T.C.
MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES IN
PURE AND APPLIED SCIENCES

THERMAL SPRAYED AND FUSED ALUMINIUM COATINGS

Mehmet Burak YILMAZ

THESIS

FOR THE DEGREE OF MASTER OF SCIENCE
IN
METALURGICAL AND MATERIALS ENGINEERING

SUPERVISOR
Assoc. Prof. Dr. Recep ARTIR

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ACKNOWLEDGEMENT

I would like to;
Thank my supervisor Assoc. Prof. Dr. Recep ARTIR for his patience and leadership.
Thank my company Senkron for its possibilities.
Thank my family for their supports.
Thank science for thermal spray.
Thank God for my life.

June, 2009 **M. Burak YILMAZ**

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ÖZET

TERMAL PÜSKÜRTME VE ERGİTME YÖNTEMİYLE ALUMİNYUM KAPLAMA

Metallerin aluminyum kaplanması atmosferik korozyon,kimyasal korozyon ve yüksek sıcaklık dayanımı açısından bilinen ve uygulanan bir prosestir. Fakat aluminyum kaplamanın uygulamadaki zorluğu ve getirdiği sınırlandırmadan dolayı kutu sementasyonu ve termal sprey gibi sadece birkaç proses ile uygulamak mümkündür. Aluminyum kaplama uygulamaları arasında en pratik ve ekonomik yöntem termal spreydir. Özellikle yapı çeliklerinde aluminyum kaplama sonrasında yüksek sıcaklık ve korozyon dayanımında gelişme görülür. Termal sprey ile uygulanmış aluminyum kaplamalar tekrar yüzey işlem görerek modifiye edildiklerinde ise servis ömürleri daha uzun ve çalışma performansları daha yüksek olmaktadır.

Bu çalışmada düşük karbon çeliği üzerine aluminyum kaplama ve kaplama ergitme yöntemleri kullanılmıştır. Kaplama sonrası numunelere katı hal difüzyonu uygulanarak daha iyi korozyon ve oksidasyon direncine sahip olmaları sağlanmıştır.

Bu teknik yapı çelikleri ve çelik boruların deniz suyu korozyonu ve yüksek sıcaklık korozyonuna karşı dayanımlarını iyileştirmek amacıyla kullanılabilir.

Haziran, 2009 **M.Burak YILMAZ**

ABSTRACT

THERMAL SPRAYED AND FUSED ALUMINIUM COATINGS

Aluminium coatings are well known processes and have wide range of application areas for protection of metals from atmospheric corrosion, chemical corrosion and high temperature resistance. But because of the diffuculty and limitations at the applications, only a few methods which called pack cementation and thermal spray are suitable for aluminium coatings. The most suitable and economic method for aluminium coatings is thermal spray processes. Especially at production steels, corrosion and high temperature resistance gets better after thermal spray coatings. Surface modified aluminium coatings have better performance then the other ones like more service life and more performance.

In this study aluminium alloy coatings were performed onto low carbon steel substrate with or without fusing. After coating, samples were heat treated to obtain solid state diffusion layer into steel for a better oxidation and corrosion resistance.

This technique could be used for ordinary construction steels and pipes in contacting sea water and working against moderate temperature oxidation environments.

June,2009 **M.Burak YILMAZ**

SYMBOLS

α **:** Goethite

γ **:** Lepidocrocite

μm **:** Micrometer

e^0 **:** Interstitial Electron

M^{z+} 0 **:** Interstitial Metal Ion

M^{z+} **:** Cation Vacancy

$e^{\square}$: A Positive Hole

T **:** Temperature (°C)

V **:** Volts

ABBREVIATIONS

HVOF : High Velocity Oxygen Fuel

RPM : Rotate Per Minute

HRC : Rockwell hardness C Scale

DC : Direct Current

KG : Kilogram

DB : Decibel

MM : Millimeter

AH : Ampere Hour

BAR : Bar

PSI : Pressure Square Inch

SEM : Scanning Electron Microscope

SEM-BEI : Scanning Electron Microscope - Backscattered Electron Image

OM : Optical Microscopy

EDS : Energy-dispersive X-ray spectroscopy

KV : Kilovolts

FIGURES

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I. INTRODUCTION AND AIM

Thermal spray coatings are often used because of their high degree of hardness relative to paint coatings. Their hardness and erosion resistance make them especially valuable in high-wear applications. The hardness and density of thermal spray coatings are typically lower than for the feedstock material from which the coatings were formed. In the case of thermal spray metallic coatings, the hardness and density of the coating depend on the thermal spray material, type of thermal spray equipment, and the spray parameters.

Metallic thermal spray coatings may be either anodic or cathodic to the underlying metal substrate. Because corrosion occurs at the anode, anodic coatings will corrode in corrosive environments and the cathode will not. Anticorrosive coating systems are generally designed such that the coating material is anodic to the substrate metal. Anodic coatings will corrode or sacrifice to protect the substrate. In some cases, the corrosion resistance of the thermal spray material itself is important. For very high temperature applications and for chemical exposures, the thermal spray coating must be very corrosion resistant. For such applications, the coating provides a corrosion resistant barrier to protect the substrate.[1]

Protective coatings are probably the most widely used products for corrosion control. They are used to provide longterm protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions.Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. The workpiece becomes a composite material exhibiting properties generally not achievable by either material if used alone. The coatings provide a durable, corrosion resistant layer, and the core material provides the load bearing capability.[6]

Thermal spray coatings, primarily zinc, aluminium, zinc-aliminum alloys and aluminium metal matrix composites have been successfully used to combat corrosion in a wide range of applications. Steel structures and components that have been zinc or aluminium sprayed include television towers, antennea, radar, bridges, light poles, girders, ski lifts and countless other similar structures.[7]

Spray and fuse is a modification of the cold spray method. The materials used for coating the self fluxing alloys. The Spray and Fuse coatings have been metallurgically developed to perform at their peak after having undergone an intense fusing stage. This line of coatings combines the ease of application of a thermal sprayed coating with the tough, high stress wear characteristics of a hardface weld overlay.[8-10]

II. GENERAL DESCRIPTION OF THERMAL SPRAYING

Thermal spraying is a group of processes wherein a feedstock material is heated and propelled as individual particles or droplets onto a surface.[1]

The earliest records for thermal spraying are patents by the Swiss engineer M. U. Schoop, originating in the early 1900s. At first lead and tin wires were melted in a welding torch by the energy of an acetylene/oxygen flame. The torches then were modified for the use of powdered materials. The wire-arc spraying process was patented around 1908, also by Mr. Schoop, making the deposition of more, and various metals possible. Due to the development of thermal plasmas, and the increasing demand of high temperature and wear resistant materials and coating systems, the thermal spraying technologies expanded in the 70s . Since the 80s the major developments are leading towards increasing particle velocities. Nowadays thermal spraying includes all processes where coating materials are partially, or totally molten, either inside or outside of a spray torch, and the liquid or solid particles are deposited onto a surface, where the arriving droplets form a coating.[2]

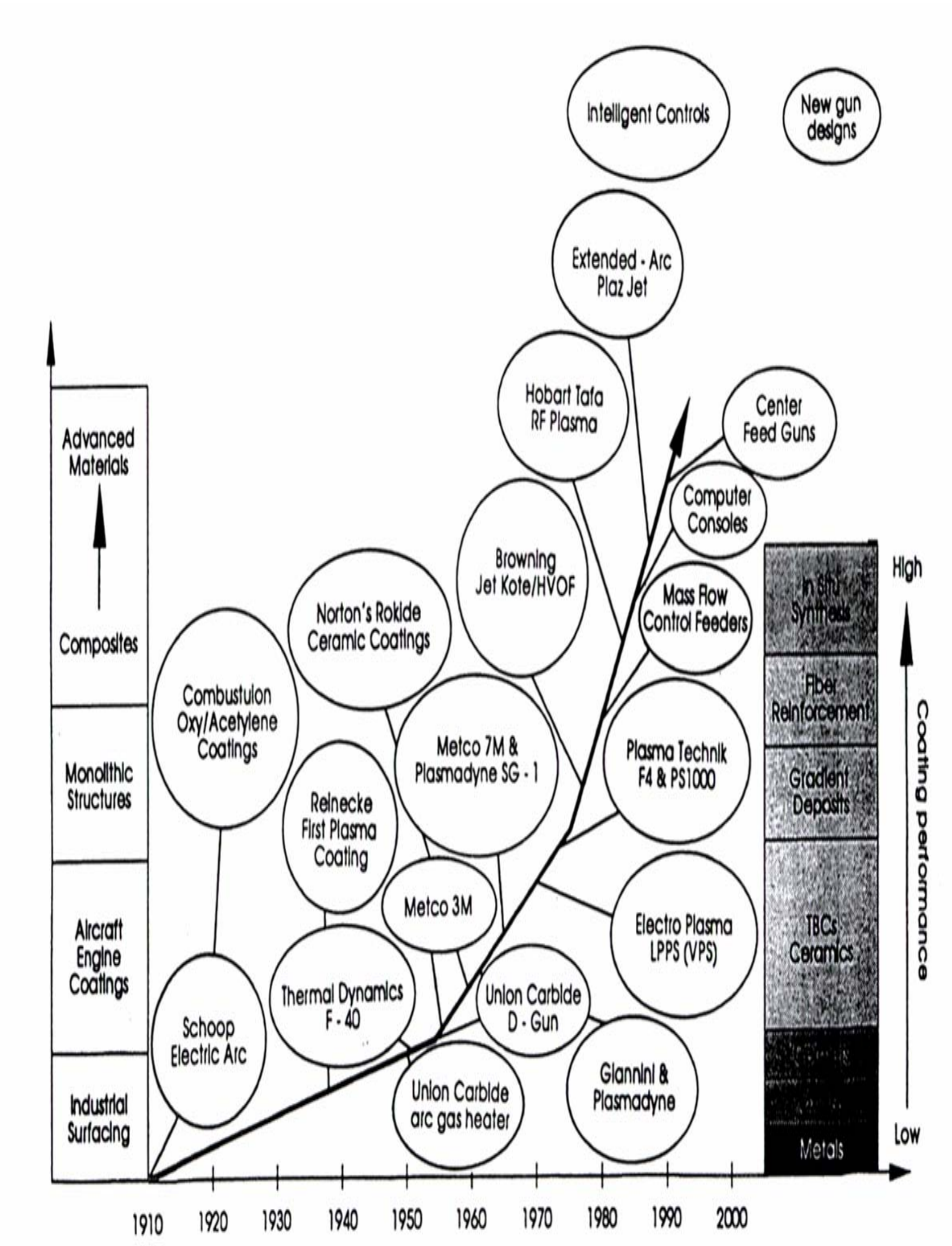


Fig.II.1. Historical development of thermal spraying equipment, processes, and materials.[2]

The thermal spray gun generates the necessary heat by using combustible gases or an electric arc. As the materials are heated, they are changed to a plastic or molten state and are confined and accelerated by a compressed gas stream to the substrate. The particles strike the substrate, flatten, and form thin platelets (splats) that conform and adhere to the irregularities of the prepared substrate and to each other. As the sprayed particles impinge upon the surface, they cool and build up, splat by splat, into a laminar structure forming the thermal spray coating. Fig.II.2. illustrates a typical coating cross section of the laminar structure of oxides and inclusions. The coating that is formed is not homogenous and typically contains a certain degree of porosity, and, in the case of sprayed metals, the coating will contain oxides of the metal. Feedstock material may be any substance that can be melted, including metals, metallic compounds, cements, oxides, glasses, and polymers. Feedstock materials can be sprayed as powders, wires, or rods. The bond between the substrate and the coating may be mechanical, chemical, or metallurgical or a combination of these. The properties of the applied coating are dependent on the feedstock material, the thermal spray process and application parameters, and posttreatment of the applied coating.[1]

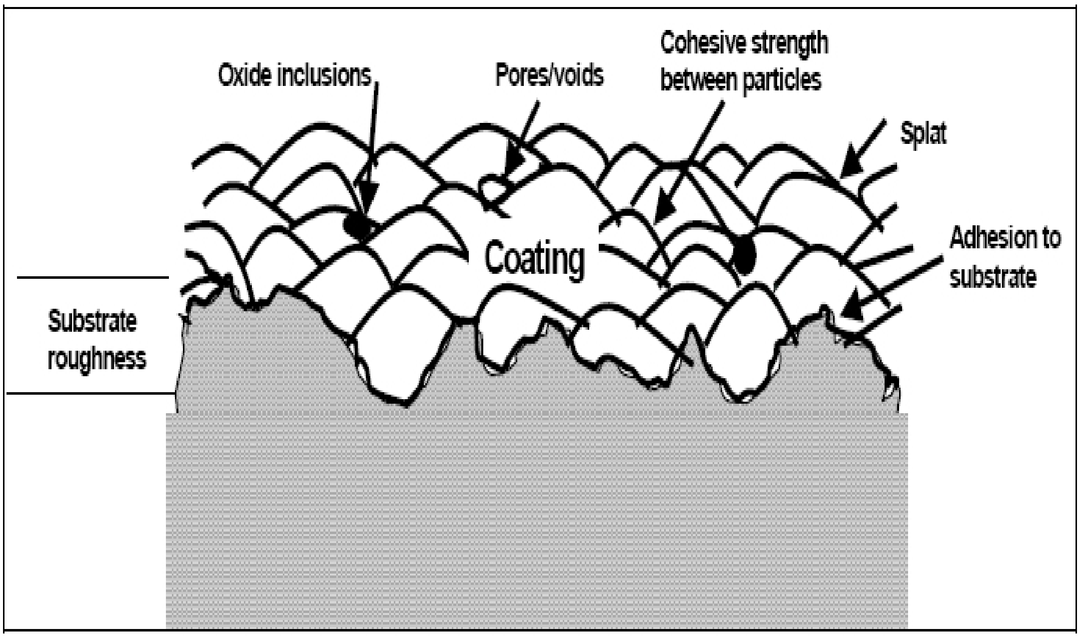


Fig.II.2. Typical cross section of a thermal spray coating[1]

II.1. The Bonding Mechanisms of Thermally Sprayed Coatings

During the rapid solidification of the spray particles there is a close contact between particles and/or the substrate surface. This leads to bonding effects due to mechanical interlocking, adhesion, diffusion, chemical reactions, and sometimes partial fusion of the contact surfaces. Mechanical interlocking is the main mechanism of thermal spray coating adhesion/adherence, if the substrate temperature is kept within the above mentioned range. The bond between impacting particles and the substrate surface is established to a high degree through the arriving droplets liquid flowing and solidifying around the substrate asperities/roughness. Usually these asperities are formed by mechanical means such as abrasive blasting, grit blasting, or rough turning, which also activate and clean the surfaces prior to coating. The quenching stresses within the spray particles increase the interlocking effects.[2]

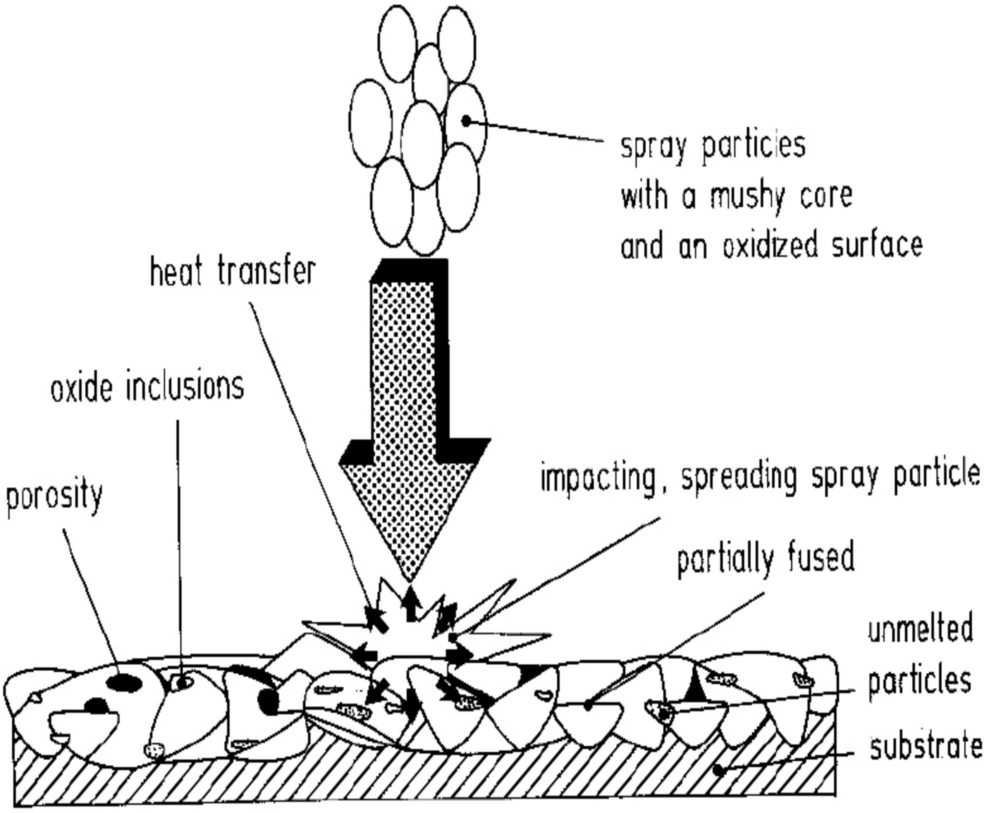


Fig.II.3. Schematic of a typical structure during thermal spray coating.[2]

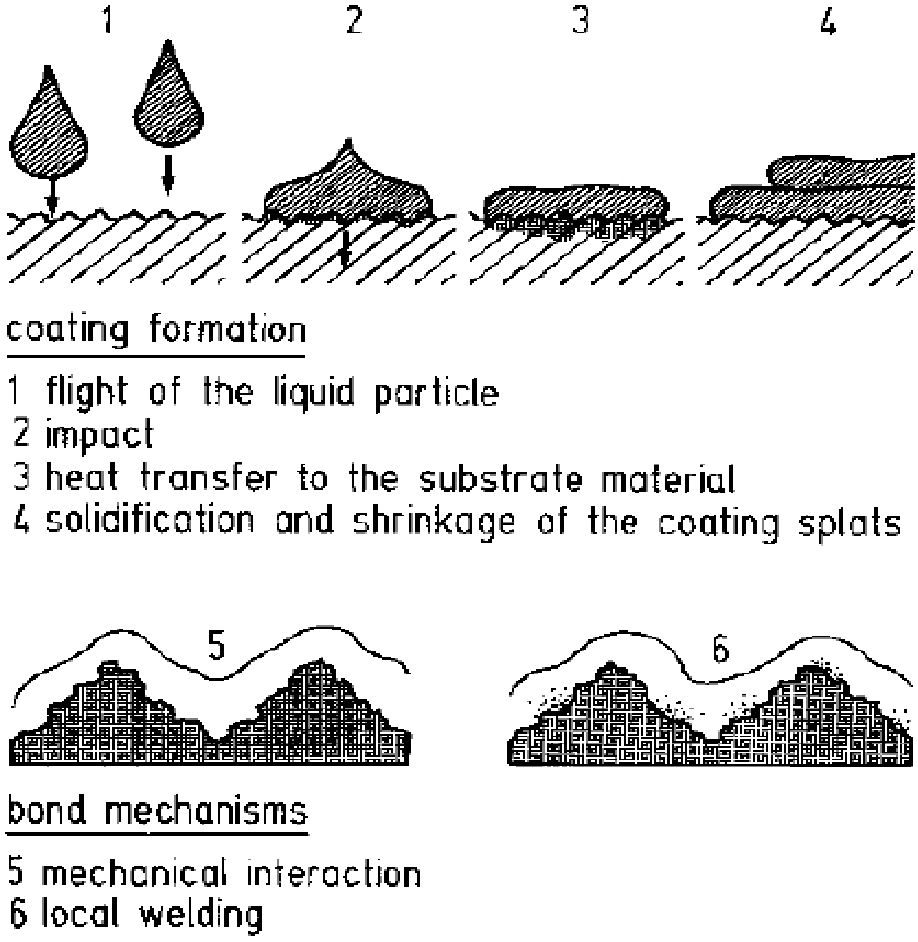


Fig.II.4. Bonding interactions within a spray coating.[2]

The adhesive bonding mechanisms are effective at microcontact areas between particles and/or substrate. These forces correspond to the atomic attractive forces within crystalline solid matter, since the particles approach one another as close as atomic levels. Depending on the type of atomic bonding, on the one hand van der Waals forces (physisorption) and on the other hand an exchange of valence electrons (chemisorption) may take place. Between spray particles, as well as between spray particles and the substrate, melting and diffusion within micro dimensions may occur due to the interface temperature being somewhat higher than the melting point of the substrate, despite the high cooling rates. The industrial applications of thermally sprayed coatings largely depend on the bond quality between the coating and substrate.

Therefore, a thorough substrate surface preparation is a necessity. Contaminants such as rust, scale, grease, moisture, etc., must be removed from the surface. After leaning, usually a roughening of the substrate surface follows to ensure coating adhesion. Common methods for surface roughening, which are often combined, are:

- Dry abrasive grit blasting.
- Machining or macro roughening.
- Applying a bond coat.

The thermal spray coating process should start as soon as possible after the surface preparation is completed, since the prepared surface is very active, and oxidation, recontamination, etc., should be avoided. In some cases, preheating of the substrate materials may be necessary just prior to the coating in order to drive moisture from the substrate. For this purpose substrate preheating in air up to 150 – 200°C for approximately 60 seconds is sufficient.[2]

II.2. Thermal Spray Processes

Thermal spray processes may be categorized as either combustion or electric processes. Combustion processes include flame spraying, HVOF spraying, and detonation flame spraying. Electric processes include arc spraying and plasma spraying.

II.2.1. Combustion Processes

II.2.1.1 Flame Spraying

The oldest form of thermal spray, flame spraying, may be used to apply a wide variety of feedstock materials including metal wires, ceramic rods, and metallic and nonmetallic powders. In flame spraying, the feedstock material is fed continuously to the tip of the spray gun where it is melted in a fuel gas flame and propelled to the substrate in a stream of atomizing gas. Common fuel gases are acetylene, propane, and methyl acetylene-propadiene. Air is typically used as the atomization gas. Oxyacetylene flames are used extensively for wire flame spraying because of the degree of control and the high temperatures offered by these gases. By gauging its appearance, the flame can be easily adjusted to be an oxidizing, neutral, or reducing flame. The lower temperature propane flame can be used for lower melting metals such as aluminum and zinc as well as polymer feedstocks. The basic components of a flame spray system include the flame spray gun, feedstock material and feeding mechanism, oxygen and fuel gases with flowmeters and pressure regulators, and an air compressor and regulator.

II.2.1.2. Wire Flame Spraying

The wire flame spray gun consists of a drive unit with a motor and drive rollers for feeding the wire and a gas head with valves, gas nozzle, and air cap that control the flame and atomization air. Compared with arc spraying, wire flame spraying is generally slower and more costly because of the relatively high cost of the oxygen-fuel gas mixture compared with the cost of electricity. However, flame spraying systems, at only one-third to one-half the cost of wire arc spray systems, are significantly cheaper. Flame spray systems are field portable and may be used to apply quality metal coatings for corrosion protection.

II.2.1.3. Powder Flame Spraying

Powder flame operates in much the same way as wire flame spray except that a powder feedstock material is used rather than wire and there is no atomizing air stream. The melted coating material is atomized and propelled to the surface in the stream of burning fuel gas. The powder is stored in either a gravity type hopper attached to the top of a spray gun or a larger air or inert gas entrainment type detached hopper. Powder flame spray guns are lighter and smaller than other types of thermal spray guns. Production rates for powder flame spray are generally less than for wire flame spray or arc spray. Particle velocities are lower for flame spray, and the applied coatings are generally less dense and not as adherent as those applied by other thermal spray methods.

II.2.1.4. HVOF Spraying

One of the newest methods of thermal spray, HVOF, utilizes oxygen and a fuel gas at high pressure. Typical fuel gases are propane, propylene, and hydrogen. The burning gas mixture is accelerated to supersonic speeds, and a powdered feedstock is injected into the flame. The process minimizes thermal input and maximizes particle kinetic energy to produce coatings that are very dense, with low porosity and high bond strength. HVOF systems are field portable but are primarily used in fabrication shops. HVOF has been used extensively to apply wear resistant coatings for applications such as jet engine components.

II.2.1.5. Detonation Flame Spraying

In detonation flame spraying, a mixture of oxygen, acetylene, and powdered feedstock material are detonated by sparks in a gun chamber several times per second. The coating material is deposited at very high velocities to produce very dense coatings. Typical applications include wear resistant ceramic coatings for high-temperature use. Detonation flame spraying can only be performed in a fabrication shop.

II.2.2. Electric Processes

II.2.2.1. Arc Spraying

Arc spraying is generally the most economical thermal spray method for applying corrosion resistant metal coatings, including zinc, aluminum, and their alloys. Energy costs are lower and production rates are higher than they are with competing methods such as wire flame spray. Arc spraying may be used to apply electrically conductive materials including metals, alloys, and metal-metal oxide mixtures. In arc spraying, an arc between two wires is used to melt the coating material. Compressed gas, usually air, is used to atomize and propel the molten material to the substrate. The two wires are continuously fed to the gun at a uniform speed. A low voltage (18 to 40 volts) direct current (DC) power supply is used, with one wire serving as the cathode and the other as the anode. Coating quality and properties can be controlled by varying the atomization pressure, air nozzle shape, power, wire feed rate, traverse speed, and standoff distance. Arc sprayed coatings exhibit excellent adhesive and cohesive strength.

II.2.2.2. Plasma Spraying

Plasma spraying is used to apply surfacing materials that melt at very high temperatures. An arc is formed between an electrode and the spray nozzle, which acts as the second electrode. A pressurized inert gas is passed between the electrodes where it is heated to very high temperatures to form a plasma gas. Powdered feedstock material is then introduced into the heated gas where it melts and is propelled to the substrate at a high velocity. A plasma spray system consists of a power supply, gas source, gun, and powder feeding mechanism. The process may be used to apply thermal barrier materials, such as zirconia and alumina, and wear resistant coatings such as chromium oxide. [1]

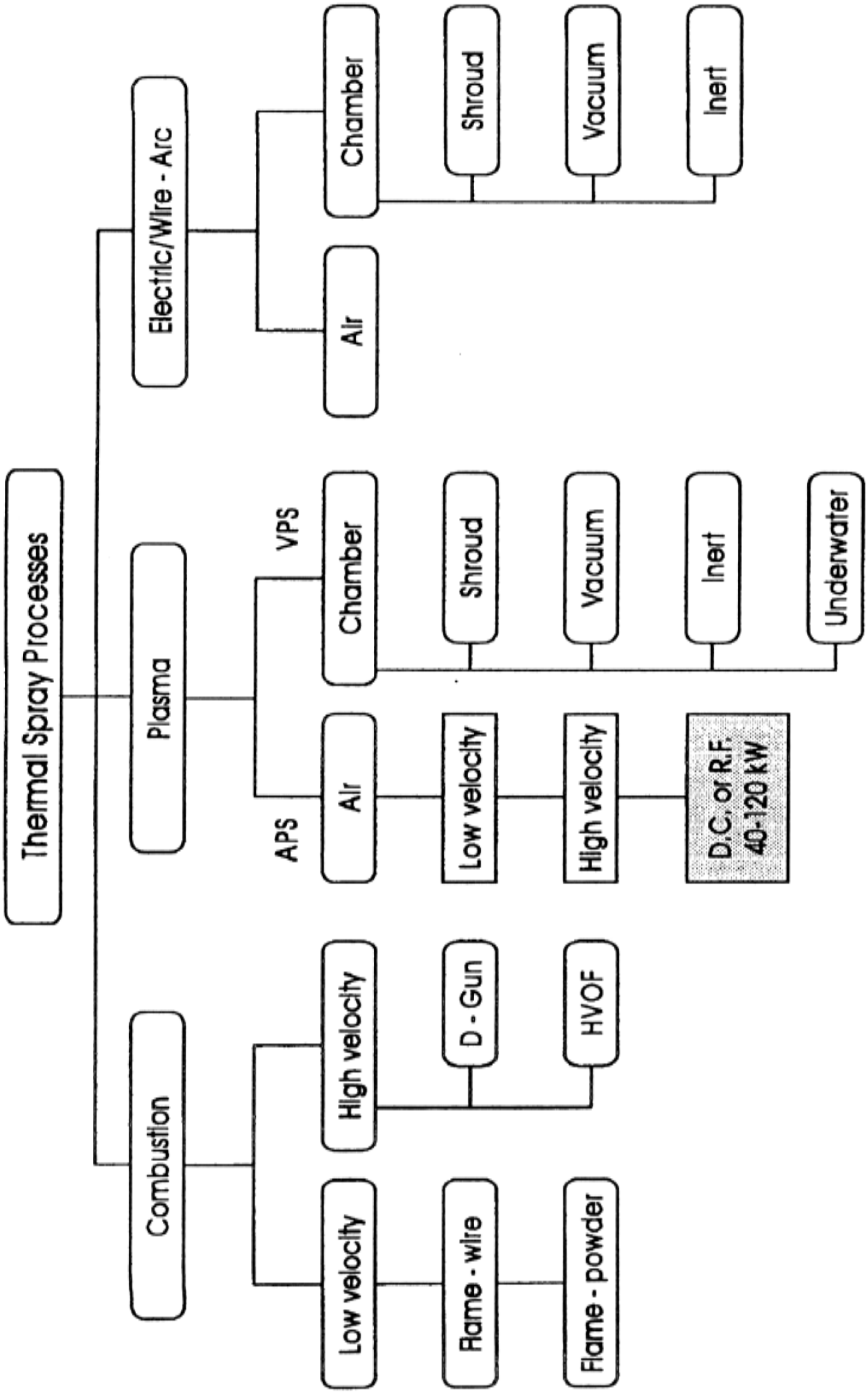


Fig.II.5. Thermal spray processes. [2]

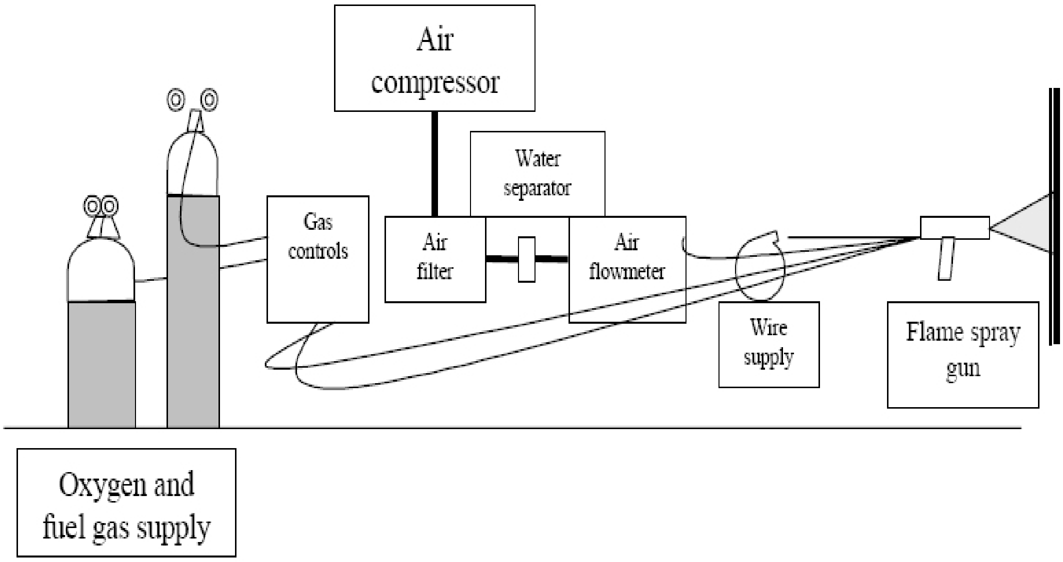


Fig.II.6. Typical flame spray system[1]

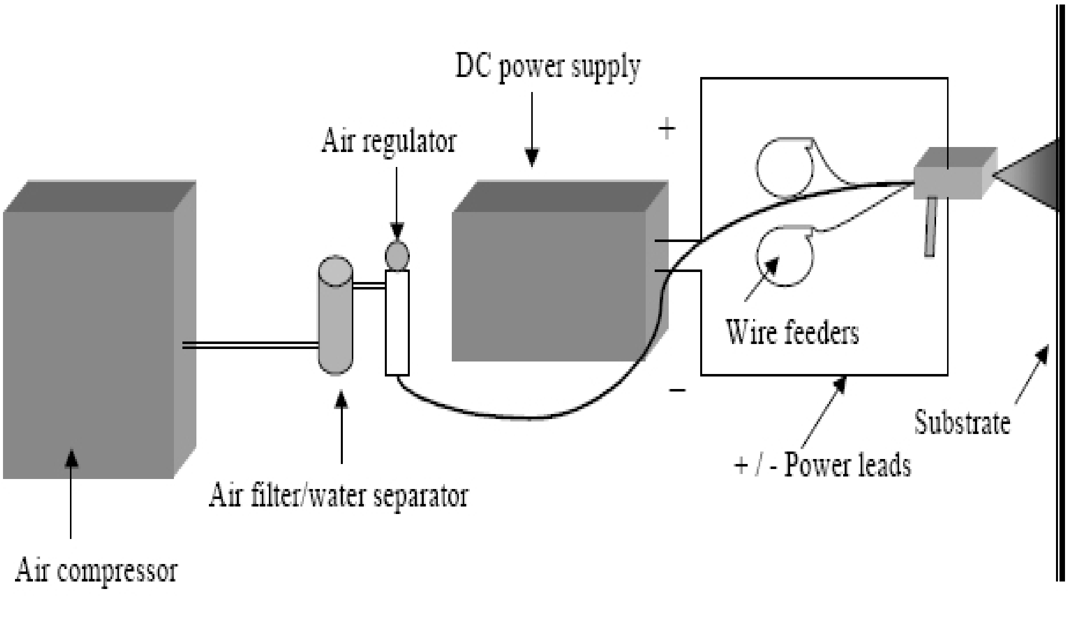


Fig.II.7. Typical two-wire arc spray system[1]

II.3. Corrosion

II.3.1. Classification of Corrosion Processes

A logical and scientific classification of corrosion processes, although desirable, is by no means simple, owing to the enormous variety of corrosive environments and the diversity of corrosion reactions, but the broad classification of corrosion reactions into ‘wet’ or ‘dry’ is now generally accepted, and the terms are in common use. The term ‘wet’ includes all reactions in which an aqueous solution is involved in the reaction mechanism; implicit in the term ‘dry’ is the absence of water or an aqueous solution. These terms are evidently ambiguous; for example, it is not always clear whether ‘wet’ is confined to aqueous solutions the ‘wetting’ of solids by mercury indicates that liquid-metal corrosion should be classified as ‘wet’. Even if the term is restricted to aqueous solutions, the difficulty arises that the mechanism of growth of magnetite scale during the reaction of the interior of a boiler drum with dilute caustic soda at high temperatures and pressures is best interpreted in terms of a ‘dry’ corrosion process. Similar considerations apply to the reactions of aluminium and zirconium with hightemperature water.

Considering oxidation as a typical ‘dry’ reaction it follows that at the interfaces:

$$\mathrm{M} \leftrightarrow (\ \mathrm{M}^{z+}\ 0/\mathbf{0}\ ) + \mathrm{z}\ (\ e^{\,0/\mathbf{0}}\ ) \qquad \text{(Eq. II.1)}$$

where $\mathrm{M}^{z+}\ 0$ is an interstitial metal ion, e^{0} an interstitial electron and **/0** indicates the metal/oxide interface .

If the metal dissolves to enter a vacant site, then

$$\mathrm{M} \leftrightarrow (\ \mathrm{M}^{z+}\ \square/\mathbf{0} + \mathrm{z}\ e^{\,\square/\mathbf{0}}\ ) \qquad \text{(Eq. II.2)}$$

where $\mathrm{M}^{z+}\square$ represents a cation vacancy and $e^{\,\square}$ a positive hole.

At the gas / oxide interface the O_2 gas ionises

$$(\ \tfrac{1}{2}\,\mathrm{O}_2 / \text{ads.}\ ) + 2\ (\ e / \mathrm{X}\ ) \leftrightarrow (\ \mathrm{O}^{2-} / \text{ads.}\ ) \qquad \text{(Eq. II.3)}$$

where / X indicates the gas / oxide interface.

By definition, these interfaces can be considered as anodes and cathodes respectively.

II.3.2. Corrosion of Iron and Steel

Steel is an alloy consisting mostly of iron, with a carbon content between 0.2% and 2.14% by weight, depending on grade. Carbon is the most cost-effective alloying material for iron, but various other alloying elements are used such as manganese, chromium, vanadium, and tungsten. [3]

Bare iron and steel are liable to rust in most environments but the extent of the corrosion depends upon a number of factors, the most important of which are the composition and surface condition of the metal, the corrosive medium itself and the local conditions.

With regard to the effect of composition, ferrous metals fall into three broad categories:

1. The ordinary cast irons, wrought irons and steels, to which no alloying elements are added, and which are vulnerable to corrosion.

2. Low-alloy steels, which contain about 2-3% of alloying elements, commonly copper, chromium and nickel. These steels still rust, but under certain conditions in the atmosphere, the rust formed becomes adherent and protective so that the corrosion rate becomes several times less rapid than with the ordinary steels mentioned above. These steels are often termed weathering steels.

3. Stainless steels, which contain high percentages of alloying elements, e.g. 18% chromium, 8% nickel and 3% molybdenum. Steels of this type are practically non-corrodible in appropriate circumstances. The discussion that follows will be concerned mainly with materials in the first of these categories. Moreover, since the corrosion of cast iron is discussed elsewhere , and since little wrought iron is produced nowadays, the subject matter will virtually resolve itself into the corrosion of ordinary carbon steels, as used in mass for general purposes.

The treatment will begin with a brief consideration of the mechanism of rusting and of the influence of variations in the steel itself. It will be completed by short surveys of present knowledge of the rusting of ordinary mild steel in the three natural media: air, water and soil.

II.3.2.1. Mechanism of Rusting

In pure dry air at normal temperatures a thin protective oxide film forms on the surface of polished mild steel. Unlike that formed on stainless steels it is not protective in the presence of electrolytes and usually breaks down in air, water and soil. The anodic reaction is:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad \text{(Eq. II.4)}$$

In de-aerated solutions, the cathodic reaction is

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(Eq. II.5)}$$

This occurs fairly rapidly in acids but very slowly in alkaline and neutral solutions. In the presence of oxygen the following reaction occurs in slightly alkaline and neutral solutions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{(Eq. II.6)}$$

This is the common form of cathodic reaction in most environments. The OH^- ions react with Fe^{2+} ions to form ferrous hydroxide:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad \text{(Eq. II.7)}$$

This is oxidised to ferric hydroxide $Fe(OH)_3$ which is a simple form of rust. The final product is the familiar reddish brown rust $Fe_2O_3.H_2O$, of which there are a number of varieties, the most common being the α form (goethite) and the γ form (lepidocrocite). In situations where the supply of oxygen is restricted, Fe_3O_4 (magnetite) or γ Fe_2O_3 may be formed.This is a simplified treatment but it serves to illustrate the electrochemical nature of rusting and the essential parts played by moisture and oxygen. The kinetics of the process are influenced by a number of factors. Although the presence of oxygen is usually essential, severe corrosion may occur under anaerobic conditions in the presence of sulphatereducing bacteria (Desulphovibrio desulphuricans) which are present in soils and water. The anodic reaction is the same, i.e. the formation of ferrous ions. The cathodic reaction is complex but it results in the reduction ofinorganic sulphates to sulphides and the eventual formation of rust and ferroussulphide (FeS).

II.3.2.2. Effect of Variations in the Steel

Ordinary steels are essentially alloys of iron and carbon with small additions of elements such as manganese and silicon added to provide the requisite mechanical properties. The steels are manufactured from a mixture of pig iron and scrap, which is treated in the molten state to remove excess carbon and other impurities. The steel may be continuously cast into strands or cast into individual ingots. The final product is then produced by rolling, drawing or forging. During hot rolling and forging the steel surface is oxidised by the air and the scale produced, usually termed millscale, may have an important influence on the corrosion of the steel.

The structure of millscale consists of three superimposed layers of iron oxides in progressively higher states of oxidation from the metal side outwards, ferrous oxide on the inside, magnetite in the middle and ferric oxide on the outside. The relative portions of the three oxides vary with the rolling temperatures. If millscale was perfectly adherent, continuous and impermeable, it would form a good protective coating, but in practice millscale soon cracks and flakes off in places. In air, the presence of millscale on the steel may reduce the corrosion rate over comparatively short periods, but over longer periods the rate tends to rise. In water, severe pitting of the steel may occur if large amounts of millscale are present on the surface. Wrought iron, which has been replaced by mild steel, contained appreciable quantities of slag and corroded at a rate about 30% less than mild steel when exposed in air.

The corrosion rates of wrought iron and mild steel when immersed in seawater or buried in soil are not significantly different when the copper contents are similar.Investigations of the effects on corrosion of mechanical working of steels indicate some influence on pitting but little on general corrosion.

II.3.2.3. Rusting in Air

II.3.2.3. Controlling Factors

The rusting of bare steel in the atmosphere is controlled by the climatic conditions at the exposure site. The main factors are the availability of moisture, and the extent to which the air is polluted, but other less important ones, such as temperature.

Moisture: the critical humidity Moisture can reach a steel surface directly in liquid form as a result of precipitation processes, i.e. rain and dew, but the water vapour that is always present in air can also, under certain conditions, cause steel to rust at relative humidities well below saturation.[4]

II.3.3. Aluminium and Aluminium Alloys

Aluminium is a soft, durable, lightweight, malleable metal with appearance ranging from silvery to dull grey, depending on the surface roughness. Aluminium is nonmagnetic and nonsparking. It is also insoluble in alcohol, though it can be soluble in water in certain forms.[5] Aluminium and the aluminium alloys lend themselves to many engineering applications because of their combination of lightness with strength, their high corrosion resistance, their thermal and electrical conductivity and heat and light reflectivity, and their hygienic and non-toxic qualities. The variety of forms in which they are available also enhances their utility.[4]

Zinc, aluminum, and zincaluminum alloy coatings are important anticorrosive coatings because they are anodic to steel. In other words, they corrode preferentially to steel, acting as sacrificial coatings preventing the corrosion of the underlying steel substrate. Zinc is a much more active metal in this respect than aluminum. On the other hand, aluminum coatings are harder, have better adhesion, and form a protective oxide layer that prevents self-corrosion. Alloys of the two metals have properties somewhere in between, depending on the ratio of zinc to aluminum. An 85-15 (percent by weight) alloy of zinc and aluminum is a widely used thermal spray coating material because it is thought to have the best combination of attributes from both metals.[1]

II.3.3.1. Composition and Mechanical Properties

Pure aluminium has good working and forming properties, high resistance to corrosion, low mechanical strength, and high ductility. The diverse and exacting technical demands made on aluminium alloys in different applications are met by the considerable range of alloys available for general and specific engineering purposes, each of which has been designed and tested to provide various combinations of useful properties. These include strength/weight ratio, corrosion resistance, workability, castability, or high-temperature properties, to mention but a few.

Composites of aluminium alloy with a thin cladding on one or both surfaces of a more anodic aluminium alloy or pure aluminium, enable sheet, plate and tube to be produced with special combinations of strength and corrosion resistance appropriate to service conditions. Although originallyapplied to high strength aircraft alloys, this principle of cladding is now utilised in several important industrial applications.

II.3.3.2. Selection of Purity or Alloy Type

II.3.3.2. Pure Aluminium

The use of the 99.8% and 99.99% grades is usually confined to those applications where very high corrosion resistance or ductility is required. The chemical industry can advantageously use these purities for handling some products, but because of their low mechanical strength they are sometimes used as a cladding material for a stronger substrate. Decreasing the purity results in increased strength for the 99% and 99.5% grades, which still retain a high resistance to corrosion. The 99% pure metal may be considered the more useful general purpose metal for lightly stressed applications such as panelling and cooking utensils.

II.3.3.3. Aluminium- Magnesium-Silicon Alloys

The corrosion resistance of the AI-Mg-Si alloys is slightly inferior to that of the Al-Mg alloys, but where maximum obtainable strength is required then a fully heat-treated Al-Mg-Si alloy would generally be preferable to an Al-Mg alloy with comparable properties obtained by cold working.

II.3.3.4. Aluminium-Zinc-Magnesium Alloys

The Al-Zn-Mg alloy system provides a range of commercial compositions, primarily for those areas where strength is a major consideration. The high strength alloys contain a Zn + Mg content well in excess of 6% and are used in specialist structures such as aircraft. The risk of stress corrosion cracking in these alloys may be accentuated by incorrect heat treatment or composition and they cannot be recommended for general use.

The other group of alloys are those with a Zn + Mg content not exceeding 6%. These have been used for general engineering, when natural ageing after welding can be utilised to permit the fabrication of strong welded structures. In particular, these medium strength Al-Zn-Mg alloys have been successfully used for transport applications and it seems probable that this will increase in the near future. With correct manufacturing procedures the risk of stress corrosion with these alloys is negligible and the resistance to unstressed corrosion is only slightly inferior to the AI-Mg-Si structural alloys.

II.3.4. Corrosion Behaviour in Aqueous Environments

II.3.4.1. Theoretical Considerations of Corrosion Behaviour

Aluminium is a very reactive metal with a high affinity for oxygen. The metal is nevertheless highly resistant to most atmospheres and to a great variety of chemical agents. This resistance is due to the inert and protective character of the aluminium oxide film which forms on the metal surface. In most environments, therefore, the rate of corrosion of aluminium decreases rapidly with time. In only a few cases, e.g. in caustic soda, does the corrosion rate approximate to the linear. A corrosion rate increasing with time is rarely encountered with aluminium, except in aqueous solutions at high temperatures and pressures.The corrosion resistance of aluminium and its alloys is largely due to the protective oxide film which within seconds attains a thickness of about 10 Å on freshly exposed metal; continuation of growth is markedly influenced by the environment, being accelerated by increasing temperature and humidity. Immersion in water results in rapid oxide thickening. The behaviour of the oxide may be modified by impurities or alloying additions.

II.3.4.2. Corrosion in Natural Environments

II.3.4.2. Atmospheric

The aluminium alloys as a group weather outdoors to a pleasant grey colour, which deepens to black in industrial atmospheres. Superficial pitting occurs initially but gradually ceases, being least marked on high-purity aluminium. With some alloys, including the copper-bearing alloys and the medium-strength AI-Zn-Mg alloys, additional protection, e.g. painting, is desirable in the more aggressive atmospheres to avoid any risk of intercrystalline corrosion.

Gases such as hydrogen sulphide and carbon dioxide do not increase the corrosivity of the atmosphere towards aluminium. Service experience extends over 70 years and includes such well-known examples. Twenty-year tests at selected marine, industrial and rural sites have shown that the greater part of the attack takes place in the first year or two and that thereafter the rate of attack maintains a low value. The relatively high percentage strength losses are due to the extremely thin test specimens. The falling-off in rate of pitting with time is in sharp contrast to the behaviour of the older-established structural metals which have a fairly uniform corrosion rate throughout their life, and indicates that the relative merit of aluminium increases with scheduled life.

II.3.4.3. High-temperature Corrosion

II.3.4.3. Dry Atmospheres

When exposed at high temperatures in dry atmospheres aluminium is highly resistant to corrosion by most of the common gases, other than the halogens or their compounds.

II.3.4.3. High-Temperature Aqueous Systems

When aluminium corrodes at temperatures below 90°C in aqueous systems, attack is usually by pitting. At temperatures between 90 and 250°C (for the attainment of high considerable pressures are needed) uniform attack is the commonest form of aqueous corrosion. Above about 250°C, uniform attack is merely the prelude to highly destructive intergranular attack. The corrosion products from the uniform attack form a film which includes a barrier layer and a bulk film analogous to those formed during anodising it is the bulk film which controls the corrosion rate, which is not significantly affected by most common dissolved ions. The onset of intergranular attack occurs at about the same time as the crystallisation of the amorphous barrier layer oxide. Kinetic studies indicate that over the temperature range from 100 to 363 °C the oxidation rate law is successively inverse logarithmic, parabolic and linear.[4]

II.4. Protective Coatings

Protective coatings are probably the most widely used products for corrosion control. They are used to provide long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials to preserve their strength and integrity. The main function of a protective coating is to isolate structural reactive elements from environmental corrosives. The fact that protective coatings occupy only a very small fraction of the total volume of a system is quite telling of the heavy requirements imposed on these materials.

A coating must provide a continuous barrier to a substrate, and any imperfection can become the focal point for degradation and corrosion of the substrate. Metal finishing comprises a wide range of processes that are practiced by most industries engaged in manufacturing operations using metal parts. Typically, metal finishing is performed on manufactured parts after they have been shaped, formed, forged, drilled, turned, wrought, cast, and so forth. A“finish” can be defined as any final operation applied to the surface of a metal article to alter its surface properties and achieve various goals. The quality of a coating depends on many factors besides the nature of the materials involved. Metal finishing operations are intended to increase corrosion or abrasion resistance, alter appearance, serve as an improved base for the adhesion of other materials, enhance frictional characteristics, add hardness, improve solderability, add specific electrical properties, or improve the utility of the product in some other way.

II.4.1. Coatings and Coating Processes

Coating fundamentals makes reference to a multitude of concepts and properties. A critical property of antifouling paint is, for example, the inhibition of living organism growth on the coating. A fire-resistant coating, on the other hand, should resist or retard the burning of the substrate. From a corrosion point of view a coating is rated on the resistance it provides against corrosion in a specific environment, and because there are many variations in environment corrosivity, there is also a great variety of corrosion protective coatings. These can be broadly divided into metallic, inorganic, and organic coatings.

II.4.1.1. Metallic Coatings

Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. The workpiece becomes a composite material exhibiting properties generally not achievable by either material if used alone. The coatings provide a durable, corrosion-resistant layer, and the core material provides the load-bearing capability. The deposition of metal coatings, such as chromium, nickel, copper, and cadmium, is usually achieved by wet chemical processes that have inherent pollution control problems. Alternative metal deposition methods have replaced some of the wet processes and may play a greater role in metal coating in the future. Metallic coatings are deposited by electroplating, electroless plating, spraying, hot dipping, chemical vapor deposition, and ion vapor deposition. Some important coatings are cadmium, chromium, nickel, aluminum, and zinc. Copper, gold, and silver are also used in electrical equipment and occasionally for specialty fastener applications. Copper is used as a base layer in multiple-plate electroplating, silver is used for antifretting purposes, and both silver and gold are sometimes used to provide electrical conductivity in waveguides and at contacts.[6]

II.4.2. Coatings for Corrosion Resistance

Thermal spray coatings, primarily zinc, aluminium, zinc-aliminum alloys and aluminium metal-matrix composites have been successfully used to combat corrosion in a wide range of applications. Steel structures and components that have been zinc or aluminium sprayed include television towers, antennea, radar, bridges, light poles, girders, ski lifts and countless other similar structures. In addition thermal spray coatings, primarily aluminium offers years of protection in marine applications, such as buoys and pylons. Aluminium spraying has been used in offshore oil rigs for well head assemblies, flare stacks, walkaways, and other structural steel components.

II.4.2.1. High Temperature Protection

There are several specific applications in the hot sections of engines where corrosion and high temperature metal fatigue occur together. If substrate temperatures can be held down at critical moments of engine activity, there is an oppornity to raise combustion temperatures with resulting improvements in engine performance.[7]

II.4.3. Properties and Applications of the Main Metallic Elements Used for Protective Coatings

II.4.3.1. Aluminium

Aluminum coatings can be applied to steel by hot dipping, cementation, ion vapor deposition, and spraying. Ion vapor deposition is a relatively new process, and spraying is the only process that has been used extensively over a long period of time. Pack cementation is widely used for gas turbine components. In soft waters aluminum is cathodic with respect to steel; however, in seawater or some fresh waters containing chloride ions or sulfate ions, aluminum may become anodic to steel, and aluminum coatings should therefore corrode sacrificially and provide cathodic protection to steel. However, as noted below, this may not always be the case. Sprayed aluminum coatings provide an adherent, somewhat absorbent film about 100 to 150 μm thick. They provide very good protection to steel, and they may be sealed with organic lacquers or paints to provide further protection and delay the formation of visible surface rust. The surface of the steel must first be grit-blasted to provide a rough surface to aid adhesion. Unfortunately the thickness and relative roughness of the coatings make them unsuitable for close tolerance parts. Ion vapor-deposited aluminum coatings have been used on a variety of parts including steel and titanium fasteners, electrical connectors, engine mounts and stator vanes, landing gear components, integrally machined wing skins, and a large number of miscellaneous components. These coatings are soft and ductile and are prepared using commercially available aluminum feed wire that is melted, vaporized, and ionized in a glow discharge created by an inert gas. The process is applied in a batch mode, where parts to be coated are held at a high negative potential relative to the evaporation source. The positively charged gas ions bombard the surface of the part and perform a final cleaning action. When this is done the aluminum is vaporized and ionized, and the ionized aluminum is accelerated toward the part surface where it plates as a dense, tightly adherent coating. Minimum coating thickness are in the range 8 to 25 μm, and coatings may be used as prepared or with a supplementary chromate treatment. The thinner coatings are used when close tolerances are required such as on threads, intermediate thickness coatings are used on interior parts or where only mildly corrosive environments are expected, and the thicker coatings are used for exterior parts operating in highly corrosive environments and for engine parts. Ion vapor-deposited aluminum has been considered as a replacement for diffused nickel cadmium and aluminum pigmented paints for use in the cooler sections of gas turbines, where temperatures are less than 454°C. The process has also been considered as an alternative to pack cementation for the preparation of aluminide coatings on hot-section components. In this case the ion vapor-deposited aluminum is diffused into the nickel-based superalloy substrates to form the nickel aluminide coating.Ion vapor deposition of aluminum is attractive because it avoids the environmental and toxicological problems associated with cadmium. It does not cause hydrogen embrittlement of steel or solid metal embrittlement of steel or titanium, and it should be more galvanically compatible with aluminum alloy structure and avoid the exfoliation corrosion of sensitive aluminum alloy structure. However, views on the ability of aluminum to protect steel fasteners appear to vary. A view is that the presently available pure aluminum coatings are not able to provide adequate sacrificial protection to steel in a chloride ion environment, and for this reason a recommendation is made for the development of aluminum coatings containing small amounts of zinc or other elements for improved protection.

II.4.3.1. Pack Cementation

Diffusion coatings are formed by depositing a layer of aluminum on the metal surface and then heating the component in a furnace for a period of time. During this heat treatment, the aluminum and metal atoms migrate, or diffuse, into each other, which is the reason these coatings are called diffusion coatings. This processing is usually performed by a pack cementation process in which the aluminum deposition and the heat treatment occur simultaneously. Pack cementation is widely used to confer oxidation resistance on ferrous alloys. Usually relatively expensive aluminum or binary alloys grade reagent is used during the pack process with aluminum as a source. Pack cementation processes include aluminizing, chromizing, and siliconizing. Components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. In the aluminizing process, a source of aluminum reacts with a chemical activator on heating to form a gaseous compound (e.g., pure Al with NaF to form AlF). This gas is the transfer medium that carries aluminum to the component surface. The gas decomposes at the substrate surface, depositing aluminum and releasing the halogen activator. The halogen activator returns to the pack and reacts with the aluminum again. Thus, the transfer process continues until all of the aluminum in the pack is used or until the process is stopped by cooling. The coating forms at temperatures ranging from 700 to 1100°C over a period of several hours. Pack cementation is the most widely used process for making diffusion aluminide coatings. Diffusion coatings are primarily aluminide coatings composed of aluminum and the base metal. A nickel-based superalloy forms a nickel-aluminide, which is a chemical compound with the formula NiAl. A cobalt-based superalloy forms a cobalt-aluminide, which is a chemical compound with the formula CoAl. It is common to incorporate platinum into the coating to improve the corrosion and oxidation resistance. This is called a platinum-aluminide coating. Diffusion chrome coatings are also available. Diffusion aluminide coatings protect the base metal by forming a continuous, aluminum oxide layer, Al_2O_3, which prevents further oxidation of the coating. (Actually, oxidation continues but at much slower rates than without a continuous aluminum oxide scale.) When part of the Al_2O_3 scale spalls off, the underlying aluminide layer is exposed to form a new Al_2O_3 scale. Thus, the coating is self-healing. Pack cementation can also be used to produce chromium-modified aluminide coatings. The addition of chromium is known to improve the hot corrosion resistance of nickel-based alloys. Although chromium can be codeposited with aluminum in a single-step process, a duplex process is frequently used to form the chromium-modified aluminide. The component is first chromized using either pack cementation or a gas phase process, and this is then followed by a standard aluminizing treatment. The final distribution of the chromium in the coating will depend on whether a low- or high-activity aluminizing process is employed. For a platinum-aluminide coating, a thin layer of platinum is first deposited onto the substrate, usually by a plating process. The second step involves aluminizing for several hours using the conventional packed cementation process to form the platinumaluminide coating. Conventional pack cementation processes are unable to effectively coat internal surfaces such as cooling holes. The coating thickness on these internal surfaces is usually less than on the surface due to limited access by the carrier gas. Access can be improved by pulsing the carrier gas, or by use of a vapor phase coating process. Another method of coating both the internal and external surfaces involves generating the coating gases in a reactor that is separate from the vessel the parts are in. The coating gases are pumped around the outside and through the inside of the parts by two different distribution networks. Internal passages can be coated by filling them with the powder used in the pack. Slurry processes can also be used to deposit the aluminum or the aluminum and other alloying elements. The slurry is usually sprayed on the component. The component is then given a heat treatment, which burns off the binder in the slurry and melts the remaining slurry, which reacts with the base metal to form the diffusion coating. After coating, it is usually necessary to heat treat the coated component to restore the mechanical properties of the base metal. Thermal spraying. Energy surface treatment involves adding energy into the surface of the work piece for adhesion to take place. Conventional surface finishing methods involve heating an entire part. The methods described in this section usually add energy and material into the surface, keeping the bulk of the object relatively cool and unchanged. This allows surface properties to be modified with minimal effect on the structure and properties of the underlying material. Plasmas are used to reduce process temperatures by adding energy to the surface in the form of kinetic energy of ions rather than thermal energy.

Advanced surface treatments often require the use of vacuum chambers to ensure proper cleanliness and control. Vacuum processes are generally more expensive and difficult to use than liquid or air processes. Facilities can expect to see less-complicated vacuum systems appearing on the market in the future. In general, use of the advanced surface treatments is more appropriate for treating small components (e.g., ion beam implantation, thermal spray) because the treatment time for these processes is proportional to the surface areas being covered. Facilities will also have to address the following issues when considering the new techniques. Coatings can be sprayed from rod or wire stock or from powdered materials. The material (e.g., wire) is fed into a flame, where it is melted. The molten stock is then stripped from the end of the wire and atomized by a high-velocity stream of compressed air or other gas, which propels the material onto a prepared substrate or workpiece. Depending on the substrate, bonding occurs either due to mechanical interlock with a roughened surface, due to localized diffusion and alloying, and/or by means of Van der Waals forces (i.e., mutual attraction and cohesion between two surfaces). The basic steps involved in any thermal coating process are substrate preparation, masking and fixturing, coating, finishing, inspection, and stripping (when necessary). Substrate preparation usually involves scale and oil and grease removal, as well as surface roughening. Roughening is necessary for most of the thermal spray processes to ensure adequate bonding of the coating to the substrate. The most common method is grit blasting, usually with alumina. Masking and fixturing limit the amount of coating applied to the workpiece to remove overspray through time-consuming grinding and stripping after deposition. The basic parameters in thermal spray deposition are particle temperature, velocity, angle of impact, and extent of reaction with gases during the deposition process. The geometry of the part being coated affects the surface coating because the specific properties vary from point to point on each piece. In many applications, workpieces must be finished after the deposition process, the most common technique being grinding followed by lapping. The final inspection of thermal spray coatings involves verification of dimensions, a visual examination for pits, cracks, and so forth. Nondestructive testing has largely proven unsuccessful. There are three basic categories of thermal spray technologies: combustion torch (flame spray, high velocity oxy-fuel, and detonation gun), electric (wire) arc, and plasma arc. Thermal spray processes are maturing, and the technology is readily available. Environmental concerns with thermal spraying techniques include the generation of dust, fumes, overspray, noise, and intense light. The metal spray process is usually performed in front of a “water curtain” or dry filter exhaust hood, which captures the overspray and fumes. Water curtain systems periodically discharge contaminated wastewaters. Noise generated can vary from approximately 80 dB to more than 140 dB. With the higher noise-level processes, robotics are usually required for spray application. The use of metal spray processes may eliminate some of the pollution associated with conventional tank plating. In most cases, however, wet processes, such as cleaning, are necessary in addition to the metal coating process. Therefore, complete elimination of tanks may not be possible. Waste streams resulting from flame spray techniques may include overspray, wastewaters, spent exhaust filters, rejected parts, spent gas cylinders, air emissions (dust, fumes), and wastes associated with the grinding and finishing phases.

II.5. Surface Preparation

It is well recognized that you can make a poor coating perform with excellent pretreatment, but you cannot make an excellent coating perform with poor pretreatment. Surface pretreatment by chemical or mechanical means is also important in painting, and the methods used are designed to ensure good adhesion of the paint to the alloy surface. Surface engineering for increased material performance is one important element in the world of metal finishing. Most metal surface treatment and plating operations have three basic steps:

1. Surface cleaning or preparation, which involves the use of solvents, alkaline cleaners, acid cleaners, abrasive materials, and/or water

2. Surface modification, which involves some change in surface properties, such as application of a metal layer or hardening

3. Rinsing or other workpiece finishing operations to produce the final product.[6]

II.6. Spray and Fuse Coatings

The Spray and Fuse coatings have been metallurgically developed to perform at their peak after having undergone an intense fusing stage. This line of coatings combines the ease of application of a thermal sprayed coating with the tough, high stress wear characteristics of a hardface weld overlay.[8]

The Spray and Fuse process consists of spraying a powdered alloy or wire on a part and then the sprayed overlay is fused to the base metal by torch or furnace heat. This creates a smooth, nonporous, welded hard surface that can then be ground and lapped to a low surface roughness finish.[9]

Spray and fuse is a modification of the cold spray method. The materials used for coating the self-fluxing alloys. These materials contain elements that react with oxygen to oxides to form low-density oxides that float to the surface, thus improving density, bonding. They have relatively low melting points and require post spray heat treatment. In general, these are nickel- or cobalt-base alloys that use boron, phosphorus, or silicon, either singly or in combination, as melting-point depressants and fluxing agents. In practice, parts are prepared and coated as in other thermal spray processes and then fused. There are two variants: Spray and fuse, and spray-fuse. In spray and fuse, the fusion is done after deposition using one of several techniques, such as flame or torch, induction or vacuum, inert, or hydrogen furnaces. In spray-fuse, the deposition and fusion are done simultaneously.

The alloys used generally fuse between 1010 to 1175 °C, depending on composition. Reducing atmosphere flames should be used to ensure a clean, well-bonded coating. In vacuum and hydrogen furnaces, the coating may have a tendency to wick or run onto adjacent areas. Several stop off materials are commercially available to confine the coating. It is recommended that test parts be coated and fused whenever the shape, coating alloy, or lot of material is changed, to establish the minimum and maximum fusing temperatures. Fusing temperature is known to vary slightly between lots of spray material. On vertical surfaces, coating material may sag or run off if the fusing temperature is exceeded by more than a few degrees. These coatings are fully dense and exhibit metallurgical bonds. Excessive porosity and nonuniform bonding are usually indicative of insufficient heating.

Spray-and-fuse coatings are widely used in applications where excessive wear combined with high stresses on the coating/substrate (shear or impact) are a problem. These alloys generally exhibit good resistance to wear and have been successfully used in the oil industry for sucker rods and in agriculture for plowshares. In many applications, these coatings make possible the use of less expensive substrate materials. Coating harnesses can be as high as 65 HRC. Grinding is usually necessary for machining a fused coating because of the high hardness. Use of spray-an-fuse coatings is limited to substrate materials that can tolerate the 1010° C fusing temperatures. Fusing temperature may alter the heat-treated properties of some alloys. However, the coating will usually withstand additional heat treatment of the substrate. Slower cooling rates may be required to reduce cracking where greater thicknesses are needed or where there is a substantial difference in the thermal expansion coefficients between the coatings and the substrate.[10]

II.6.1. Fusing of Thermal Sprayed Coatings

It is good practice to begin the fusing operation immediatly after the spraying is completed. The work is already hot, and this heat is wasted if fusing is delayed. Also, on low-expansion steels there is a possibility that the coating will crack during cooling and it is not always easy to "heal" these cracks.

Fig.II.8. Spraying of workpiece before fusing process. [9]

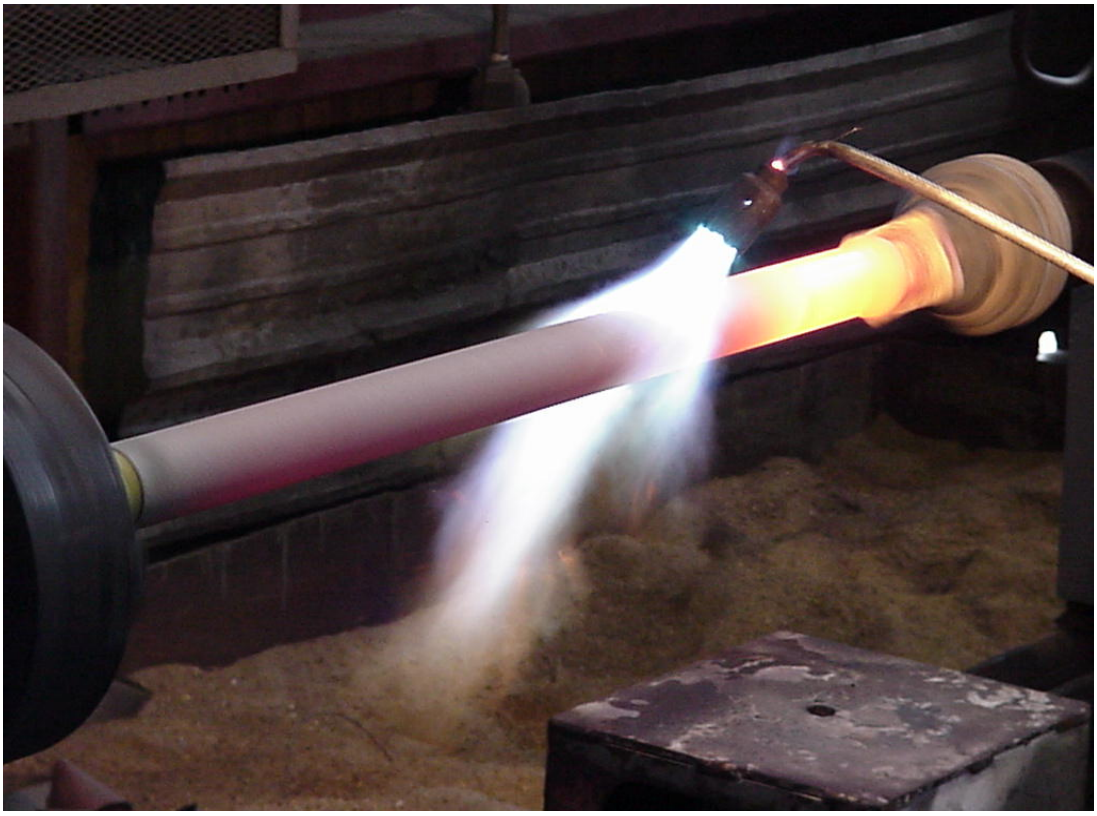


Fig.II.9. Fusing of thermal sprayed workpiece. [9]

II.6.1.1. Torch Fusing

The most widely used fusing method is with acetylene torches. Prophane is sometimes used, and while it offers a slight economic advantage it generally has a somewhat stronger oxidizing effect.

Fusing technique varies widely with the size, shape, and composition of the base material but there are a few basic rules which should be observed:

a. Avoid excessive heat concertration when heating prior to fusing. As sprayed, the coating is in tension but if the torch is immediately brought up close to the surface, and held in one place, the coating may expand much faster then the base material and the bond may be destroyed before fusing is accomplished. If the coating loosens from the base, oxidation of the base prevents "wetting" and the coating cannot then be fused to the base.

b. Make sure that the base material is heated throughout, to a temperature close to the melting point of the coating. Otherwise the base is not fully expanded and so will contract much less than the coating during cooling. This can result in cracking.

c. Always use a neutral or slightly reducing flame. With the nickel-base alloys a slight “feather” is desirable; with the cobalt base alloys it is essential to maintain a “feather” three to five times the lenght of the inner cone. Flow reading ratios of 3 oxygen to 4 acetylene are satisfactory with the nickel-base alloys. Slight higher acetylene to oxygene ratios should be used with the cobalt base alloys.

d. Always use a torch or torched with ample capacity, with a fairly “soft” flame. A high velocity flame may cause the molten surface to flow unevenly. Also, it is poor economy to use excessive flame velocities.

e. Avoid overheating. This causes sagging or running with the straight self-fluxing alloys and may cause gassing withcarbide coatings. The fusion point is easly recognised as the coating “glistens” when fusing temperature is reached.

II.6.1.2. Furnace Fusing

Nearly all high temperature furnace brazing is done using a dry hydrogen atmosphere, and this is the ideal atmosphere for furnace fusing of flame-sprayed hard surfacing alloys. Combusted gas atmospheres can be used for some work, but good control is necessary and the atmosphere must be free of excess oxygen. Because of the many variables involved, it is recomended that furnace fusing problems be treated on an individual basis.

II.6.1.3. Induction Fusing

This method is useful principally for repetitive work. For production applications, induction heating equipment should be consulted. [11]

III. THE STUDY

III.1.Selection of The Coating Material and Application of Processes

In this study St-37 mild steel has been coated with wire flame spray and electric arc spray methods with a specified aluminum alloy. The coating wires are 1.62 and 3.20 mm diameters Al-6Si alloy. After spraying, surface of some selected specimens have been fused by propane torch. Fusing process is needed to melt the surface of the coated specimens to improve density of coating and reduce porosity concentration of the specimens. Therefore, a lower surface area and a better bonding can be obtained after fusing process.

Flame spray and electric arc spray methods are the processes that wire can be used as coating material. Because of that, both processes, depending on wire feeding systems have been used in this study. Usage of wire at coating process is cheaper than powder processes and at industrial applications production costs are very important. The specifications of the alloy which have been used is Al-6Si. The Al-6Si wire that specifically design for electric arc spray applications has a size of 1.62 mm diameter. This aluminum wire has a wide range of applications. Al-6Si wire with a 3.2 mm diameter is used for flame spray applications. This aluminum wire is recommended for repair and restoration of aluminum based substrates and for low temperature abradable seal applications in compressors. The addition of silicon in the aluminum alloy provides improved machining capability over coatings of pure aluminum. Coating hardness will vary with application temperature and during the service life of the coating.[12]

At the coating process Metco 12E wire flame spray gun and Senkron Arcjet 95 guns were used. The Metco 12E combustion wire spray process employs a set of drive rolls powered by an air turbine to draw a metal alloy wire through the combustion spray gun. At the gun nozzle, fuel gas of acetylene, propane, hydrogen is mixed with oxygen in precise volumetric proportions using a siphon plug and ignited to create a flame, which is then shaped at the gun’s air cap by compressed air. The metal wire is fed concentrically into the flame, melted and atomized by the compressed air, and the molten droplets are propelled towards a prepared surface where they solidify and bond to the substrate to form a coating.[13]

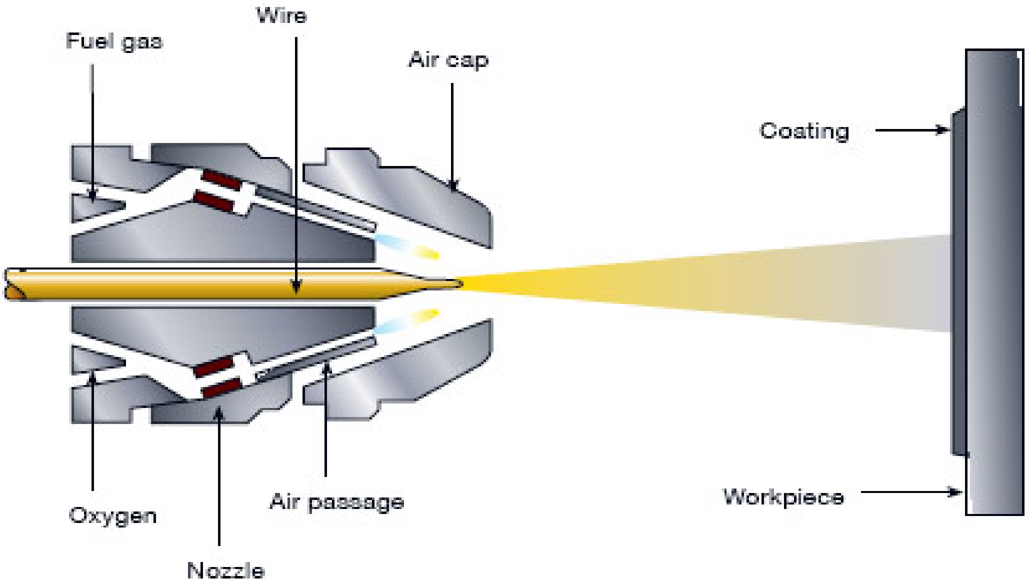


Fig. III.1. Schematic cross-section of a typical combustion wire spray gun [13]

Combustion wire spray is a common choice for machine element repair and corrosion coatings. Either hard (higher melt temperature) or soft (lower melt temperature) wires can be used.[13]

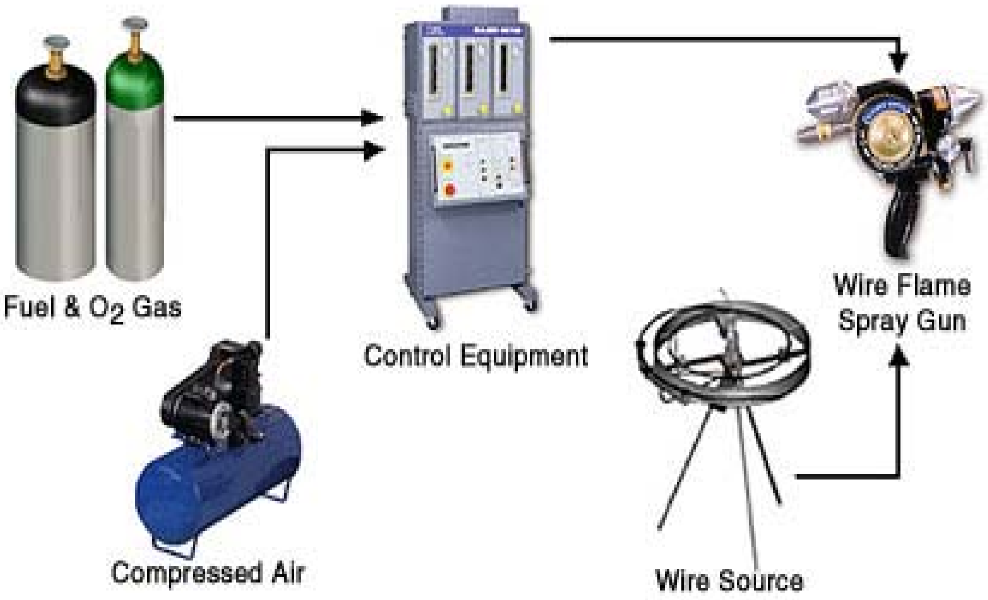


Fig. III.2. Key components of combustion wire spray system [13]

Fig. III.3. Metco 12E gun while coating process.[14]

The Senkron Arcjet 95 gun uses two metallic wires, usually of the same composition, as the coating feedstock. The two wires are electrically charged with opposing polarity and are fed into the arc gun at matched, controlled speeds. When the wires are brought together at the contact point, the opposing charges on the wires create enough heat to continuously melt the tips of the wires. Compressed air is used to atomize the now molten material and accelerate it onto the workpiece surface to form the coating.[15]

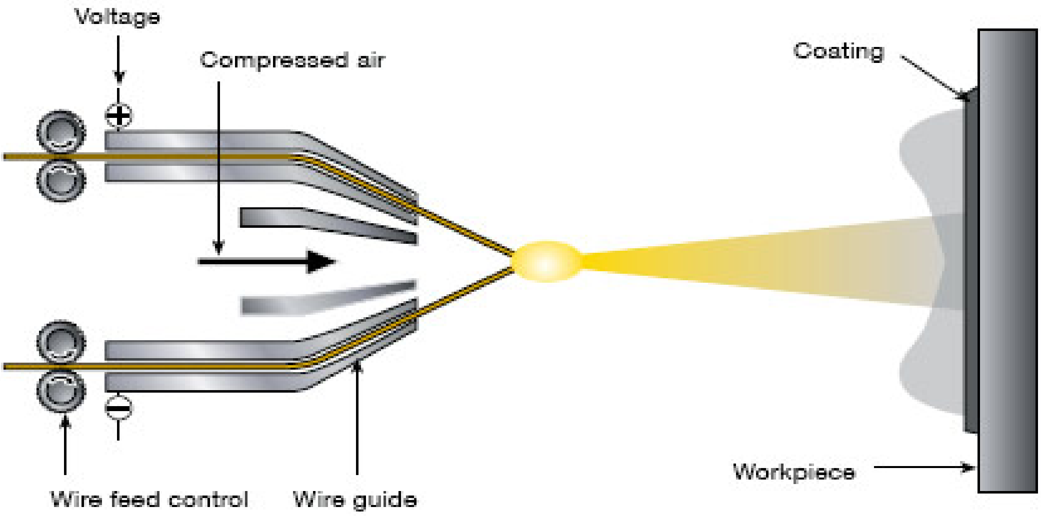


Fig. III.4. Schematic cross-section of a typical electric arc wire spray gun[15]

In electric arc wire spray system, the weight of coating that can be deposited per unit of time is a function of the electrical power (amperage) of the system and the density and melting point of the wire. Depending on the columnar strength of the wire, 'push', 'pull' or 'push/pull' mechanisms can be used to feed the wire at a constant rate.[15] The Senkron Arcjet 95 gun has a pull wire feeding system. Wire feeding is done by a air motor which has a 2500 RPM. Also this gun has a melting capacity about 8,6 Kg per hour. The power supply of this gun is about 450 Ah and while coating process with 1.62 mm size wire it uses about 180-200 Ah and 25-30 volts.

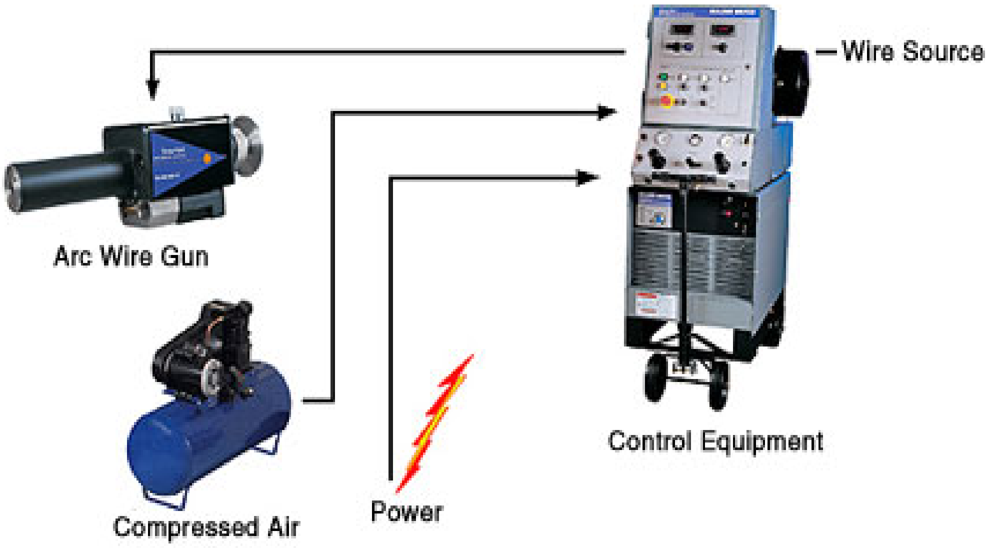


Fig. III.5. Key components of electric arc wire spray system.[15]

The pressure of the spray air is about 6 bars and for wire feeding speed it is about 2 bars. These are the parameters of arc spray gun. Coating thickness is about 250 μm to 350 μm.

For the surface preparation of samples, brown Al_2O_3 sand has been used. This sandblasting material has a number of 36. And the diameter of sandblasting nozzle is 8 mm. The spray air for sandblasting is about 6- 7 bars.

The same coating thickness has been used at the flame spray process. Spray distance for both of the coatings are 15- 17cm. The rpm of lathe while coating process is 180 and while fusing process it is 60 rpm. The heat of the specimens while coating has not been exceeded 80 °C and while fusing, temperature is about 750 – 850 °C degree. At the coating process, the moving speed of the guns are both same and it is about 10 m/s. But this speed is up to melting at fusing process and controlled by technicians due to their experiences.

At wire flame spray process acetylene fuel has been used and flow rate of the gas is about 40-45 psi .The pressure of the gasses are 4 bars for oxygen, 1.5 bars for acetylene and 5 bars for spraying air.

After coating process the samples were heat treated using PYROX VIK 150/18 electric heated furnace for 8 hours at 950 °C under vacuum ($10^{-1.5}$ mbar) with a heating rate of 10 °C/min for diffusion process to take place.

Corrosion behavior of coatings was evaluated by salt spray corrosion test. The test unit was operated by 5 % NaCl distilled water solution. WEISS SC 450 was used to perform corrosion resistance of coating for 72 hours by 24 hours intervals. This practice provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber.

Oxidation test was also performed on both after diffusion and coated only samples at 850 °C for 24 hours in air atmosphere and weight of samples was measured before and after oxidation test to monitor weight changes during oxidation.

For microstructural investigation after coating and melting processes the specimens have been cut into 1 cm wide with a disc grinder and they have been polished by Struers Labopol-6 with an rpm of 800 and the grit sizes of 320, 600, 800 and 1000 silicon carbide grinding papers. At polishing process 1-3 µm Al_2O_3 paste has been used.

For the microstructural investigations, Nikon Eclipse series microscope has been used for optical studies. Jeol JSM - 5910 LV series scanning electron microscope was employed for back scattered and EDS analysis.

IV. RESULTS AND DISCUSSIONS

IV.1. Corrosion Test Results

For corrosion tests WEISS SC 450 salt spray equipment has been operated by 5 % NaCl distilled water solution. Total test time is 72 hours with 24 hours intervals.

Test conditions and results of samples are given in Table IV.1.

Table IV.1. Test conditions and test results of samples.

Sample Number	**Coating Equipment**	**Coating Method**	**Coating Material**
1	Arc Spray	Sprayed and Fused	Al6Si
2	Arc Spray	Sprayed	Al6Si
3	Flame Spray	Sprayed and Fused	Al6Si
4	Flame Spray	Sprayed	Al6Si
5	None	None	None

There is no indication of any red or brown rust on the coated samples revealing that coating is protective against salt spray test.

Table IV.2. Salt spray specimens before test.

 Sample 1	 Sample 2
 Sample 3	 Sample 4
 Sample 5	

Table IV.3. Salt spray specimens after 48 hours.

 Sample 1	 Sample 2
 Sample 3	 Sample 4
 Sample 5	

Table IV.4. Salt spray specimens after 72 hours.

 Sample 1	 Sample 2
 Sample 3	 Sample 4
 Sample 5	

After salt spray tests, weight changing by percentage is given below on the table:

Table IV.5. Weight change of salt spray samples by % .

Sample Number	**Weight chance (%)**
1	0
2	0
3	0
4	0
5	- 0.502

After salt spray tests sample 1,2,3 and 4 have no changes on their weight. Possible reasons of that non changing weight is, chemical resistance of coated aluminium layer onto steel substrate. That means a lower corrosion has been seen on samples . Aluminium has good stability in NaCl salt solution. But sample 5 which was not coated and in as received condition had a weight loss suggesting, steel has been reacted with salt solution and rust formed on the surface of sample. Dissolution of iron atoms into solution and formation of rust from sample surface, has lead to the weight loss. However, according to results of this experiment, generally aluminium coatings on steel surfaces which have been fused or not fused showing good corrosion resistance behavior in salt solutions.

IV.2. Oxidation test results

Oxidation test was carried out on selected samples in air atmosphere furnace, at 850 °C for 24 hours. Mass of all samples was recorded before and after the test to evaluate the weight changes and oxidation behaviour. The weight % changes of samples was given in Table IV.6. The effect of oxygen on samples at high temperature has been investigated in this experiment.

Samples with fusing treatment exhibited higher oxidation resistance than coated only samples with no fusing treatment. This result was shown in the Table IV.6 in samples 1 and 3.

These results suggested that after fusing process lower porosity concentration and a better bonding can be obtained resulting in lower oxidation.

Table IV.6. Weight changes % of oxidation test samples.

Sample Number	**Weight change after coating (%)**
1	4.47
2	5.10
3	5.63
4	6.16
5 (Non coated steel)	8.25

IV.3. Optical Metallographic Results

Optical microscope images were given below figures at 100x zoom.

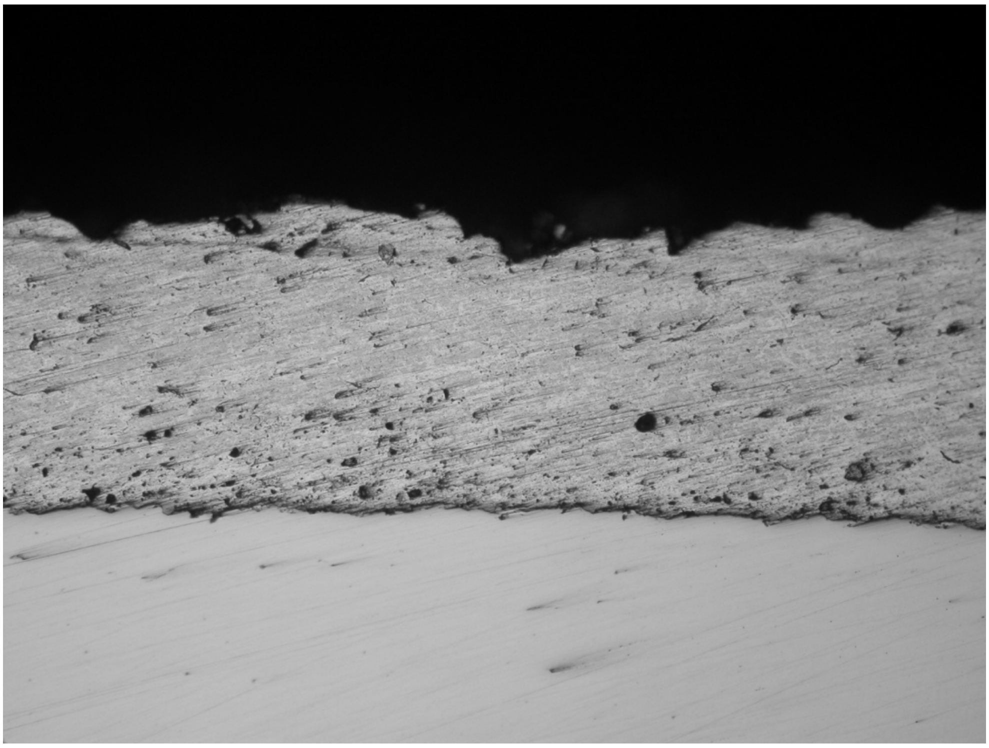


Fig. IV.1. Optical Microscopy of arc wire sprayed Al-6Si at 100x.

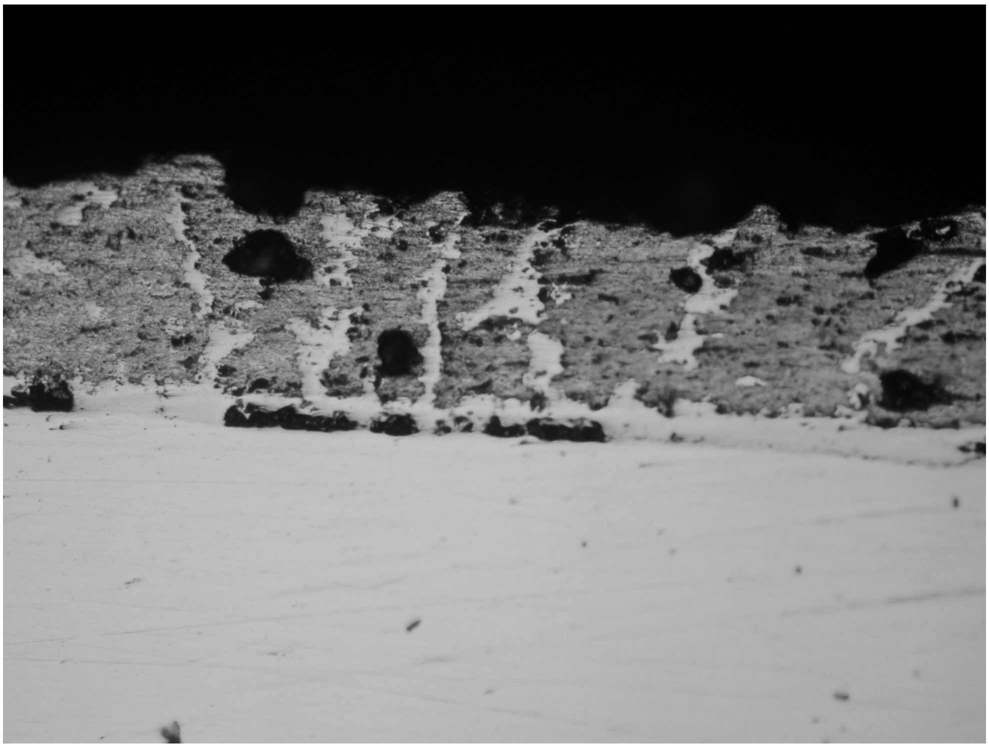


Fig. IV.2. Optical Microscopy of arc wire sprayed and fused Al-6Si at 100x.

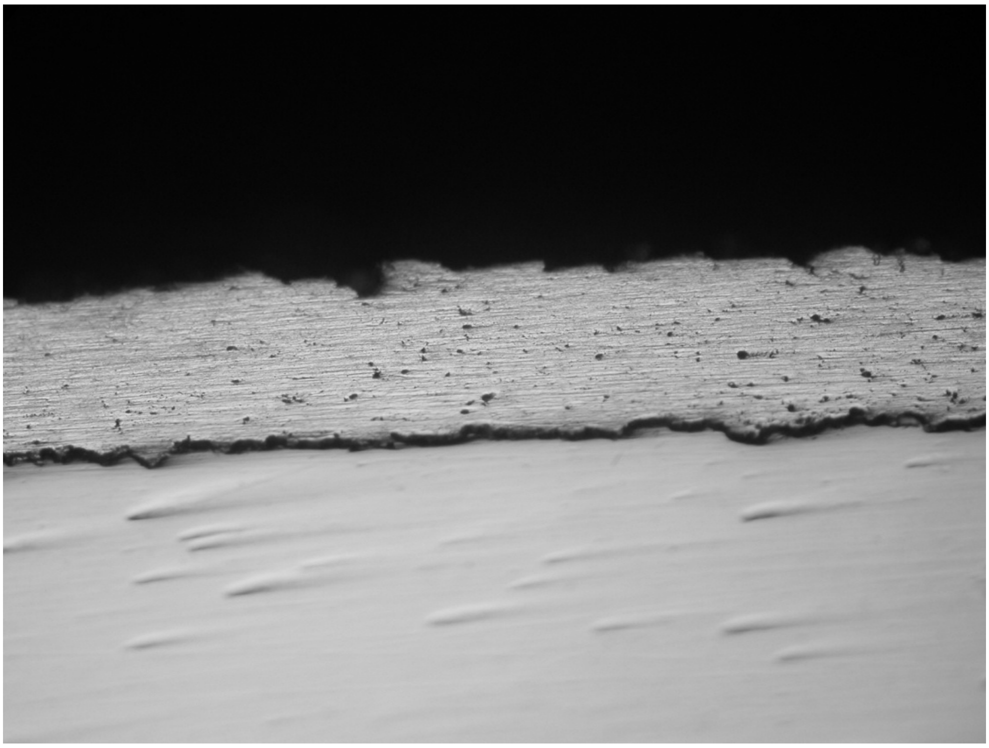


Fig. IV.3. Optical Microscopy of wire flame sprayed Al-6Si at 100x

Fig. IV.4. Optical Microscopy of wire flame sprayed and fused Al-6Si at 100x

In the optical microscopy results which were given in Figs IV. 1, 2,3,4,5 and 6 Al alloy coating can be seen with a thickness of 250-350 µm. Some reaction products were clearly identified as Fe and Al intermetallics which will be evaluated in the next section. Porosities were formed during thermal spray processes which are not homogenously distributed and because of fusing process porosities are got together forming larger porosities compared to after thermal coating. Because of the lack of bonding after sand blasting and coating between substrate and the Al alloy coating layer the mechanical properties of that kind of coating could be lower. However, after fusing treatment carried out by acetylene torch physical bonding was transformed into chemical bonding but some of the porosities were enlarged their diameter by rejoining to each other.

On the other hand, reaction products were formed after coating and diffusion heat treatment revealing different contrast in the microstructure as shown in Fig. IV.2. and the Fig. IV.4.

For a clear view of aluminium and steel structure, samples have been etched with %1 Nital solution. Etching time has been set to 30 seconds. After etching process, microstructure of steel has been revealed and no changes have been seen on aluminium coatings.

The optical view of etched samples are:

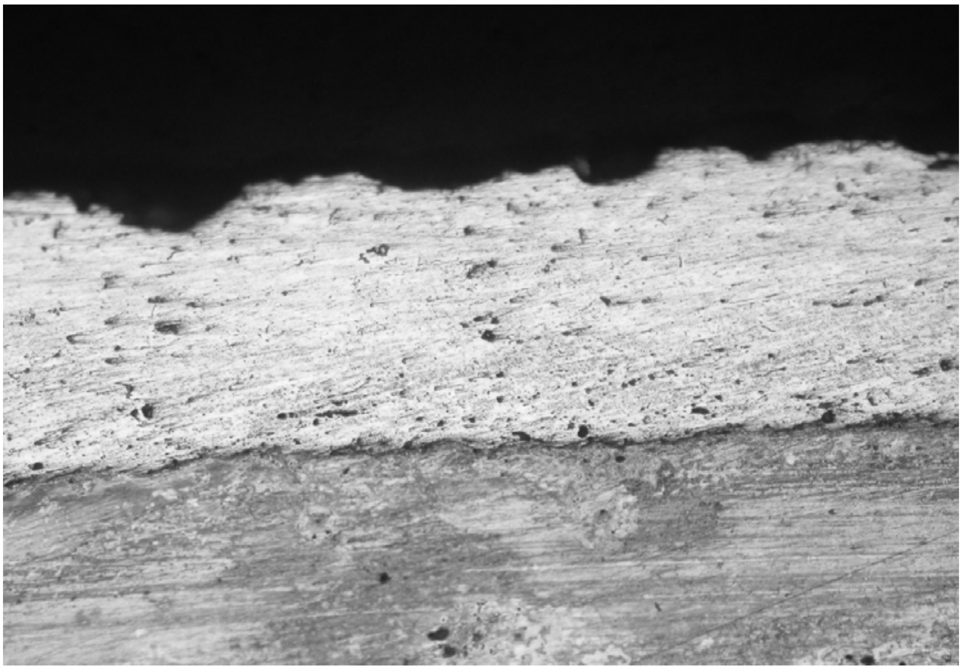


Fig. IV.5. Optical Microscopy of arc wire sprayed and etched Al-6Si at 100x

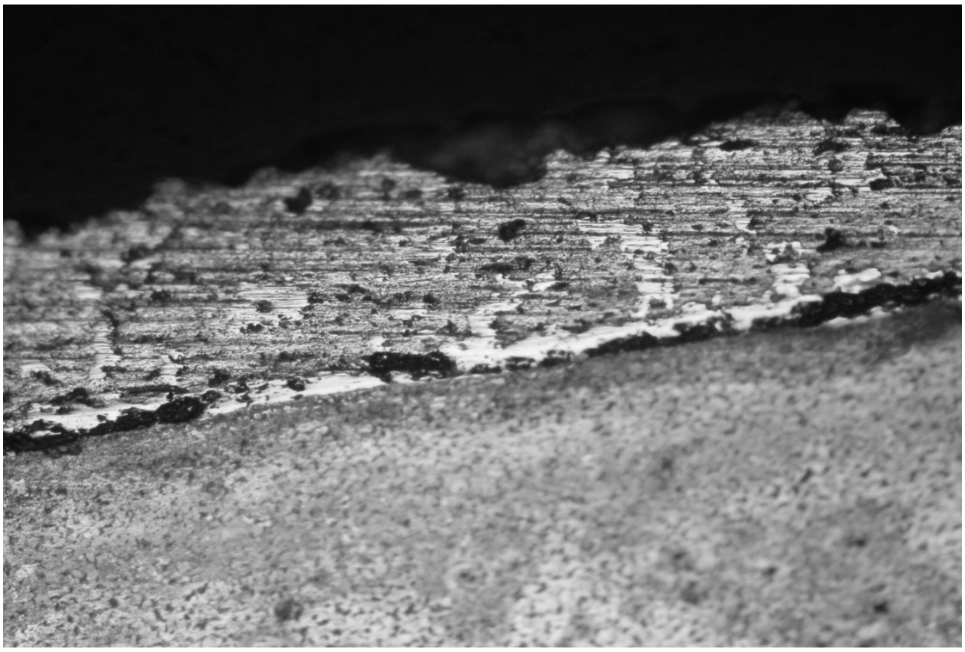


Fig. IV.6. Optical Microscopy of arc wire sprayed, fused and etched Al-6Si at 100x

IV.4. Scanning Electron Microscopy Results

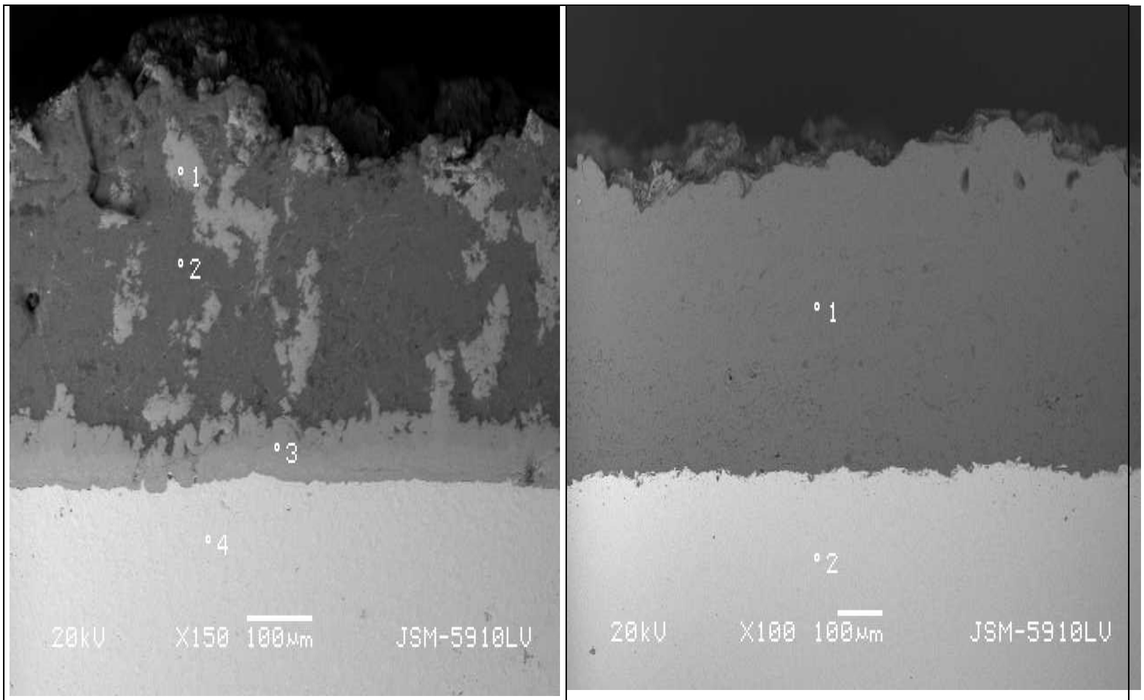
Samples have been classified into two groups before SEM study. First group is coated with no heat treatment ones and the second one is heat treated samples. Heat treatment was peformed for lowering porosity concentration and investigating the effect of diffusion of aluminum on steel. Optical and SEM investigations revealed a sucesssful diffusion process by heat treating under vacuum at 950 °C with a thickness of nearly 200-250 micron. Thus diffusion of aluminum was found to be is easier because of the lower oxygen concentraion than open air atmosphere.

Explanations of samples are given on Table IV.7.

Table IV.7. Explanation of thermal sprayed and heat treated samples.

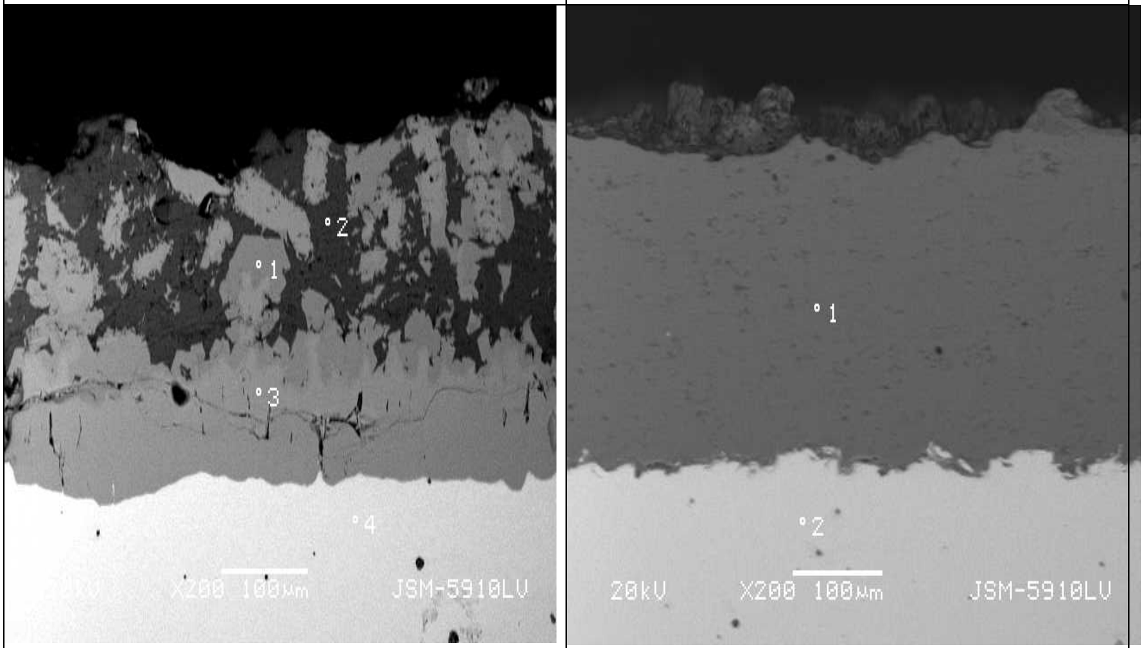
Sample Number	Coating Equipment	Coating Method	Heat Treatment
1	Arc Spray	Sprayed and Fused	No
2	Arc Spray	Sprayed	No
3	Flame Spray	Sprayed and Fused	No
4	Flame Spray	Sprayed	No
5	Arc Spray	Sprayed and Fused	Yes
6	Arc Spray	Sprayed	Yes
7	Flame Spray	Sprayed and Fused	Yes
8	Flame Spray	Sprayed	Yes

As a general observation after thermal spray coating of Al , Fused coatings were found to be relatively more denser and displayed better bonding compared to sprayed only samples as shown in optical microscopy Figures Fig. IV.2. , Fig. IV.4. and Fig. IV 6. Some selected SEM –BEI images and their EDS analysis were given below in the figures Fig. IV.7. and Fig. IV.8. and Fig. IV.9- Fig. IV.19 respectively.



Sample 1

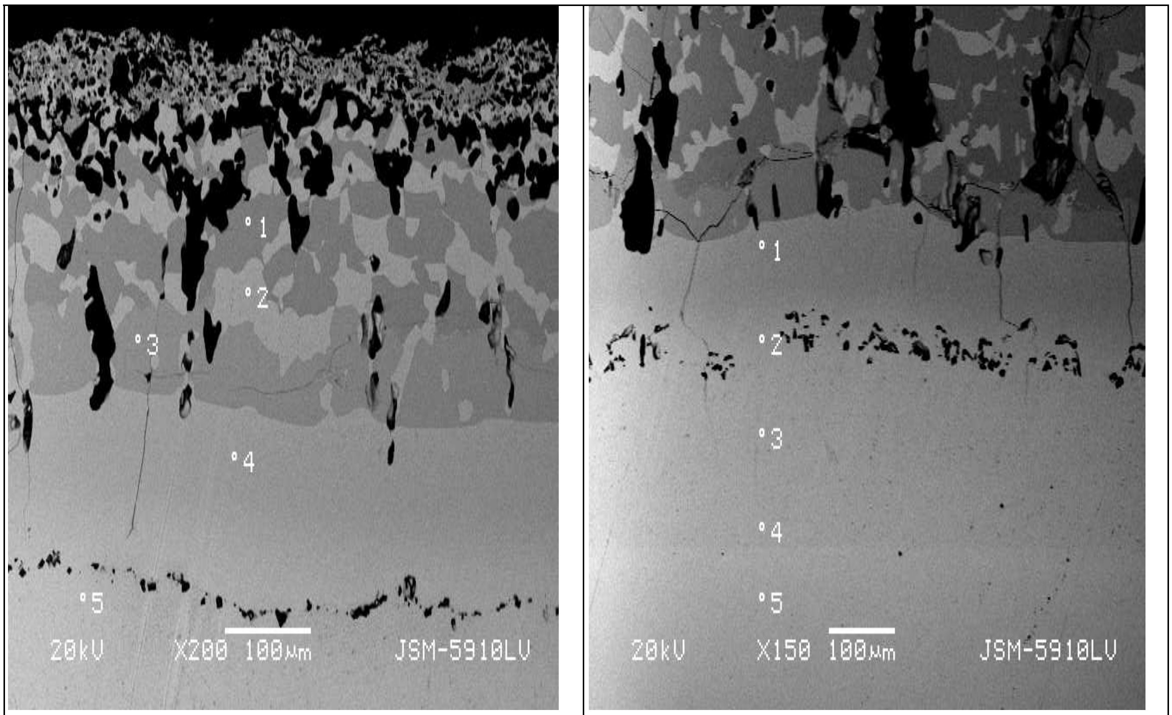
Sample 2



Sample 3

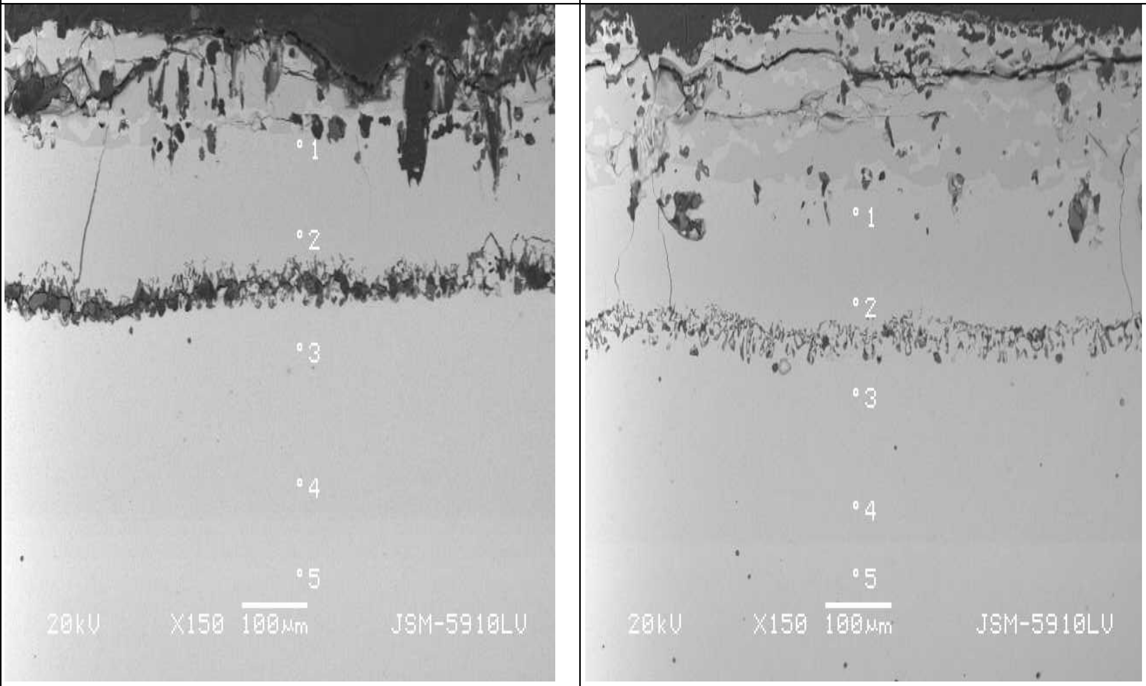
Sample 4

Fig. IV.7. SEM images of sample 1,2,3 and 4. without heat treatment.



Sample 5

Sample 6



Sample 7

Sample 8

Fig. IV.8. SEM images of sample 5, 6,7 and 8. after heat treatment.

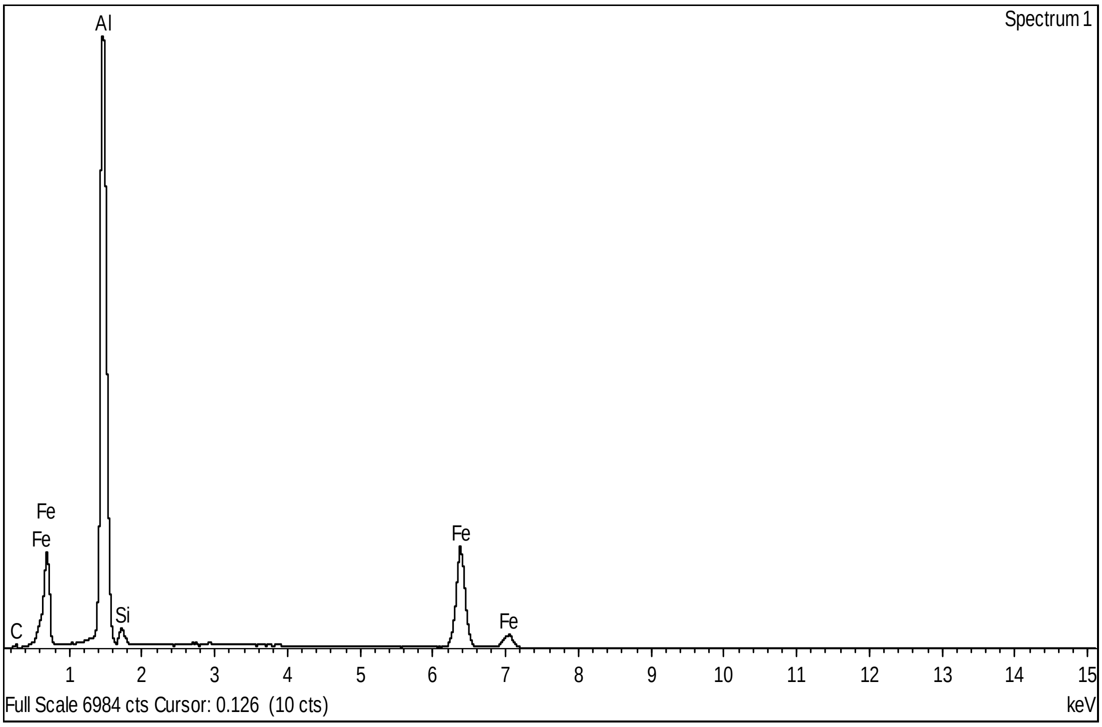


Fig. IV.9. Spectrum analysis of sample 1 point 1.

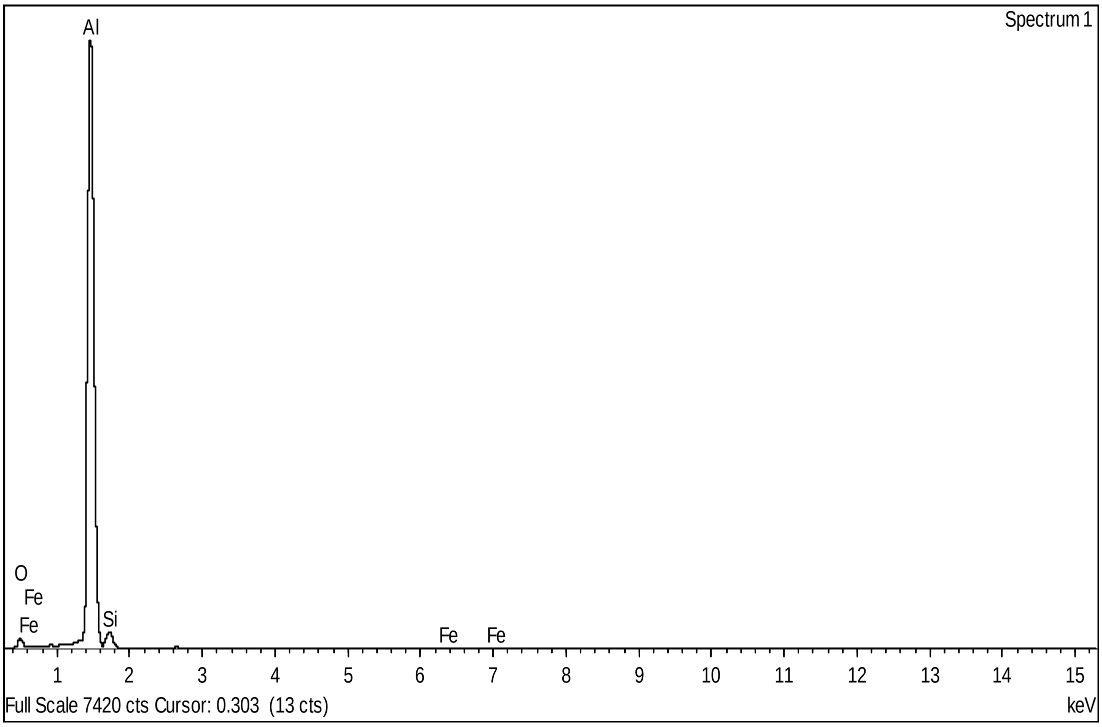


Fig. IV.10. Spectrum analysis of sample 1 point 2.

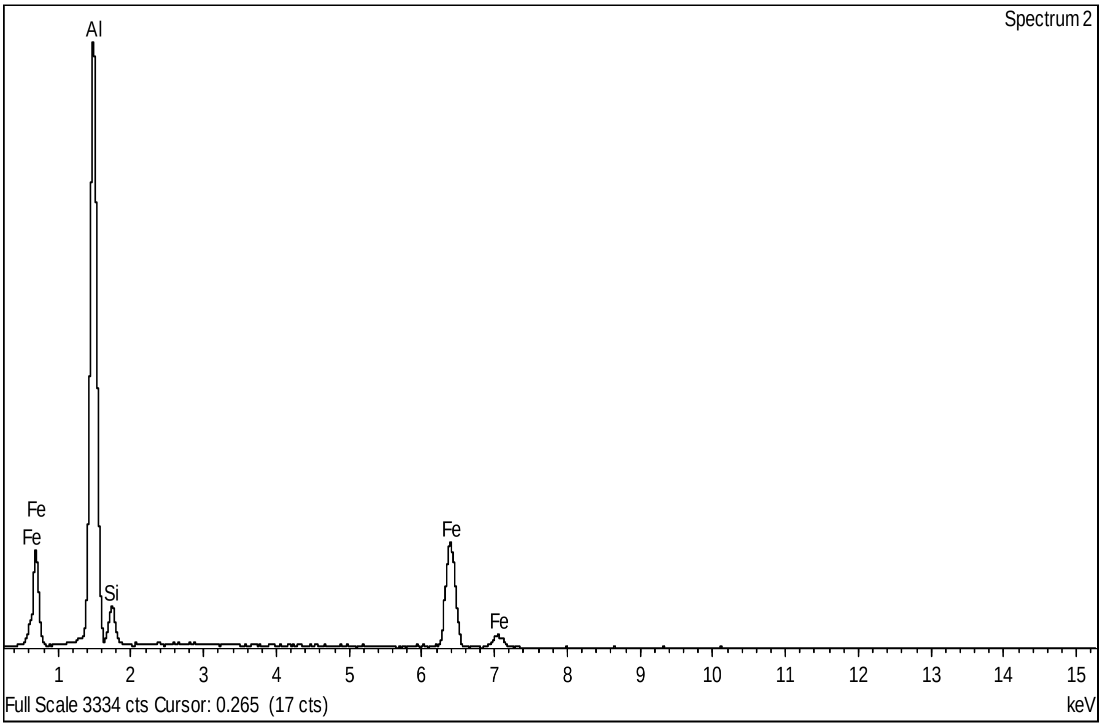


Fig. IV.11. Spectrum analysis of sample 1 point 3.

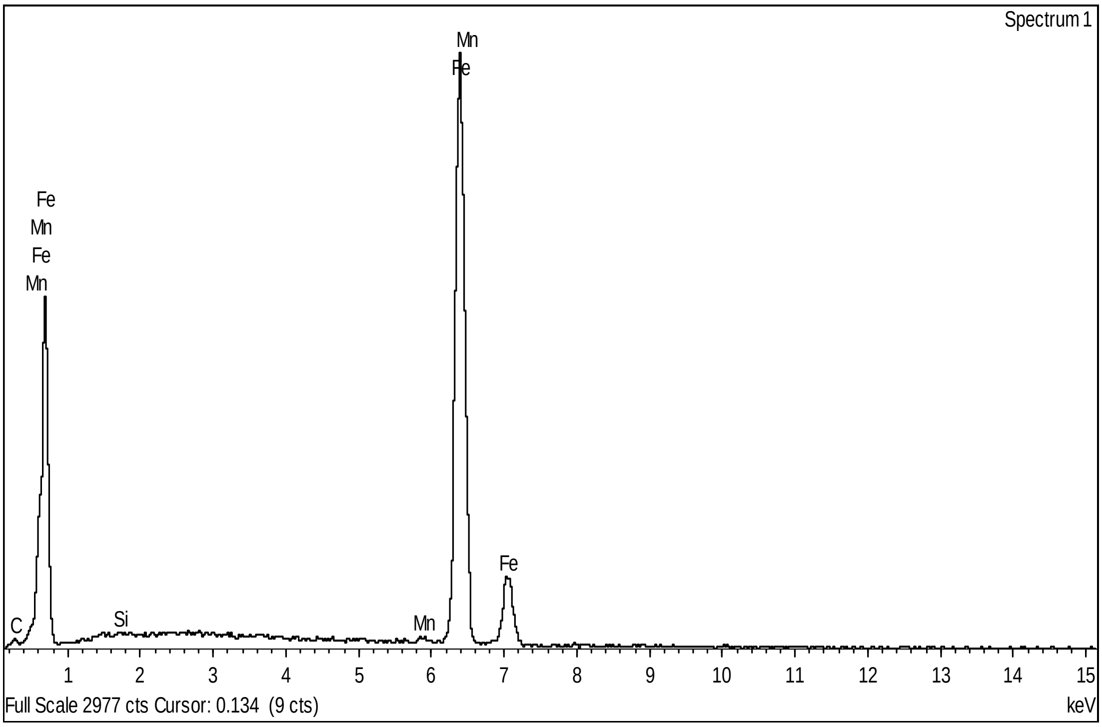


Fig. IV.12. Spectrum analysis of sample 1 point 4.

Table IV.8. EDS analysis of sample 1.

Sample 1	Analysis point	Elements %						
			O	C	Al	Si	Mn	Fe
		1	0	0.7	56.2	6.4	0	36.5
		2	9	0	83.5	6.5	0	0.8
		3	0	0	56	6	0	37.8
		4	0	0.6	0	0	0.7	98.5

Depending up to fusing process, the melted aluminium coating layer has been formed some phases. These phases explains that a chemical reaction became and bonding of coating layer got better adhesion. As seen on point 1 and point 3, there is an elemental ratio suggested that possible phase on these points would be Fe_2Al_3.

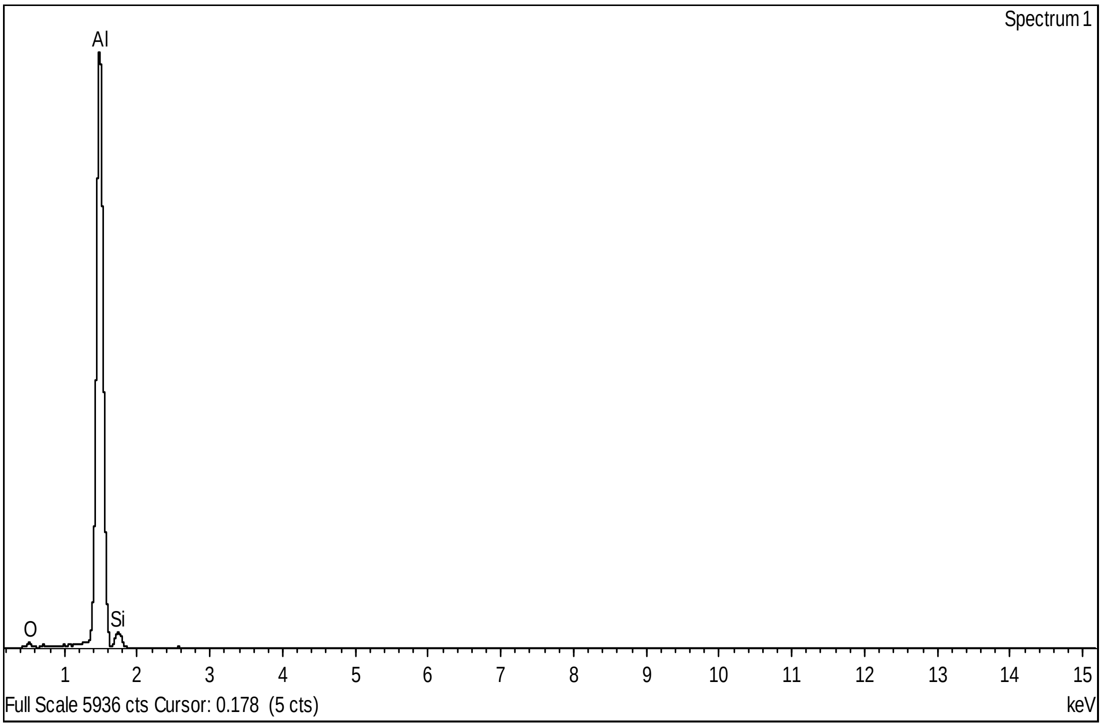


Fig. IV.13. Spectrum analysis of sample 2 point 1.

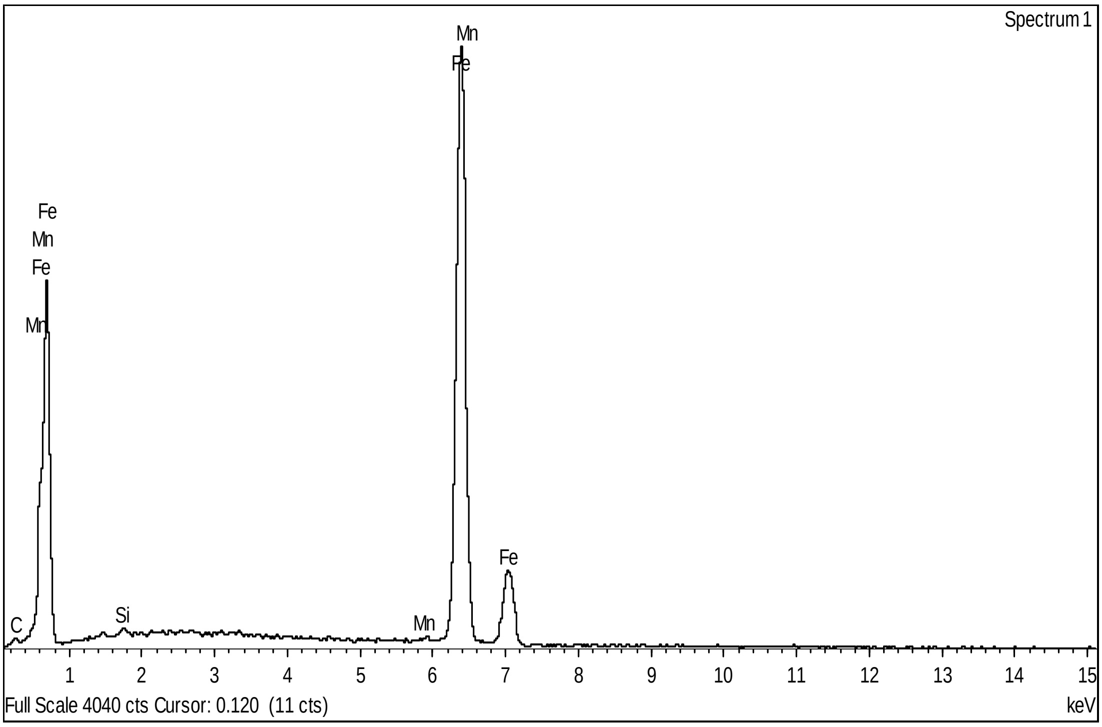


Fig. IV.14. Spectrum analysis of sample 2 point 2.

Table IV.9. EDS analysis of sample 2.

Sample 2	Analysis point	Elements %						
			O	C	Al	Si	Mn	Fe
		1	4.5	0	88.2	7.2	0	0
		2	0	0.4	0	0.3	0.5	98.6

According to EDS analysis of sample 2 some evidence of Al oxidation was determined suggesting a oxide layer formation on the surface of coating. Normally sample was coated by Al-Si alloy with no oxide contamination.

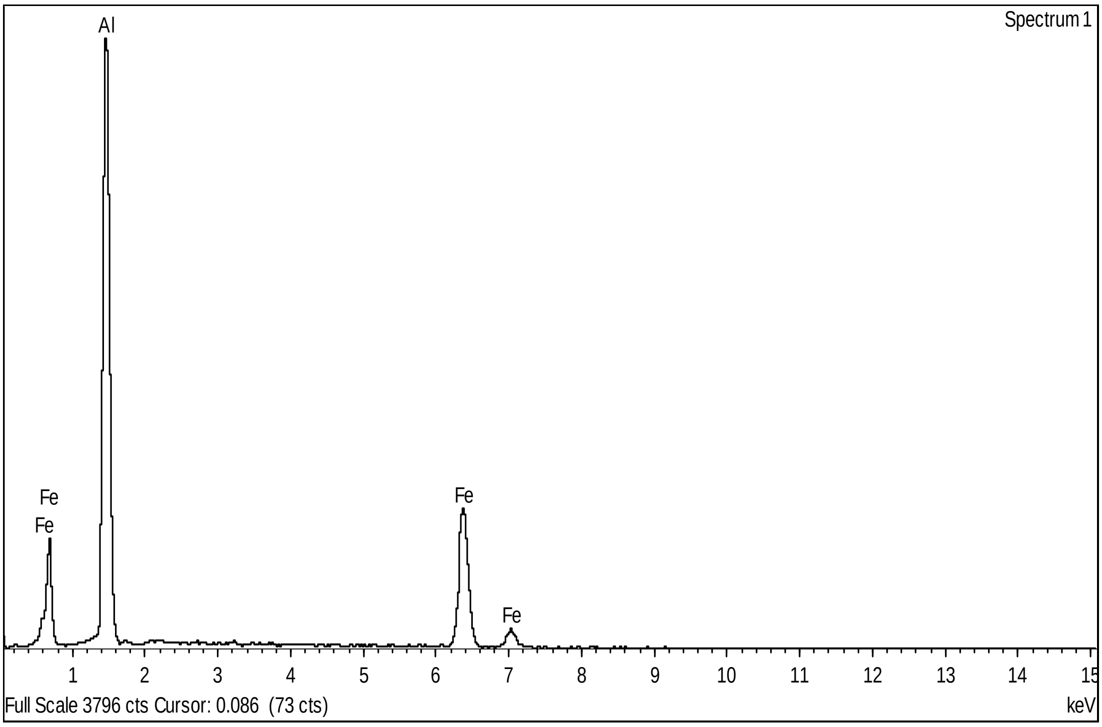


Fig. IV.15. Spectrum analysis of sample 5 point 1.

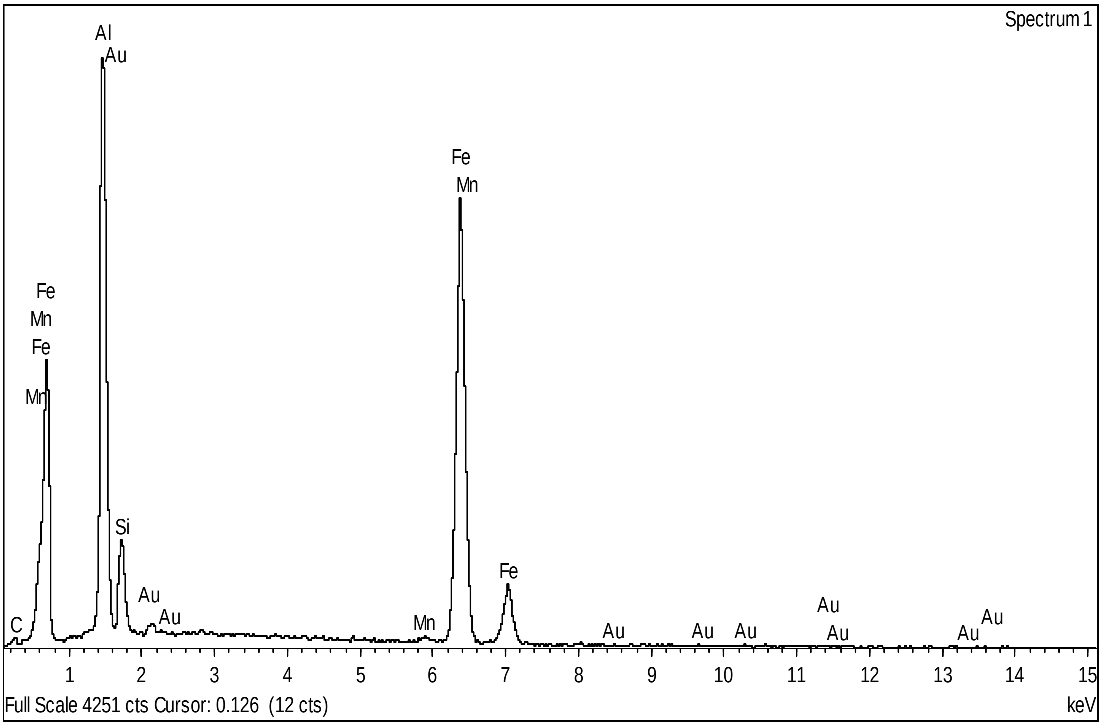


Fig. IV.16. Spectrum analysis of sample 5 point 2.

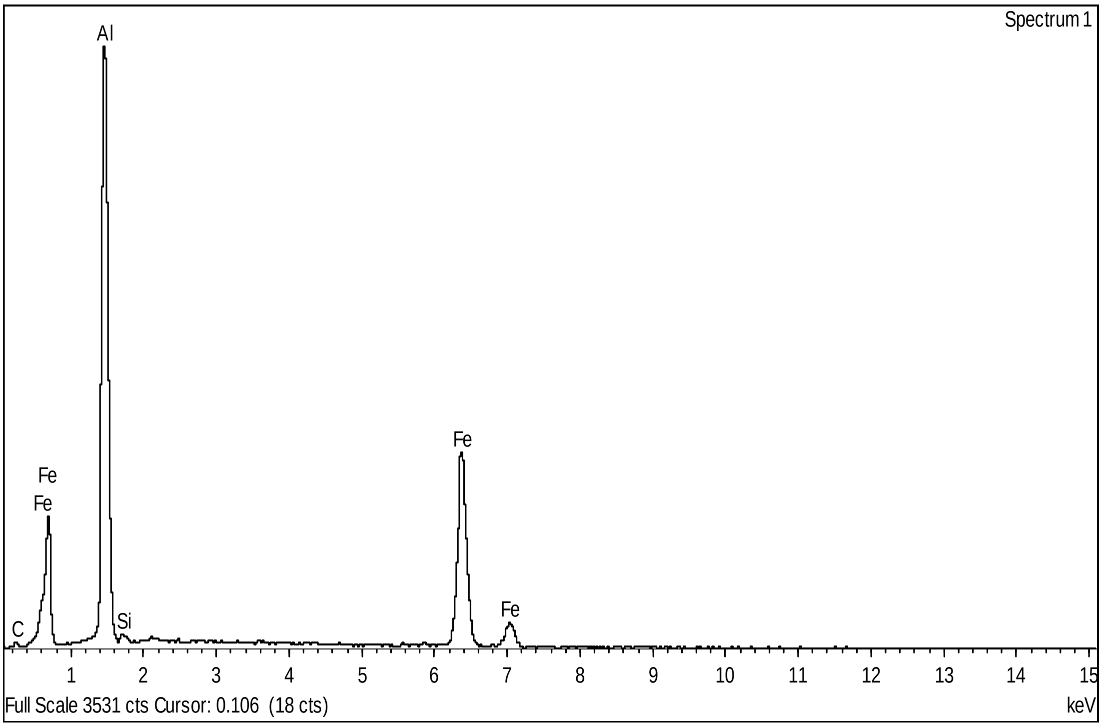


Fig. IV.17. Spectrum analysis of sample 5 point 3.

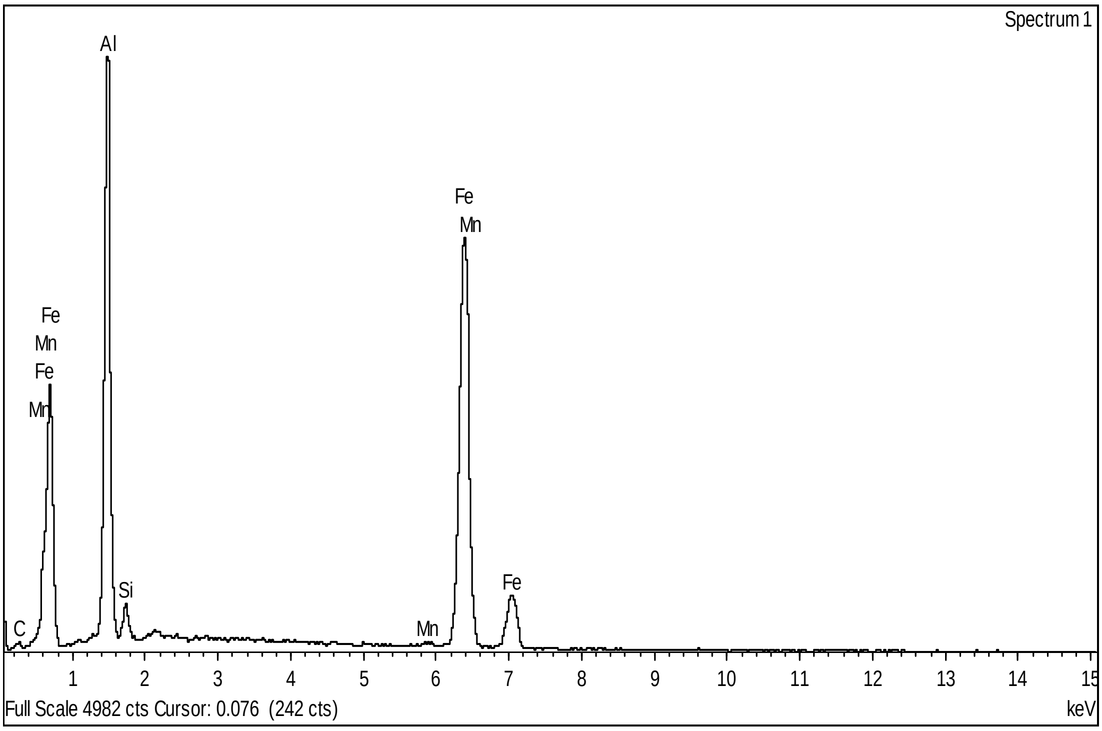


Fig. IV.18. Spectrum analysis of sample 5 point 4.

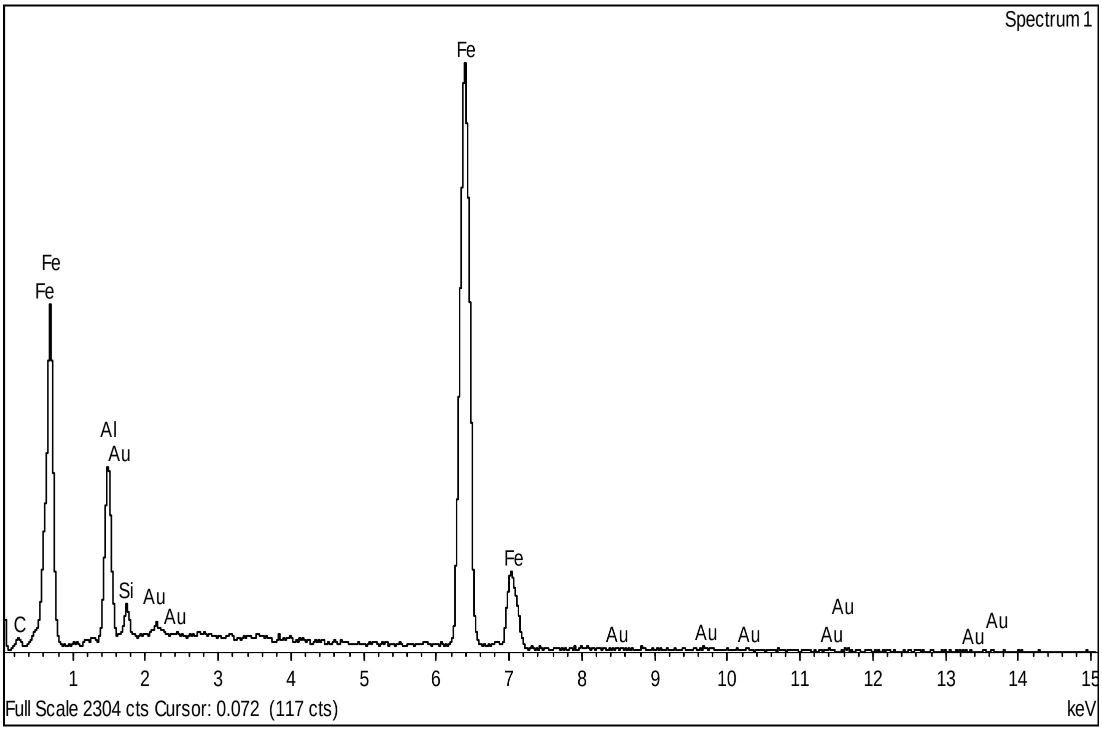


Fig. IV.19. Spectrum analysis of sample 5 point 5.

Table IV.10. EDS analysis of sample 5.

Sample 5	Analysis point	Elements %						
			O	C	Al	Si	Mn	Fe
		1	0	0	54.8	0	0	45.1
		2	0	0.4	27.7	5.4	0.4	65.9
		3	0	0.3	45.1	0.9	0	53.5
		4	0	0.4	30.3	2.1	0.4	66.5
		5	0	0.9	10	1.6	0	87.3

Table IV.11. EDS analysis of sample 6.

Sample 6	Analysis point	Elements %						
			O	C	Al	Si	Mn	Fe
		1	0	0.7	29.2	3.1	0	66.8
		2	0	0.7	23	2.9	0	23.2
		3	0	0.9	9.3	1.4	0.6	87.6
		4	0	0.9	3.1	0.6	0	95.2
		5	0	0.3	0	0	0.4	99.2

On sample 5 and 6 it can be clearly seen that there are different phases on each point. Different contrasts and different concentrations on EDS analysis of points verify these phases. After vacuum furnace process, the porosities which have been lined up on to substrate have been joined to each other and that shows a clearly porosity line. This line can be seen on sample 5 over point 5 and on sample 6 around point 2. Also the porosities in the coating layer have been came together and moved to surface of the material. So big porosity holes formed because of this reaction. Heat treatment process made the coating layer more denser and better adhesion than only coated samples. This more denser coating layer proves a better chemical and hot temperature corrosion resistance to material. When the material meets hot temperatures, diffusion process continues and resistance of materials improved . Thickness of phase points proves diffusion layer too. Diffusion layer thickness was found to be thicker than thermal spray coating layer. At the bottom of sample there is a white border line. This line indicates the end of diffusion process layer. This explanation is based on the aluminium concentration at this point which was obtained by EDS . On sample 6 at point 5, EDS analysis shows aluminium concentration % 0 and this data proves that there is no diffusion of aluminium under this point.

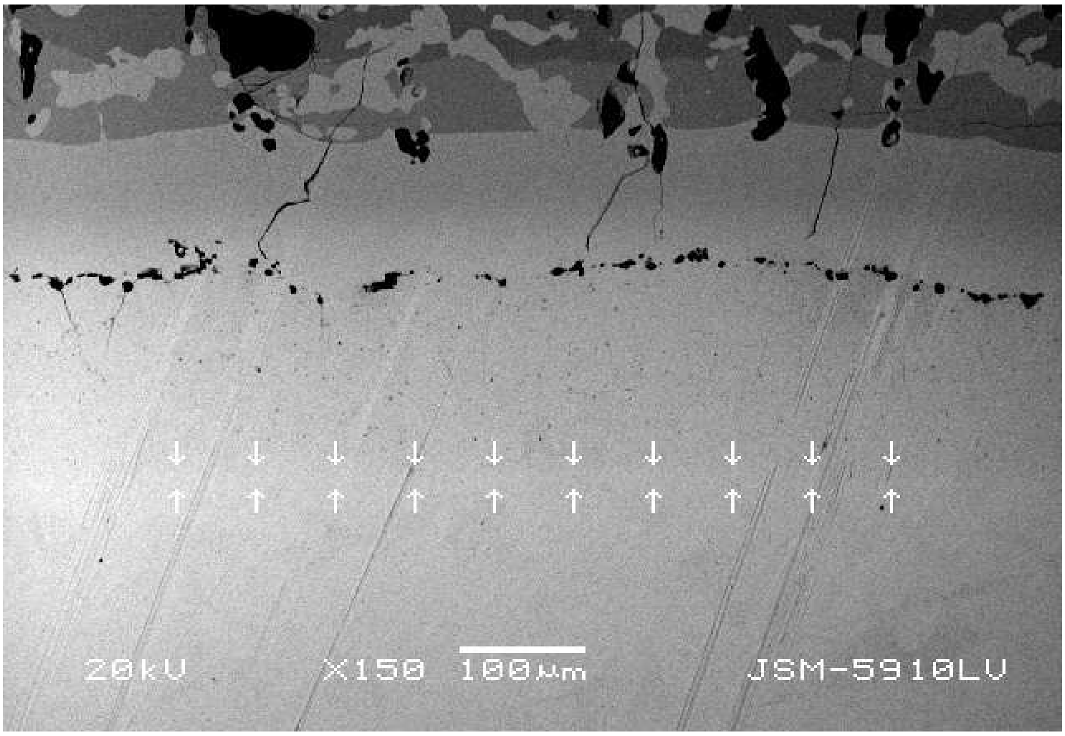


Fig. IV.20. End of diffusion zone on sample 5 after heat treatment.

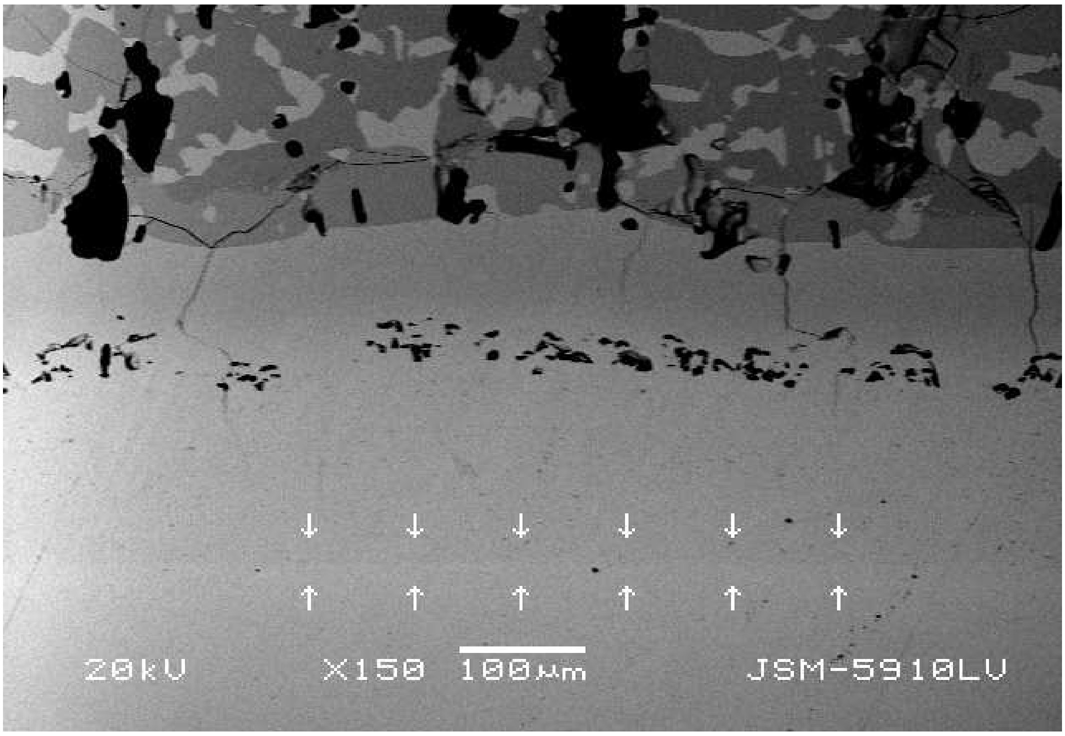


Fig. IV.21. End of diffusion zone on sample 6 after heat treatment.

In Fig IV.20. and IV.21. the end of diffusion zone was displayed which is an indication of diffusion layer boundary ranging from 200- 250 microns. White arrows in the pictures donate for this layer boundary. Diffusion layer shows the extent of aluminium atoms diffusion into the steel substrate. Possible intermetallic phases formed after diffusion process may be named as FeAl, Fe_2Al_3, $FeAl_2$ and Fe_2Al_5.

IV.5. Micro Hardness Test Results

Micro Hardness tests were conducted starting from the outer surface to inner zone to evaluate the hardness test changes. Hardness tests done by Wolpert model 930/250 micro hardness testing machine. Load weight is 200 grams and load time is 12 seconds. As expected the Vickers hardness values were gradually changed in heat treated samples through the diffusion layer suggesting intermetallic phase formation between Fe and Al alloy. The hardness values for steel substrate with no coating and diffusion layer was 70 Kg/mm^2 whereas Al coated regions and diffusion layer hardness values was varying from 130 Kg/mm^2 and 350 Kg/mm^2 respectively.

V. CONCLUDING REMARKS AND RECOMMENDATIONS

In this study aluminium alloy coatings were performed onto low carbon steel substrate with or without fusing. After coating samples were also heat treated at 950 °C under vacuum for 8 hours to obtain solid state diffusion layer into steel for a better oxidation and corrosion resistance.

After coating and heat treatment samples were characterized by using corrosion test, oxidation test, microhardness tests, optical microscopy and SEM and EDS analysis. Following conclusions can be drawn from this investigation,

1-Aluminum alloy coating was successfully obtained onto steel substrate.

2- Heat treatment under vacuum was performed and favorable diffusion layer was obtained with a thickness of ranging from 200 up to 250 microns for all samples.

3- Various intermetallic phases or phases were formed after diffusion process. These phases were identified by optical and SEM and EDS analysis. Also micro hardness results were revealed hardness changes and increase in comparison with steel substrate suggesting intermetallic phase formation of between Fe and Al.

4- After thermal spray coating of Al , Fused coatings were found to be relatively more denser and displayed better bonding compared to sprayed only samples

5- Salt spray corrosion test results revealed that aluminium coatings on steel surfaces which have been fused or not fused showing good corrosion resistance behavior in salt solutions compared to bare steel sample without coating

6- Oxidation test samples with fusing treatment exhibited higher oxidation resistance than coated only samples with no fusing treatment. These results suggested that after fusing process lower porosity concentration and a better bonding can be obtained resulting in lower oxidation.

7- As a concluding remark, by performing a surface modification of an ordinary low carbon steel by Al alloy coatings with fusing process and consecutive diffusion can demonstrate better resistance against oxidation and sea water corrosion. Therefore this technique could be used for ordinary construction steels and pipes in contacting sea water and working against moderate temperature oxidation environments.

Recommendation for further studies can be summarized as follows

a) Various kinds of aluminum alloys could be tried in coatings and characterization studies would be performed

b) Wear test was not carried out in this investigation. Wear test would be performed by applying different diffusion temperature and time.

c) Characterization of coatings and performance tests could be accomplished by varying the diffusion temperature and time under vacuum.

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- (Paper) Termal Sprey Kaplama Teknolojisindeki Gelişmeler ve Trendler: Çevresel Bariyer ve Termal Bariyer Kaplama Uygulamaları, Doç. Dr Fatih ÜSTEL, Met. Malz. Müh. Mehmet Burak YILMAZ, Sakarya Üniversitesi Müh. Fak. Metalurji ve Malzeme Mühendisliği Bölümü, Sakarya, 2006.
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