings permit the pass of the electrolyte due to the stresses generated during coating deposition and the corresponding crack formation between different layers. Thinner coating let the electrolyte go through the coating because it is not thick enough to correctly protect the base steel. Hence, it was concluded that the optimization of spraying parameters and stress relaxation processes will be as important as thickness when protection of the base steel is needed with cermet coatings.

### *4.3 Mechanical properties of cermet coatings*

The porosity and weak interface adversely affect the erosion property and the cracks allow corrosive substance in the environment to attach the protective coating [31]. One of the important applications of HVOF coatings is their use in dynamic components in various off-shore and oil and gas industrial equipments [32]. In service, these components are subjected to severe cyclic loading under an aggressive environment. Consequently, investigations of fatigue properties of HVOF coating are of utmost importance. This led to considerable research studies have been carried out to investigate various affecting parameters on the fatigue properties of HVOF-coated surfaces.

The effects of $Cr_3C_2$-25NiCr and WC-10Ni- HVOF coatings and hard chromium electroplating on the fatigue strength, abrasive wear and corrosion resistance of AISI 4340 steel was evaluated [33]. $Cr_3C_2$-25NiCr results in higher fatigue strength when compared to chromium electroplated coatings. With respect to WC-10Ni thermal spray coated, insignificant influence on the fatigue strength was detected. Salt spray test results showed that $Cr_3C_2$-25NiCr HVOF thermally sprayed coating has better corrosion resistance in comparison to WC-10Ni. It was also concluded that coatings $Cr_3C_2$- 25NiCr and WC-10Ni presented better abrasive wear resistance with lower wear weight loss than chromium electroplated.

In the HVOF process, it is the end-product quality that matters; in this case, coating structural homogeneity, adherence to the substrate underneath, and operational durability are the main concerns in ensuring the coating quality [16]. Consequently, investigations into the mechanical properties of coating becomes important for improving the durability of coating and also in order to better understand the influence of composition and microstructure on these properties, it is necessary to evaluate quantitatively the mechanical properties of the coatings [17]. Mechanical properties of HVOF coating were investigated by Brandt [34]. He showed that carbide coatings by the HVOF process with porosity levels of less than 1% behave like a homogeneous material with improved ductility. Fracture toughness of HVOF-sprayed WC–Co coating was investigated by De Palo et al. [35]. They indicated that Vickers indentation method was useful and it became a convenient technique for fracture toughness measurement of coatings. Fatigue properties of a 4340 steel with HVOF coating were studied by Herna´ndez et al. [36]. They showed that crack nucleation sites are associated with the presence of alumina particles left over from the grit blasting prior to coating. Mechanical properties and residual stress distribution of thermal spray coating were examined [37]. They showed that HVOF coating had more rigidity than coating by the atmospheric plasma spraying process. Fatigue behavior of HVOF-coated 4140 steel was investigated [38]. It was indicated that the possible existence of tensile residual stresses in the vicinity of the substrate–coating interface would assist in the propagation of the fatigue cracks nucleated at the alumina particles.

### *4.4. Applications of cermet coating*

A new application for thermally sprayed cermet coatings is as replacements for hard chrome plating. Hard chrome plating can produce a wear resistant coating with good surface finish at cost effective price. However, there are growing environmental concerns associated with the disposal of the effluents from the used plating solution and these concerns have caused the cost of the process to increase. Cermet coatings have a wear resistance which is between 2.5 and 5 times better than hard chrome plating and do not suffer from effluent disposal problems. They are therefore finding increasing use at the expense of hard chrome plating, particularly if wear resistance is important or if a thick coating is required on a large part, [25]. In corrosive media the wear resistance of cermet coatings depends on the corrosion resistance of the metallic binder. Other factors influencing the coating deterioration are the corrosivity of the media and any galvanic interaction from the surrounding material. The corrosion resistance of the metallic binder should be comparable to the material of the rest of the system. This is especially important when the surrounding materials are corrosion resistant alloys as stainless steels, where the coatings otherwise will act as an anode. [24]

## 5. TYPES OF THERMAL SPRAY COATING PROCESSES

Here are some of thermal spray coating processes, for example: APS is the most common thermal spray process to deposit ceramic coatings. However, HVOF methods can produce metallic coatings with low porosity and excellent wear resistance. The deposition methods most frequently used for the erosion protective coatings are super detonation gun (D-gun), the least appearing in literature, air plasma spraying (APS), and high- velocity oxygen-fuel (HVOF) flame spray processes. In the D-gun the gases (acetylene and oxygen) are mixed along with a pulse of powder introduced into the barrel. Detonation using a spark generates waves of high temperature and pressure which heat the powder particles to their melting point or above. Particle velocities of about 750 m/s, can be achieved. This process is a non-continuous process by the fact that after each detonation the barrel is purged with nitrogen and the process is repeated at up to 10 times per second [27]. The APS process is basically the spraying of molten material onto a surface to form a coating [47]. Sprayed material in the form of powder is injected into a very high temperature plasma flame, where it is rapidly heated and accelerated. The melted droplets would impact on the substrate surface, flatten, spread and rapidly cool down, forming the so-called splats. The final coating consists of number of splats. However, the layers deposited by plasma spray process have some disadvantages, e.g. micro-cracks, poor adhesion between the coating and substrate, phase changes due to high-temperature exposure, non-uniformity in the coating density, and improper microstructural control, which could result in failure of the implanted system. The HVOF process [27] comprises a mixture of fuel (propane, propylene, hydrogen or acetylene) and oxygen which are burned in the chamber and because of the expansion the gas velocity can become supersonic. Powder is introduced axially, heated, melted and accelerated. The powder normally reaches velocities of around 550 m/s. A great advantage of HVOF on conventional thermal spraying such as APS is high particle velocity and low thermal energy [10] (lower temperature (1900–3000K)) which reduces the chance of carbide particles changing or oxidizing during the process (decarburization) [27].

Generally these methods have their own characteristics such as different spray particle velocities and temperatures which results in coatings having different microstructure and properties [3]. During the spraying processes and the cooling of deposits complex chemical transformations of the materials occur. The main phenomena which occur during APS or HVOF spraying of cermets are the thermal decomposition of the tungsten monocarbide WC or chromium carbide $Cr_3C_2$ and the carbide reactions with the metallic binder [3]. The decarburization of WC, followed by the formation of undesirable carbides like $W_2C$, complex Co-W-C and metallic tungsten occur often during APS because of the high temperature of the plasma flame and the oxidizing spray atmosphere. With a significant lower flame temperature and higher particle velocity the HVOF spraying leads to less phase transformation and produces denser coatings with lower porosity. Due to the technology improvement that has occurred during the last years, HVOF provides coatings with better compaction and low chemical decomposition, especially for WC- based coatings [5]. In addition, one of the great advantages of the HVOF process is the higher velocity reached by the particles and the low temperatures involved which minimizes any potentially damaging effects to the coating and substrate [28].

### *5.1 High Velocity Oxy-fuel (HVOF) spray coating*

This method is the state-of-art-technology in the heat spray sphere where oxygen and kerosene are the heat energy source. Typical materials for HVOF spraying are cermets (ceramic-metal), most often tungsten carbides and chrome based. Wear and tear resistant and corrosion resistant coatings in different environments are typical applications, [20–39]. The high velocity oxygen fuel (HVOF) powder spray process represents the state-of-the-art for thermal spray metallic coatings and can result in very dense, tightly adherent coatings with little or no oxidation during the application and low residual stresses, [23]. Deposition of coatings by thermally activated processes like HVOF thermal spraying has been successfully used for producing nanocrystalline (NC) coatings. Nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate, [4]. Ceramic coatings are attractive as they possess good thermal and electrical properties, and are more resistant to oxidation, corrosion, erosion and wear than metals in high-temperature environments. Nanoparticles of diamond as well as chemical compounds used for hard coatings (SiC, $ZrO_2$, and $A1_2O_3$) are commercially available, with typical particle sizes in the range 4-300 nm. Within tribology, a new development has been to deposit nano-coatings from colloids, e.g. of graphite. Nano-sized silica has proved to be an alternative to toxic chromate conversion coating. [4, 22]

The HVOF spraying WC-based cermet hard coatings such as WC-Co, WC-CoCr and others have been investigated by W. Fang et al [5] for obtaining the coatings of high hardness, wear resistance, thermal stability and corrosion resistance. The surface properties, such as microstructure, hardness and porosity of WC-CrC-Ni coatings prepared by optimal coating process (OCP) have been investigated. In particular, the friction and wear behaviors are analyzed for the WC-CrC-Ni coatings, EHC (electrolytic hard chrome) and the substrate Inconel 718 (IN 718) both at 25 and 450 ◦C. They found that the HVOF WC–CrC–Ni coating is very protective for alloy surface. [5]

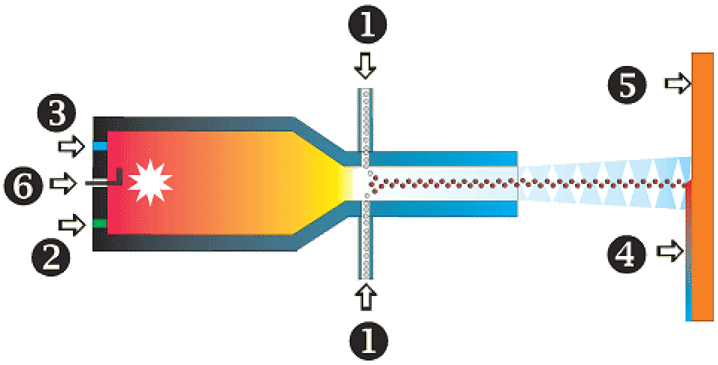

**Figure 1**. HVOF spray coating device [40].

1. Added material – Powder 2. Kerosene inlet 3. Oxygen inlet
4. Spray 5. Background 6. Sparkling plug

Substitution of hard chromium coatings with new HVOF cermet coatings has been studied by L. Fedrizzi et al [23] and they found that this process involves very high benefits for the environment, as the proposed HVOF technique allows to substitute some highly polluting surface treatment technologies, such as chromium-plating, with a perfectly "clean" process from an environmental point of view. In addition, the replacement should bring some important benefits such as sensible reduction in wastewater pollution caused by chromium-plating processes and the increase of the performance (corrosion and wear resistance) with respect to chromium plated. Tribo-corrosion phenomena involving mechano-chemical degradation were studied using electrochemical and weight loss measurements. The apparatus used to study wear-corrosion has been very effective because the combination of both electrochemical and mechanical analyses allowed analyzing the degradation mechanisms, [41-43]. Hard chromium degradation was found to be determined mainly by a wear of an adhesive type mechanism. But weight loss measurements clearly showed a synergistic effect due to the combined wear and corrosion degradation. Electrochemical data suggested that the corrosion rate of chromium coatings is increased by almost one order of magnitude by the mechanical damage. Degradation mechanisms of the HVOF coatings appeared to be quite different. In this case the presence of a large ceramic component in the composite coating made the corrosion degradation less important. The active-passive behavior is really important for the hard chromium coating and is no more fundamental in the case of the HVOF coating even if the metal matrix is NiCr made.

The use of nano-sized powders improves the good behavior of the conventional powders mainly because of a decrease of the interconnected porosity, a lower roughness, and a better distribution of the chromium carbides in the metal matrix, [23].

### *5.2 Electric Arc Spray (E Arc) Coating*

In the electric arc spray process (also known as the wire arc process), two consumable wire electrodes connected to a high-current direct-current (dc) power source are fed into the gun and meet, establishing an arc between them that melts the tips of the wires. The molten metal is then atomized and propelled toward the substrate by a stream of air. The process is energy efficient because all of the input energy is used to melt the metal. Spray rates are driven primarily by operating current and vary as a function of both melting point and conductivity. Generally materials such as copper-base and iron-base alloys spray at 4.5 kg (10 lb)/100 A/h. Zinc sprays at 11 kg (25 lb)/100 A/h. Substrate temperatures can be very low, because no hot jet of gas is directed toward the substrate. Electric arc spraying also can be carried out using inert gases or in a controlled-atmosphere chamber, [44]. Another consequence of the highly localized heating is that the heat input to the substrate is low, primarily because there is no hot gas or plasma jet directed at the substrate. Hence, wire arc spraying can be used to form coatings on materials such as polymers that would not withstand the heat input from other thermal spray processes, [45].

As shown in Fig 2 during the electric arc spray is the added material melted while coming into the spray gun as two wires. The compressed air flow accelerates the melted material and sprays it on the prepared surface of machine part. Added material wires can be either from the same material or different composition. Using nitrogen or argon can reduce the oxidation of such surface. [40]

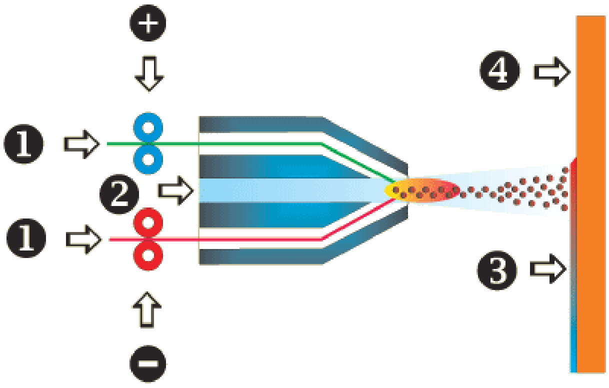

**Figure 2**. Electrical arc coating device.

1. Added material - Wire No. 1
2. Added material - Wire No. 2 (same or different as wire No. 1)
3. Background
4. Surface

### *5.3 Atmospheric Plasma Spray (APS) Coating*

This is the state-of-art-technology of surfacing which subject matter is the electric arc generated between tungsten electrode and surfacing material. During this generation is from incoming inert gas - argon - created a high concentrated plasma flow of high temperature. The powder material is added in this flow and creates the surface, [39,46]. The conventional plasma spray process is commonly referred to as air or atmospheric plasma spray (APS). Plasma temperatures in the powder heating region range from about 6000 to 15,000 °C (11,000 to 27,000 °F), significantly above the melting point of any known material. To generate the plasma, an inert gas-typically argon or an argon-hydrogen mixture is superheated by a dc arc. Powder feedstock is introduced via an inert carrier gas and is accelerated toward the workpiece by the plasma jet. Provisions for cooling or regulating the spray rate may be required to maintain substrate temperatures in the 95 to 205 °C (200 to 400 °F) range. Commercial plasma spray guns operate in the range of 20 to 200 kW. Accordingly, spray rates greatly depend on gun design, plasma gases, powder injection schemes, and materials properties, particularly particle characteristics such as size, distribution, melting point, morphology, and apparent density, [44]. Ying Chun Zhu et al, [46] have characterized nanostructured WC–Co coating deposited by (APS). The result shows that the structure of the plasma sprayed WC–Co coating is very complicated. The main structure of the coating is composed of WC grains with a mean particle size of 35 nm. In some regions, the structure is composed of WC grains with a mean particle size of 10 nm embedded in an amorphous matrix, which is formed by the melting of the WC–Co powders. Moreover, some regions of the coating are constituted completely of amorphous phase. It was also found that WC grains have grown to 100 nm in some regions of the coating. Second recrystallization occurred, strip-shaped and square shaped structures are formed in some regions of the nanostructured WC coating. The as-prepared WC-Co coating is composed mainly of WC phase with minor phases of a-W2C, b-WC1-x, and $W_3Co_3C$. The hardness of nano WC-Co coating is about 18 GPa, which is apparently improved comparing with conventional WC-Co coatings, [46].

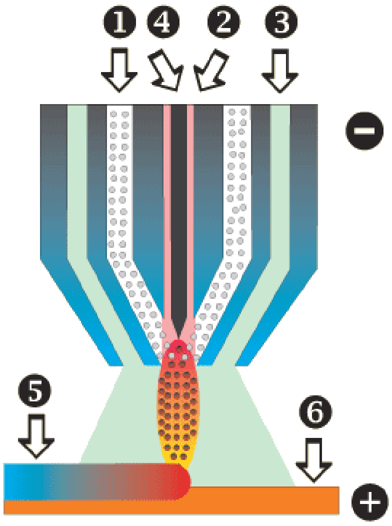

**Figure 3**. APS coating principles.

1. Added material – powder, 2. Plasma gas – argon 3. Gaseous shield - nitrogen
4. Tungsten electrode 4. Surface 5. Background

**Table 1.** Comparison of Thermal Spraying Processes and Coating Characteristics

| Process | Particle Velocity (m/s) | Adhesion (MPa) | Oxide Content (%) | Porosity (%) | Deposition Rate (kg/hr) | Typical Deposit Thickness (mm) |
|---|---|---|---|---|---|---|
| Arc | 100 | 10 – 30 | 10 – 20 | 5 – 10 | 6 – 60 | 0.2 – 10 |
| Plasma | 200 – 300 | 20 – 70 | 1 – 3 | 1 – 8 | 1 – 5 | 0.2 – 2 |
| HVOF | 600 – 800 | > 70 | 1 – 2 | 1 – 2 | 1 – 5 | 0.2 – 2 |

The influence of metallic matrix composition and spray powder size distribution of different WC-Co-Cr coating compositions deposited by HVOF process on the erosion-corrosion properties have been studied [12]. It has been found that powders having a narrow powder grain size distribution give coatings of higher quality than powders with wider grain size distributions. This is explained by the different melting behavior of powder grains of different size. Small grains are more easily over heated than larger grains. Over heating may give phases with low erosion resistance and therefore coatings of poor quality.

Nanocrystalline coatings with grain sizes in the nanometer range are also known to exhibit superior hardness and strength. The search for nanostructured coatings is driven by the improvement in coating technologies and the availability of various kinds of synthesized nanopowders. Such nanopowders can be used as feedstock materials for thermal spray processes; these include plasma spraying and HVOF spraying. Thermal spraying involves particle melting, rapid cooling and consolidation in a single-step operation. Thermal-sprayed nanocrystalline coatings with moderate hardness are found to possess better wear performances than their counterparts fabricated from microcrystalline powders. HVOF is particularly suited to deposit dense nanocrystalline ceramic coatings as opposed to plasma spraying because of its lower spraying temperature. Today, HVOF allows tailoring nanocrystalline coatings with low porosity, higher bond strength and increased wear properties, [48]**.**

### *5.4. Benefits of Thermal Spraying*

Among all thermal spraying processes, the main benefits of these processes can be summarized as follows:

1. Comprehensive choice of coating materials: metals, alloys, ceramics, cermets and carbides.
2. Thick coatings can be applied at high deposition rates.
3. Coatings are mechanically bonded to the substrate-can often spray coating materials which are metallurgically incompatible with the substrate, e.g., materials with a higher melting point than the substrate.
4. Components can be sprayed with little or no pre- or post-heat treatment, and component distortion is minimal.
5. Parts can be rebuilt quickly and at low cost, and usually at a fraction of the price of a replacement.
6. By using a premium material for the thermal spray coating, coated components can outlive new parts.
7. Thermal spray coatings may be applied both manually and automatically.

### *5.5. Advantages of coating*

The general advantages of coating applied by thermal-spraying processes have been summarized in earlier work [49]. These advantages include:

1. Protection of equipment and structures from the environment by acting as a barrier between the substrate and the aggressive environment, such as the marine and industrial environments.
2. Control of marine fouls; certain constituents in coating control the growth of mildew and marine fouling in seawater.
3. Reduction in friction; coating reduces friction between two contacting surfaces.
4. Pleasant appearance; certain types of coatings provide a pleasant appearance and produce attractive surroundings.
5. Visibility; many combinations of colors because of their visibility from large distances are used on TV and radio towers to warn aircraft.
6. Modification of chemical, mechanical, thermal, electronic and optical properties of materials.
7. Application of thin coatings on low-cost substrates results in increased efficiency and cost savings.

### *5.6. Erosion Test*

Erosion–corrosion related problems occur in power plants, oil and gas processing and chemical plants where there is an interaction between solid particles, corrosive fluid and a target material. The problem has been reported to affect static equipment for example pipelines, valves, heat exchangers, pressure vessels and various rotating equipment namely compressors, turbines and pumps. The importance of material selection for applications in these environments cannot be overstated as component wear can be accelerated by the aggressive conditions in these harsh environments. Synergy is the additional wear rate experienced by a metal under the combined action of erosion-corrosion conditions which is higher than the sum of wear rate due to pure erosion and flow corrosion, [19].

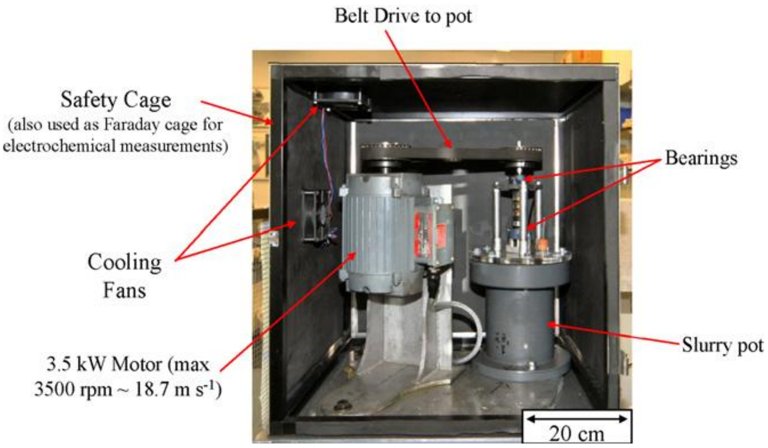

**Figure 4**. Assembled slurry pot erosion tester enclosed in a Faraday cage (pot capacity 4.0 L) [19].

S.S. Rajahram et al [19] used a slurry pot erosion tester to perform erosion- corrosion experiments. Fig. 4 [19] shows the diagram of the assembled slurry pot enclosed in the Faraday cage.

The rig is driven by a 3.5kW motor which is connected to the slurry shaft through a toothed belt and two pulleys (on the shaft and on the motor).

Cylindrical test samples are inserted between two nylon-coated arms at the end of the shaft as shown in Fig. 5 [19]. The speed of the motor is controlled through a variable speed drive with maximum rotation speed of up to 3500rpm. The pot is made of uPVC with a maximum capacity of 4 litres and has a cup type design copper cooler which allows the temperature of the slurry to be controlled by the circulation of hot/coldwater. The pot is designed with baffles in it, to allow mixing of solid particles in the slurry, preventing it from settling at the bottom of the pot. The rig assembly is enclosed within a Faraday cage which allows electrochemical measurements to be made and also acts as a protective safety barrier when running experiments [19]. It was found that the measurements and slurry pot erosion rig provide repeatable and reproducible test results with high confidence levels. Increasing the velocity and the sand concentration produced higher mass loss rates in erosion conditions. The increase in kinetic energy of the particles is suggested to be the reason for the higher mass loss rates.

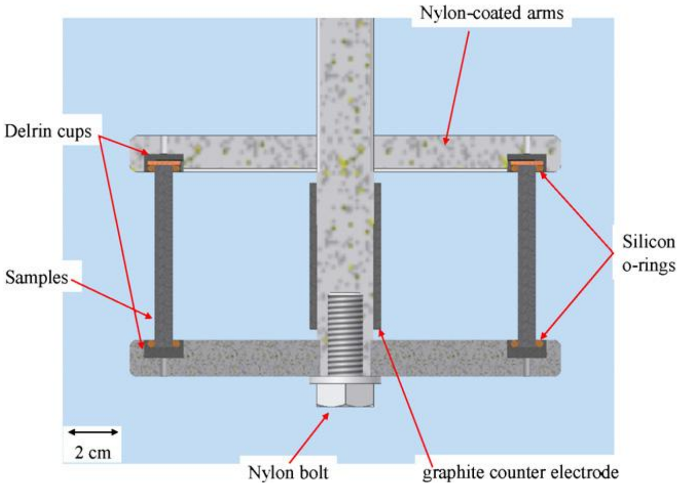

**Figure 5**. Placement of samples on two nylon-coated arms, secured with o-rings to prevent slurry ingress [19].

## 6. ELECTROCHEMICAL CORROSION TEST

With the increased use of cermet coatings and solid cermets in applications where corrosion can play a part in the degradation process, it is becoming increasingly important to be able to assess the effects of the joint corrosion as the same in erosion processes.

V.A. de Souza, A. Neville [29] used electrochemical analysis in conjunction with weight-loss analysis to determine the total material loss (TWL) and to isolate the contributions due to pure corrosion (*C*). The corrosion rate was measured in situ using a three-electrode electrochemical cell comprising a Ag/AgCl reference electrode connected by means of a salt bridge and a platinum counter electrode. DC anodic polarization tests (in static conditions or under the impinging jet) involved scanning the potential of the working electrode (the specimen under examination) from the free corrosion potential (*E*corr) in the more noble (positive) direction at a fixed rate of 0.25 mV/s. The potential was scanned in the positive direction until the current flowing in the external circuit between the working and counter electrodes reached a value of 500 A/cm2. The anodic polarization tests were started after 30 min exposure to static saline solution or the impinging jet. [29]

The impingement apparatus comprised a liquid–solid jet generated using a re-circulating rig as shown in Fig. 6 and described elsewhere [29,50]. The rig comprised a dual nozzle system. They demonstrated that WC–CoCr thermal sprayed coatings can provide good protection against wear and corrosion in liquid–solid impingement when compared with stainless steels.

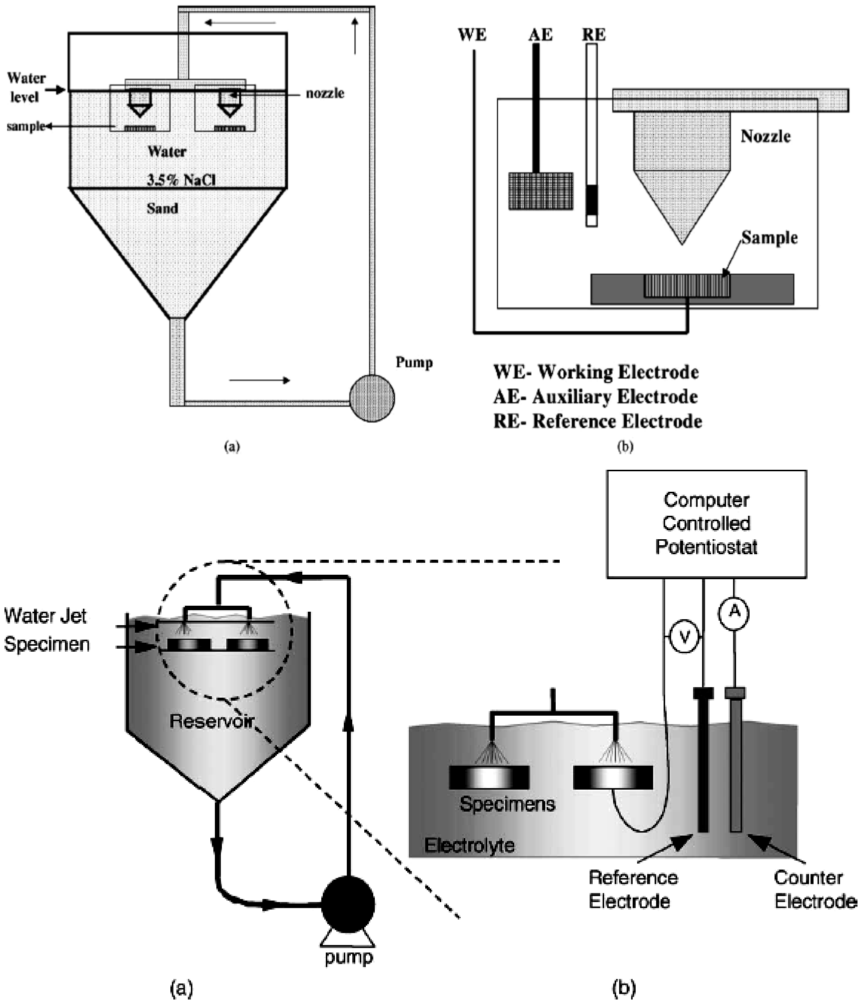

**Figure 6**. (a) The rig configuration used in the experiments and (b) the electrochemical set up on the nozzle [29,50].

## 7. EROSION-CORROSION TEST

It was found in various publications [28–30, 49, 51] that the total degradation due to erosion-corrosion has been divided into three principal components as defined below:

(a) Corrosion (*C*): electrochemical charge transfer leads to material loss. The charge transfer rate can be accentuated by the increased mass transfer or mechanical impacts as a result of an impinging flow.

(b) Erosion (*E*): mechanical damage due to impacts of a high-energy flow or suspended solids within a flow. The material removal does not involve any corrosion processes.

(c) Interactions or synergy (*S*): the enhanced material damage as a result of corrosion enhancing erosion. In this instance the corrosion processes affect the integrity of the material and render it more susceptible to mechanical damage.

### *6.1. Experimental details*

N. Espallargas et al [30] used in their investigation the erosion–corrosion equipment shown in Fig. 7 for testing Cr3C2–NiCr and WC–Ni coatings obtained by HVOF.

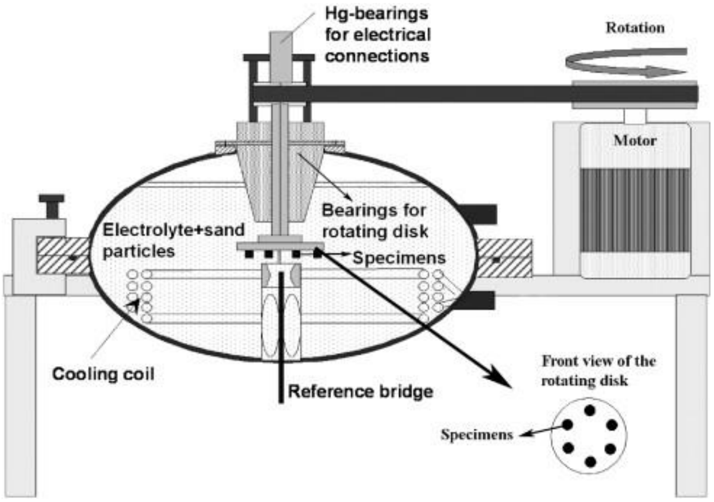

**Figure 7**. Scheme of the erosion–corrosion equipment, [30].

Six cylindrical samples were fixed to a rotating disk. The disk was rotated in a 65 L mixture made of 3.4 wt.% NaCl solution and 0.25 wt.% silica sand with average grain size 250 μm. The samples were electrically insulated from the disk and from each other. For each sample a conductor through an Hg cup was connected to a potentiostat for electrochemical measurements. The erosivity was varied by applying different rotation velocities: 14.3 and 22.9 m $s^{-1}$.

**Table 2.** Conditions used for erosion-corrosion tests, [30]

| **Test Solution** | **Condition A** | **Condition B** |
|---|---|---|
| | Mixture of 0.25 wt.% sand and 3.4 wt.% NaCl | |
| **Velocity (m $s^{-1}$)** | 22.9 | 14.3 |
| **Temperature ($^{o}$C)** | 20 | 20 |

The total material loss caused by erosion–corrosion was determined by weighing the samples before and after the tests. All tests were run for 24 h. The experimental conditions of erosion–corrosion experiments are summarized in Table 1. The samples were exposed to 0–90° impact angles due to their cylindrical shape and the impeller-like flow. [30]

The corrosion resistance of all coatings was evaluated by electrochemical measurements. The electrochemical measurements were done both during and after rotation. A saturated calomel electrode (SCE) was used as a reference electrode and the 22Cr–5Ni (wt.%) duplex stainless steel wall of the apparatus was the auxiliary electrode. Each coated sample (working electrode) was fixed at the rotating disk, exposing an area of 4.71 $cm^2$ to the solution, [30].

They clearly notify in their study that the coating structure and hardness play an important role in the erosion–corrosion mechanisms at high erosive conditions. At high erosive conditions, the microstructure of tungsten carbide coatings was responsible of its high erosion–corrosion resistance compared with chromium carbide and hard chromium coatings. The relative importance of erosion and corrosion should be considered when selecting coating material for erosion–corrosion resistance. WC-based coatings show better wear resistance, resulting on a better erosion–corrosion resistance under the most erosive conditions. The best corrosion performance of $Cr_3C_2$–NiCr coatings also places them as a good alternative to hard chromium coatings under lower erosive erosion–corrosion conditions.

Chengzhi Zhuo et al [51] are focused in their study on investigating the corrosion and erosion-corrosion behaviors of two kinds of nano-particle-reinforced Ni-Cr-Mo-Cu alloying layers in slurry flow environment. An electrochemical impedance spectroscopy (EIS) was measured to study the effects of the different particulates on corrosion and erosion-corrosion behaviors. They found that with increasing the impact velocity and content of sand particles under hydrodynamic conditions, the current densities increase with fluctuations appearing for 316L stainless steel, single alloying layer and composite alloying layer. Also the results of polarization curve measurements obtained under slurry flow conditions exhibit an increase in corrosion current density and decrease in corrosion potential compared with that of obtained under static state condition, [51]. Furthermore, V.A.D. Souza, A. Neville [28] have reported the following:

- WC Co Cr thermal sprayed coatings can provide good protection against wear and corrosion in liquid–solid impingement when compared with stainless steels. The extent of the benefits offered by WC Co Cr is dependent on environment severity.
- The role of corrosion and synergy in the total damage is important on WC Co Cr HVOF coating, much more so than on the Super duplex stainless steel.
- The corrosion of small hard phase particles (WC) can accelerate the material loss under erosion–corrosion environments and is one important feature of the synergy effect.
- Because corrosion and synergy play an important role in the total damage of WC Co Cr there is scope to improve the overall erosion–corrosion performance by enhancing the corrosion behavior.
- They also demonstrated in another study [27, 29] that different microstructures of these thermal spray coatings mean that in erosion–corrosion the degradations rates and mechanisms are different. It is important to understand how erosion and corrosion factors interact. In particular:

- Synergy (ΔEc) behavior of the coatings can change depending on the environment (sand loading), composition and microstructure.
- The formation of different tungsten species, eta phases and a higher Cr amount can reduce the toughness of WC–Co–Cr coatings and reduce the corrosion rates under erosion–corrosion.

G.C. Saha et al [51] used in their investigation the impingement jet system shown in Fig. 8 which developed to perform erosion–corrosion tests. The system consisted of a plastic tank used as a reservoir, a high pressure pump, a flow velocity controller, a sand concentration controller, a stirrer, and valves. When the fluid entered the ejector at a high speed, it produced a partial vacuum due to the venting effect. The sands underneath the valve could be mixed with the flowing fluid by means of suction. A speed-adjustable mechanical stirrer was used to ensure the homogeneous mixing of sands in the solution. An electrochemical cell was incorporated into the test rig to enable in-situ electrochemical measurements. In their study the erosion–corrosion resistant behavior of a near-nanocrystalline ‘duplex Co coated’ WC-17Co coating produced by HVOF spraying was compared with a microcrystalline WC-17Co coating and an uncoated AISI 1018 carbon steel. The results showed that the combined erosion–corrosion resistance of the coated coatings was significantly higher than that of the uncoated steel. Furthermore, the near-nanocrystalline coating showed approximately 1/3 lower erosion–corrosion rate than that of the microcrystalline coating. Preliminary results showed that the erosion–corrosion mechanism in the coatings was dominated by pure erosion in the microcrystalline coating and the corrosion- enhanced erosion in the near-nanocrystalline coating. [51]

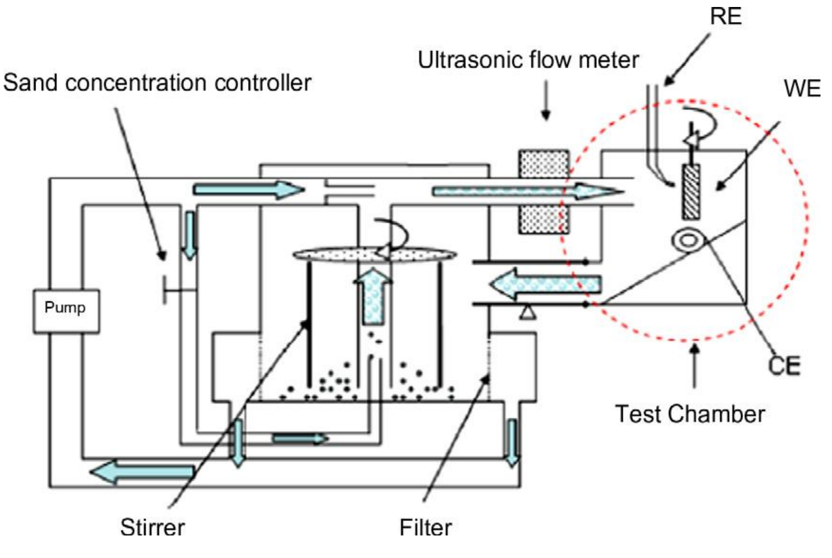

**Figure 8**. Schematic diagram of the impingement jet loop system (RE, reference electrode; WE, working electrode; CE, counter electrode). [51].

## 8. SUMMARY AND CONCLUSIONS

There are several papers in the literature dealing separately with the study of corrosion and wear resistance for different thermal spray coatings. Corrosion properties of thermal spray coatings in a corrosive media have been previously studied by different authors. They found that the absence of pores and cracks (micro and macro) is very important when corrosion resistance is required because the electrolyte penetrates through these defects to reach the substrate. When the substrate is less noble than the coating, galvanic effects can be found between coating and substrate, resulting in a significant attack of the substrate material. On the other hand, if the substrate is more noble than the coating (i.e. stainless steel) the coating acts as a sacrificial anode accelerating its corrosion.

It was concluded that chemical composition of metallic binder materials and the occurrence of micro cracks were the most important factors influencing the corrosion resistance of the HVOF sprayed WC cermet coatings in the strong acidic environment.

## ACKNOWLEDGEMENTS

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