

REVIEW ARTICLE

Research Status in Surface Melting and Related Processes for Enhancement of Surface Properties of Metallic Materials

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Abstract

The surface of industrial components may require secondary treatment to enhance its characteristics in order to perform the intended function. A number of surface treatment techniques are commonly applied to metals to achieve this through a variety of processes generally referred to as surface modification. This usually involves altering the chemistry, structure and/topology of the top surface. Literature indicates the existence of different surface modification techniques applicable to a wide range of metallic materials; but most of these treatments are material specific. Prominent among these techniques is surface melting using either arc or flame torch for surface modification. Quite extensive spectra of investigations have been conducted via either of these techniques on a wide range of materials. Therefore, in this paper, surface modification of metallic materials for improved functionalities using arc and flame melting techniques are reviewed. The review discusses investigation conducted on these techniques and provides a comparison across them. The review further highlights trends in these techniques.

Keywords: coating techniques; microstructure; substrates; surface modification; surface properties

Introduction

Coatings are generically secondary treatment products deposited on materials substrate to improve surface functionalities. [1] reported that these surface deposits are generated to improve surface properties of substrate materials including aesthetics, adhesion, corrosion resistance, wear resistance, and scratch resistance of material. Coating processes involve the deposition of an extrinsic layer (in some other instances, the layer may be a thin film) of functional material to a substrate with a view to structurally modifying the chemistry of the substrate and its properties. The structural modification thus imparts improved surface properties on the material. Literature [2,3,4] indicate that several coating techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), chemical and electrochemical processes, spraying, magnetron sputtering, and low and high energy processes are available for substrate modification. There exists significant literature information on investigations conducted on different materials using these surface modification techniques for improved wear and tribological resistances. For instance, [4] used laser surface engineering to improve the wear resistance and mechanical properties of austempered ductile iron (ADI) and reported tremendous improvement in tribological property comparable to those obtained in CVD and PVD processes. However, these reported surface modification techniques (laser, CVD, PVD and magnetron sputtering) are not only expensive but equally require high level technical expertise for a successful deposition process. Incidentally, some researchers [5, 6] have reported the use of novel low energy techniques such as flame torch melting using oxy-acetylene gas mixture and tungsten inert gas (TIG) torch melting for surface modification of substrate properties. These techniques are ordinarily deployed for flame cutting and/or joining but they have now found additional use for surface modification [7,8,9] reported the use of low temperature coating and cathodic arc deposition for surface modification in austempered ductile iron resulting in acceptable surface properties. Similarly, [5,7,10] reported the use of TIG torch technique for surface modification of plain carbon steel, low alloy steel, and commercially pure (CP) titanium. The technique generated wear resistance quite comparable to the conventional high energy beam processes. It is thus apparent that the space of arc and flame melting for surface modification is quite wide; and information on these processes are scattered and not available in a single piece. It is therefore the purpose of this paper to provide a generic and specific review of the various surface modification works available in literature.

Thermal Coating

This coating technique is a versatile process for the deposition of protective coating on a broad range of materials particularly the deposition of metals, polymers and ceramics on substrate materials. In this process, the feedstock materials be it metal, polymer or ceramic is melted by electrical plasma or arc or combustion flame and then sprayed on to a surface. The generation of thick coatings is achievable over a large area at high deposition rate when compared with other deposition processes like CVD, PVD, and electroplating as shown in Table 1 and Figure 1. Thermal spraying process is characterized with widest range of coating materials, coating thickness and coating characteristics among surface modification techniques as illustrated in Figure 1.

Coating Process	Typical Coating Thickness	Coating Material	Characteristics	Examples
Thermal Spray/PVD	0.04 – 3 mm (0.0015 -0.12 in) 1 – 5 μm (40–200 μin)	Ceramic and metallic alloy Ti(C,N)	Wear resistance, corrosion resistance Wear resistance	Bearings Machine tools
CVD	1 – 50 μm (40 – 2000 μin).	SiC	Wear resistance	Fiber coatings
Baked Polymers	1 – 10 μm (40 – 400 μin)	Polymers	Corrosion resistance, Aesthetics	Automobile
Hard Chromium Plate	10 – 100 μm (40 – 4000 μin)	Chrome	Wear resistance	Rolls
Weld Hardfacing/Overlay	0.5 – 5 mm (0.02 – 0.2 in)	Steel, Stellite	Wear resistance	Valves
Galvanize	1 – 5 μm (40 – 200 μin)	Zinc	Corrosion resistance	Steel sheet
Braze Overlay	10 – 100 μm (40 – 4000 μin)	Ni-Cr-B-Si alloys	Very hard, dense surface	Shafts

Table 1: Principal coating processes and characteristics [11].

Materials used as coating for thermal spraying are quite extensive and can be grouped into metals, alloys, ceramics, plastics and composites. This process has wider application and represents one of the surface engineering technologies with attractive attributes such as being environmentally benign, easily accessible and relatively affordable relative to other high-tech surface modification processes. Its application has grown extensively across the whole spectrum of engineering and manufacturing since it was first discovered [11]. The technique finds application in automobiles, aeroplanes, surgical implants, golf clubs, etc. Thermal spray coatings offer distinct advantages by combining versatility, cost-effectiveness, and the ability to coat complex geometries without constraints of other in-chamber processes [12].

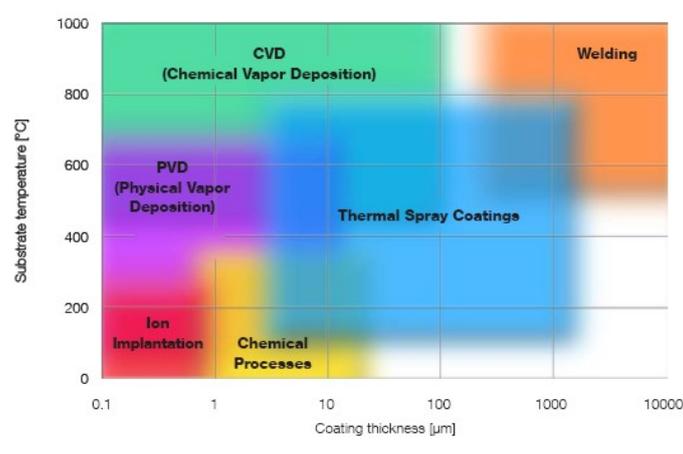


Figure 1: Comparison of coating processes [11].

Literature indicate that virtually all materials can be thermal sprayed particularly those exhibiting well-defined melting point and do not decompose when heated [13]. The schematic process of thermal spray concept is shown in Figure 2. Thermally sprayed coatings can be used to impart many surface characteristics such as: wear resistance, heat resistance, oxidation resistance, corrosion resistance, electrical resistance, electrical conductance, and restoration of size [14]

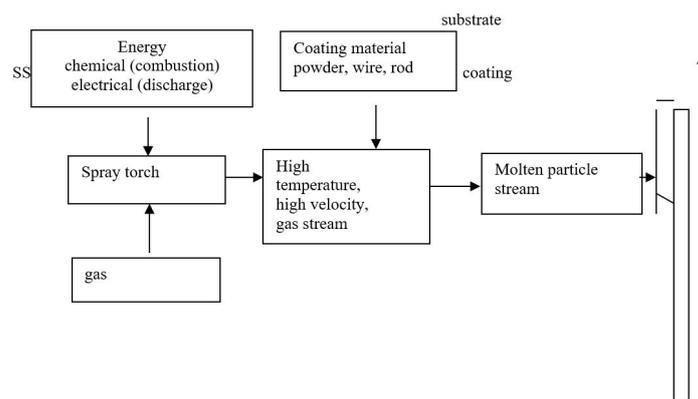


Figure2: Schematic of the thermal spray concept [14].

The process involved the melting of the feedstock coating material by a heating source, propelled by process gases, sprayed on to prepared surface of base material and solidified as solid layer as shown in Figure 3.

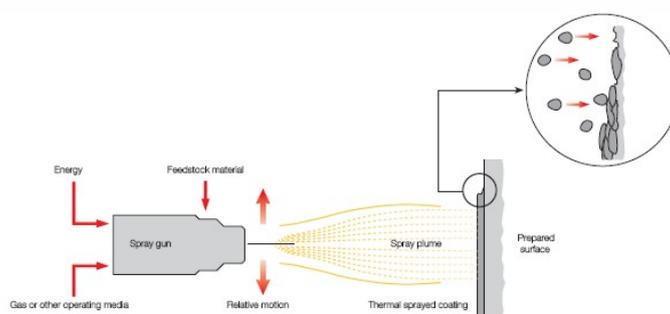


Figure3: Principle of thermal spray coating [11].

Though thermal spray is attractive for surface modification, it is prone to the generation of defects in relation to other processes. Pores formation is a common defect in thermally sprayed coating which has been found to be influenced by the contact area between the splat and the substrate or previously deposited layers. In most cases, the thickness of the inter-lamellar pores existing between layered splats, or first splats and substrate has been established to be between a few hundredths to a few tenths of micrometers. Pore formation in thermally sprayed coatings can be prevented by increasing the contact area between about 20 to 60 % with particle impact velocities, provided that the particles are not either heavily superheated or below their melting temperature [14].

Splashing of the melted particles during flattening upon impact can significantly affect the coating properties. Splats deposited on splashed material exhibit lower adhesion and this effect is more significant when spraying metals because the splashed material is oxidized rather fast due to the small droplet sizes. Substrate geometry may affect the flow of impacting and splashing particles [15].

Pores (globular) are formed during coating generation due to combination of factors involving shadowing effect, incompletely narrow holes in valleys between splats, un-molten or partially melted particles and exploded particles. These globular pores are distributed more or less homogeneously through the coating and their potential to deteriorate coating properties is proportional to their size [14]. Therefore, it is imperative to avoid the incorporation of large unmelted particles which are sufficiently heated to stick on the substrate, or of partially melted particles in the coating to minimize the likelihood of formation of pores. This can be done by choosing carefully, the particle size distribution and optimizing the particle injection. However, sometimes a compromise has to be found between having most particles fully melted but with rather high oxide content, and more un-melted particles with lower oxide content. Coatings also contain cracks formed during residual stress relaxation and that often contribute to the open

porosity of coatings.

The micro-cracks within splats result from quenching stress relaxation and are observed in ceramic materials. The macro-cracks are often due to the relaxation of an expansion mismatch stress; they run through layered splats especially at their interfaces and, so, tend to initiate inter-connected porosities. Other stress relaxations can occur but they can be avoided by optimizing spray or service conditions.

Another source of defects is the particle impact angle that reduces the normal impact velocity, resulting in elongated splats. Spraying with an angle above a certain value, depending on particle and substrate materials, will promote splashing even on substrates preheated above the so called “transition temperature”. Above this temperature, the splats exhibit a regular disk shape on a smooth substrate while below they have an irregular shape. Typically, depending on the spray process used and the material sprayed, total porosity varies between 0.5 and 15 %. This does not imply, necessarily, that porosities are inter-connected, but it does occur.

Figure 4 illustrates schematically the structure of a thermal-sprayed coating. Figure 5a presents the cross section of a stainless steel coating (304L) deposited by air plasma spraying on a low carbon (1040) steel substrate and Figure 5b that of an yttria partially stabilized zirconia (Y-PSZ). Figure 5a and Figure 5b show all the coating characteristics presented in the schematic cross section in Figure 4, except that of the Y-PSZ coating (Figure 5b); of course, oxidation and its lamellar structure is more pronounced.

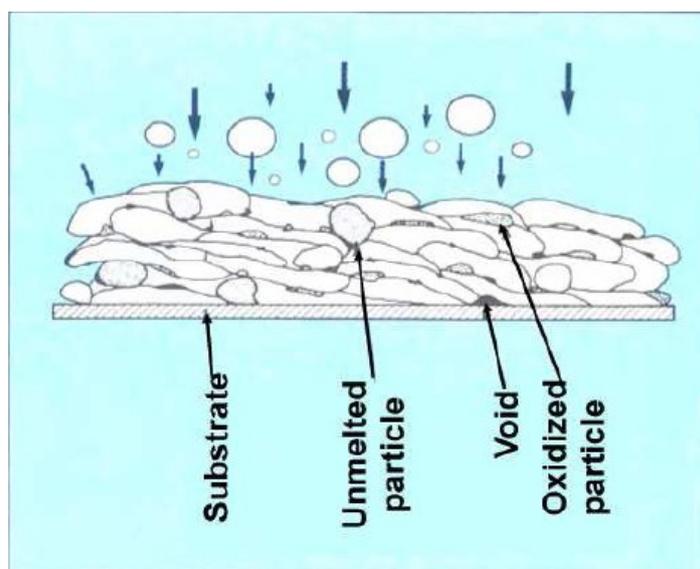


Figure 4: Schematic cross section of a thermally-sprayed coating [12].

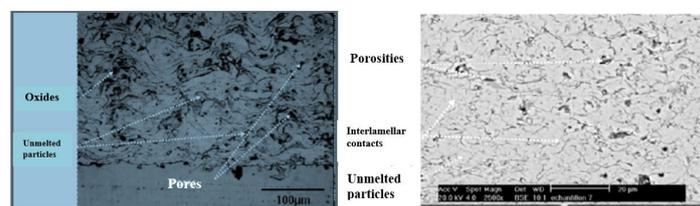


Figure 5: (a) Stainless steel coating (304L) deposited by air plasma spraying on a low carbon (1040) steel substrate, (b) Y-PSZ (8wt%) coating deposited by air plasma spraying on a super Alloy [12].

Table 2 illustrated material class, typical alloy in the class, their characteristics and examples of some engineering applications of thermally sprayed materials. It is a precondition in selection of suitable thermally sprayed coating to provide information about the materials and service environment. Additionally, performance of thermally sprayed coatings is influenced by the physical

properties of the coating such as coefficient of expansion, density, heat conductivity, melting point, particle shape, particle size distribution and manufacturing process of powder material (i.e., agglomerated, sintered, composited). Some coating materials are alloys or blends and this expand the spectrum of combination options which is achievable through experience over the years for their selection and recommendation.

Material Class	Typical Alloy	Characteristics	Example Application
Pure metals	Zn	Corrosion protection	Bridge construction
Self-fluxing alloys	FeNiBSi	High hardness, fused, minimal porosity	Shafts, bearings
Steel	Fe ₀ Cr	Economical, wear resistance	Repair
MCrAlY	NiCrAlY	High temperature, corrosion resistance	Gas turbine blades
Nickel-graphite	Ni ₃ C	Anti-fretting	Compressor inlet ducts
Oxides	Al ₂ O ₃	Oxidation resistance, high hardness	Textile industry
Carbides	WC ₁₂ Co	Wear resistance	Shafts

Table 2: Common classes of thermal spray powder materials [11].

Weld Hard facing

Metal arc Welding Surface Modification

Weld hardfacing or overlay offers a framework for improving on the desirable properties or the restoring a component's original dimension. The process involves the use of one or more metals (as hardfacing electrode or filler metal) having the requisite characteristics with respect to the base metal to deposit extra layers of coatings on the substrate. This process is also referred to as cladding, weld cladding or weld overlay cladding. It differs from general welding which is meant for joining two pieces of material together. A typical hardfacing process may be used to apply a corrosive resistant or hard facing layer onto the parent material as shown in Figure 6. The illustration was taken from the hardfacing of a cylinder for corrosion resistant in the oil sector. Weld deposition of hard facing alloys is commonly employed to enhance the tribological life of engineering components subjected to hostile environments [16]. The technique provide incentives for improving corrosion resistance, or wear resistance or strength of substrate; and the technique has been widely used to improve corrosion resistance in boilers, reactor vessels in industries. In the recent years, plasma transferred arc (PTA) surfacing is used in applications such as valve industries, hydraulic machineries, mining industries, earthmoving equipment, chemical, nuclear and thermal power plants etc.



Figure 6: Weld hardfacing of a cylinder for corrosion resistant <https://www.arcenergy.co.uk>)

PTA process can be considered as an advanced gas tungsten arc welding process more widely used for overlay applications [16].

Another variant of arc melting surface modification technique is the pulse sprayed gas metal arc welding (PSGMAW) which has

enabled the deposition of coating free of carbide precipitation. The absence of carbide precipitation in PSGMAW deposited coating which induced good ductility was attributed to fast cooling of the resolidified molten metal. This process is characterized by low dilution in overlay chemistry (typically 10% or less), crack free, minimal heat affected zone and distortion. The obtainable low dilution in overlay chemistry in this process is critical in the provision of corrosion protection by the overlay. For instance, it has been found that an overlay welding process that produces a 10% dilution when Type 309 nickel-chromium weld wire with 24% Cr was used to deposit an overlay on carbon steel substrate which yield a post deposition type 309 overlay but with reduced chromium content of about 22% Cr do possess adequate corrosion resistance as in many industrial environments with high corrosion rates of carbon or low alloy steels. But, an overlay process that produces about 30% overlay dilution which reduces the post-deposition chromium in the Type 309 overlay to about 17% was inadequate for corrosion protection in many industrial environments [17].

Laser and Electron Beam Coating

Laser and electron beam (EB) melting provides opportunity for near net shape in surface modification for enhanced functionalities in substrate materials. This melting technique was necessitated by advancement in coating technology which imposes stringent requirement of adherent and tenacious coating with minimal distortion of the substrate material. The laser and electron beam melting process is an overlay deposition process where a melting is used to deposit coating material, a powder or wire on the surface of base material via a focused and concentrated beam as illustrated in Figure 7. The two techniques fall under the same category of power beam welding, despite this, there are some fundamental variations between each welding process and its applications. EB welding is lesser-known than laser welding and this is not because it is inferior to laser but mostly because of people's perceptions.

In comparison, the EB welding uses a finely focused stream or beam of electrons, whereas laser welding uses monochromatic coherent light (photons). In both cases, the kinetic energy of the electrons or photons is turned into heat energy when they hit the surface of the metal. Also, the EB can produce deeper welds and is more efficient than laser welding. The deeper the weld penetration is and the higher the cost of the material, the more cost-effective the electron beam approach becomes compared to other welding techniques.

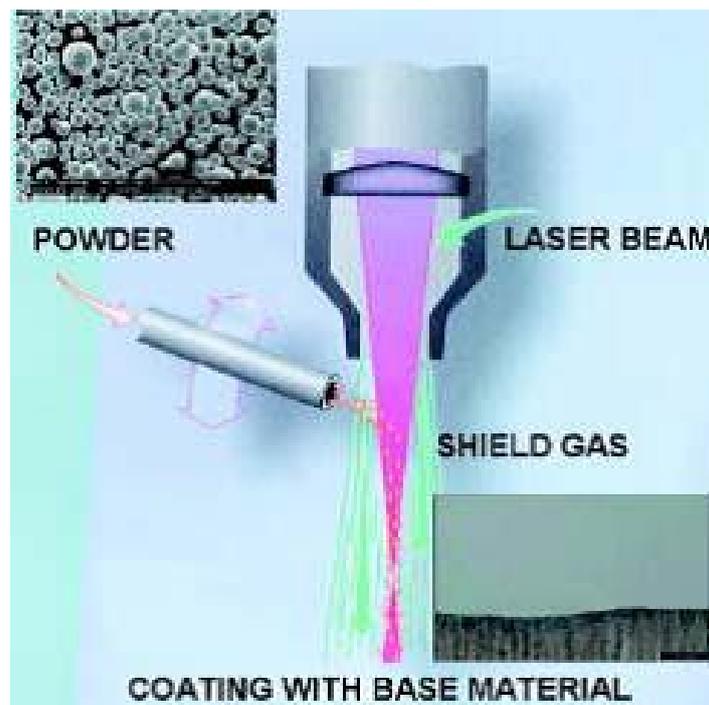


Figure 7: Principle of laser coating [18].

Table 3 compares the characteristics of laser coating with conventional weld surfacing and coating by thermal spraying. The analysis of the table indicates that laser coating technique relative to its alternatives is quite attractive arising from the combination of excellent process characteristics and the quality of its coatings. Some of these attributes include high intensity of the laser beam, controllable heat source and beam focus, excellent coating properties, low dilution, minimum distortion in the base material and very low band of heat affected zone, controllable coating thickness, and high productivity. Laser coatings have extremely dense, crack-free, non-porous, microstructures, and show excellent metallurgical bonding to the base material. It has uniform composition and coating thickness. The process equally produces very low dilution and low heat input to the component.

COATING PROCESS	COATING PROCESS PROPERTY								
	Heat source	Bond strength	Coating Structure	Heat load to workpiece	Dilution	Coating thickness	Coating material	Productivity	Cost
Thermal spraying	Combustion flame, electric or plasma arc	Low to high Mechanical bonding	Lamellar; from porous to nearly dense	Very low to moderate	Nil	0.05- some mm	Wide range of metals, alloys, ,hard metals, ceramics, polymer	Low to high	Low to high
Weld surfacing	Combustion flame, electric arc	High; metallurgical bonding	Dense; cracks and pores may exist	Very high	Moderate to high	Several mm	Metal and alloys; alloys with hard particles	Low to very high	Low to moderate
Laser cladding	High intensity laser radiation	High metallurgical bonding	Dense; crack and pore- free layer	Low to moderate	Low	Typically 0.5- 3mm	Metals and alloys; alloys with hard particles; hard metals; ceramic	Lowto moderate/ high	Moderate to high

Table 3: Comparison of thermal spraying, weld surfacing and laser coating [18].

It gives new components surfaces with high resistance against wear, corrosion and high temperatures [18]. Laser coated components find extensive application in manufacturing where they have displayed superior characteristics and performance than uncoated components; in addition to the adoption of the process for repair and maintenance of worn components. There are various options of laser surface coating depending on the source for generating the laser beam. These various options and their characteristics are presented in Table 4.

PROPERTY	LASER TYPE			
	CO ₂	Nd:YAGlamp-pumped	Nd:YAGdiode-pumped	HPDL
Wavelength (μm)	10.6	1.06	1.06	0.8-0.94
Efficiency (%)	5-10	1-3	10-12	30-50
Power (kW); max	40	5	5	6
Average power density (W/cm ²)	10 ^{6.8}	10 ^{5.7}	10 ^{6.9}	10 ^{3.5}
Service period (h)	1000 – 2000	200	5000 – 10000	5000 – 10000
Fiber coupling	No	Yes	Yes	Yes
Beam- parameter-product (mm x mrad)	12	25 – 45	12	100 – 1000

Table 4: Characteristics of high power lasers for materials processing [18].

However, [19] reported that high propensity for crack formation, which is due to rapid melt pool solidification, has been a major drawback of laser cladding processes. Cracks are detrimental to the corrosion performance of laser coatings because they act as sites for crevice and pitting corrosion. They also offer interconnected path to the substrate. Further research by [20] revealed that cracking in the laser clad layers can be avoided by optimizing the processing parameters, preheating the substrate prior to laser deposition and cladding with alloys of high ductility. Laser coatings can be prepared on several types of base materials. Most commonly, the base materials used are unalloyed steels, alloy steels, hardenable steels, stainless steels, nickel or cobalt based alloys. Also various cast irons can be coated successfully by laser process. Laser coating on copper and its alloys, on aluminum alloys and even on titanium alloys have been reported [18]. This process has been successfully deployed to produce a wide range of surface modified components to withstand abrasive, erosive and adhesive wear, wet corrosion, high temperature oxidation and corrosion environments. Such products are found in shafts, rods and seals, valve parts, sliding valves and discs, exhaust valves in engines, cylinders and rolls, pump components, turbine components, wear plates, sealing joints and joint surfaces, tools, blades and moulds productions as demonstrated in Figure 8.

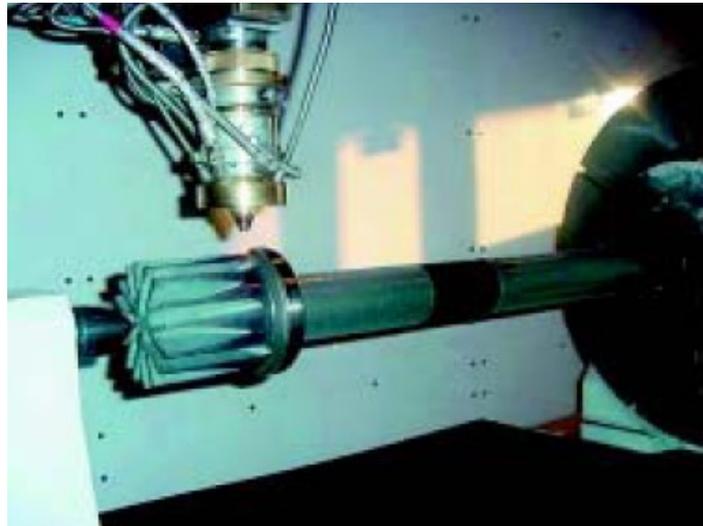


Figure 8: Laser coated by-pass valve spindle [18]

Laser coatings can be regarded as real corrosion barriers, which can protect non corrosion resistant base materials (steels) from corrosion. Figure 9 compares the corrosion properties of steel Fe 37, wrought nickel base super alloy Inconel 625 (Ni-Cr-Mo alloy) and two Inconel 625 coatings; one prepared by thermal spraying (HVOF – high-velocity oxy-fuel spraying) and the other prepared by laser coating process. The test samples were immersed in 3.5 % NaCl solution (seawater) for several hours simultaneously

measuring the potential of the sample versus time. Fe 37 steel corrodes actively, which can be seen as a change of the potential towards negative values. Wrought Inconel 625 alloy is resistant in these conditions; the potential moves to positive values with time, indicating passive behaviour. HVOF sprayed Inconel 625 coating is not resistant against corrosion in NaCl solution and the corrosion potential tries to follow the curve of the base material Fe 37. However, Inconel 625 laser coating behaves similarly with the corresponding wrought alloy; this indicates a high corrosion resistance of the laser coating. Microstructures of the two Inconel 625 coatings after the seawater immersion test are presented in Figure 9. The HVOF coating had corroded both in the coating material and the underneath base material, mainly at the coating/base material interface (Figure10a). Laser coating is still intact and shows no signs of corrosion in the coating or in the under laying steel, Figure 10b.

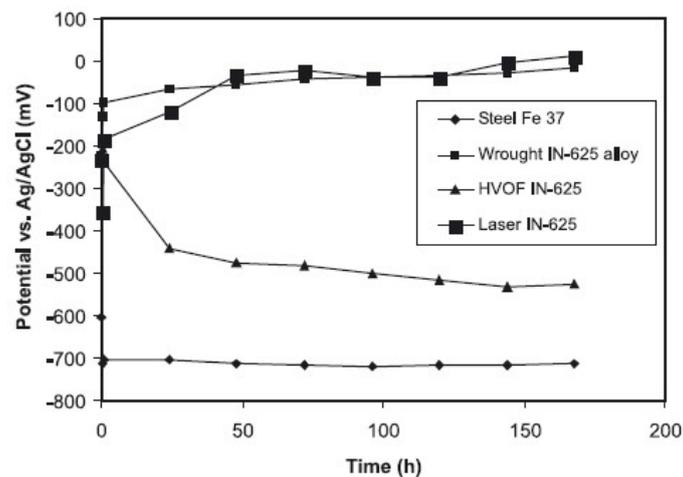


Figure 9: Open circuit potential vs. time for steel Fe 37, HVOF sprayed Inconel 625 coating, Inconel 625 laser coating and wrought Inconel 625 alloy [18].

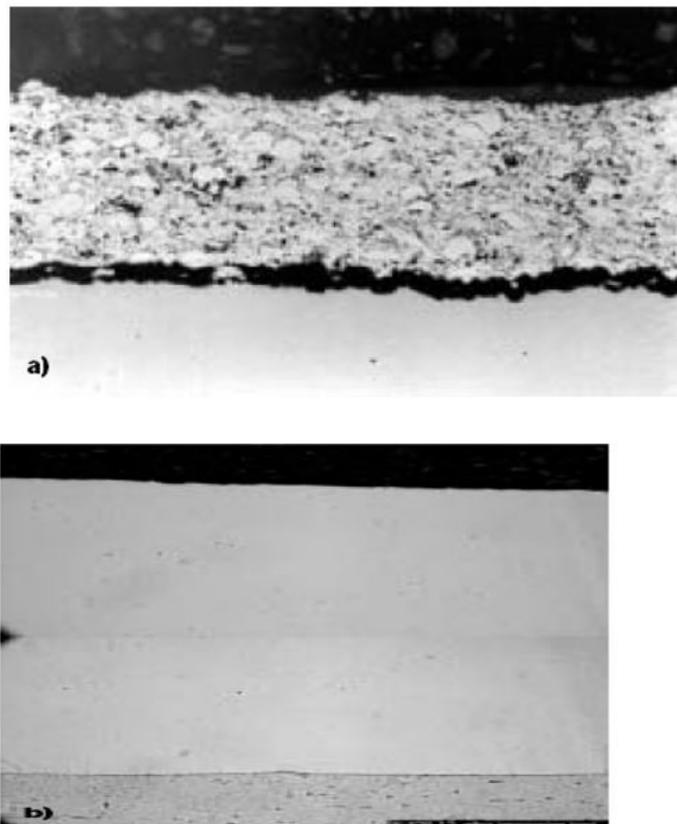


Figure 10: Inconel 625 coatings after corrosion test in 3.5 % NaCl. a) HVOF coating and b) laser coating [18].

A similar finding to that of [18] was reported by [38] who laser clad Inconel 625 wire on AISI 304 stainless steel substrate. It is significant to note that [38] were able to optimize the process parameters to obtain a commendable dilution rate of about 4.5%. However, specific material provides different requirements for coating powders, parameters and pre and post cladding treatments. These requirements must be optimized in order to obtain sound and defect-free deposits from laser cladding process.

Flame Torch Melting for Surface Modification

Flame spraying process is a thermal spraying process for the deposition of extrinsic layers on substrate materials by melting coating materials (powder, wire or rod) using the heat generated from the combustion of a fuel gas (propane, acetylene) with oxygen. This process benefits from its low capital investment, high deposition rate, ease of operation and maintenance. The main critical component in the flame torch melting process is the flame gun whose orifice determines the intensity of heat that can be exposed to the substrate material. [21] reported that most flame spray guns can be adapted to use several combinations of gases to balance operating cost and coating properties. They also indicated that flame temperatures and characteristics depend on the oxygen-to-fuel gas ratio and pressure. Flame spray' includes low- velocity powder flame, wire flame processes, high velocity processes such as HVOF and detonation gun (D-Gun). Generally, metals or metal alloys are use as the coating materials in the flame spraying where flame temperatures in the range of 2800K to 3200K [22]. The consumable used, powder and wire or rod give rise to the two variant types: powder flame spraying and wire flame spraying. A generic illustration of flame torch melting is presented in Figure 11 in which the process of the flame melting is demonstrated. The figure indicates the spread of the heat from the flame gun is dependent on the space between the gun and the substrate materials.

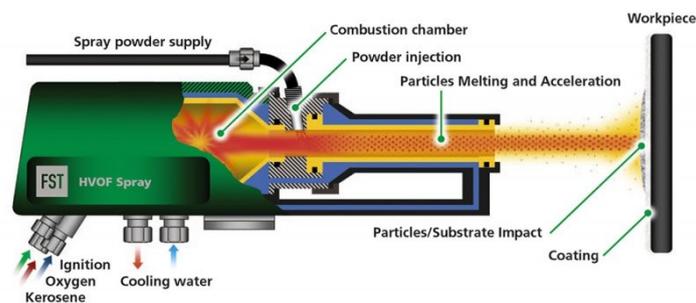


Figure 11: A schematic of a typical HVOF spray gun(Amin and Panchal, 2016).

Powder flame spraying

The powders are fed through central passage by carrier gases such as argon and nitrogen, or gravity fed from canister mounted directly on gun [22]. The powders are then transport into the combustion flame, and the mixed gases transport the material towards the prepared substrate surface. This method is however prone to high incidence of oxide formation with high content of pores at about 20% [7]. Yet, it is possible to improve the quality of coating by injecting a small jet of air into the nozzle which ensures lower pressure in the chamber connected to the powder feed hopper. This ensures that a gentle stream of gas sucked into the gun carries powder with it. The amount of powder that can be supported by a gas stream depends on many factors such as density, feed rate volume of gases, and powder characteristics. If air is not used, then the density of the supporting gas influences the feed rate and, for any particular powder, there is an optimum amount that can be carried in gaseous stream. This optimum amount depends on the velocity and volume of the gases used [23].

Wire flame spraying process

The process consists of a nozzle in which a fuel, such as acetylene or hydrogen, is mixed with oxygen and burns at the face of the nozzle. A wire is then continually fed into the flame of fuel gas – oxygen and melted; and stream of compressed air surrounding the flame atomises and propels the liquefied metal to the substrate. The process is optimized by ensuring a balance of wire feed rate and flame settings to generate the deposition of fine particulate coatings.

A wide variety of materials can be deposited using flame spraying and the vast majority of components are sprayed manually because of its low cost as well as the relative ease of application of the process. The aforementioned merits increase its application widely where a lower coating quality and bond strength are tolerated. Moreover, development in equipment technology in the last few decades has explored the possibility of increasing the particle velocities, from typically around 40 m s^{-1} to above 100 m s^{-1} [23]. Such processes, known as high velocity flame spraying, use internal combustion of the fuel and oxygen gases to create higher gas velocities, and give the much higher particle velocities [24].

Consequently, the process is characterized by high deposition efficiency, good adhesion of coatings, which have low content of oxides and low porosity [25]. Wire flame spraying finds application for wear resistant coatings, high or low friction traction coatings, anti-corrosion coatings and rebuilding of worn parts.

HVOF Flame Process

High velocity oxy-fuel (HVOF) flame process is an advanced variant of the flame deposition process in which the deposition particles are primed for delivery on the substrate material at high impact velocity. Like the parent conventional flame process, it uses a combination of oxygen with various fuel gases like hydrogen, propane, propylene and kerosene to generate the heat for the deposition process. Oxy-fuel combustion takes place in a specifically designed chamber in which the combustion gases are accelerated along a nozzle configuration to generate high velocity exhausted gas, having characteristic shock diamonds. The powder to be deposited is transported to the spray gun using a stream of carrier gas, usually argon or nitrogen, and transported to the spray gun. At this stage, it is heated and propelled by the rapidly accelerating hot gases in the combustion chamber and the nozzle, and finally ejected from the gun as a stream of molten or softened particles which are then deposited onto a surface to form a coating. Particle velocities of 400 to 800 m s^{-1} are typically obtained [23]. A schematic of a typical HVOF spray gun shown in Figure 11 accommodates powders in the size range 15 to $45 \mu\text{m}$ for metals and cermets, and 5 to $20 \mu\text{m}$ for ceramics [26].

Currently, HVOF coatings are becoming very popular in the oil and gas industry as well as aerospace and recently the automotive industry to improve the wear resistance of components [27]. The number of applications for HVOF sprayed coatings has increased steadily due to sustained growth in its use for surface engineering, together with a continual drive for improved coating performance and quality. HVOF coatings have significant advantages over conventional coatings due to the versatility of application, low coating porosity, and high adhesion between coating and substrate. Table 5 shows advantages and disadvantages of HVOF spraying compared to other thermal spraying processes. From its merits, multiple industries have the potential to benefit from HVOF coating through optimization of spray parameters of a specific coating material application.

Advantages		Disadvantages	
Characteristics	Comments	Characteristics	Comments
low level of trough-porosity (about 1-2 vol.%)	Improved corrosion protection	expensive equipment	
low oxide content (in the range of 1-2 wt%)	due to the less in-flight exposure time	need of a line of sight to the surface and spray stand off distance	difficult deposition on internal surfaces of small cylindrical components or other restricted access surfaces
higher hardness	improve the wear resistance	small powder particle sizes and narrow size distribution	high consumable cost
retention of powder chemistry	caused by a reduced time and temperature		
higher coating adhesion	higher particle velocity on impact Low levels of residual stress, can be in compression		
thicker coating (up to 2mm)			
lower levels of residual stress can be in compression	Selfpeening effect of impacting particles		

Table 5: Advantages and disadvantages of HVOF spraying over other thermal spraying [23].

The coating can be evaluated in terms of many parameters including; porosity, adhesion to substrate, hardness, fracture toughness, surface roughness, coating thickness, residual stress condition, wear resistance and corrosive resistance. Some of these coating parameters are related and based on the initial spraying conditions resulting in a delicate balance between deposition parameters

The first commercial type of HVOF spray system was the Jet-Kote process, produced by Thermadyne Stellite (now Deloro Stellite) in 1982. It is the basis of the many HVOF thermal spray processes in production today. Several alternatives of the HVOF process have been developed by a number of manufacturers, the major differences between the systems being: use of gas or liquid fuel; water or air cooling; axial or radial powder injection; combustion chamber configuration; and nozzle design and length. Operational differences comprise combustion pressure, fuel and gas flow rates, and powder feed rates. These parameters determine powder particle heating time, temperature and velocity, and ultimately the coating quality. Typical values for fuel gas flow rate, oxygen/fuel ratio and spraying distance for different spraying systems are shown in Table 6.

System	Fuel/m ³ h ⁻¹	Oxygen/ m ³ h ⁻¹	Compressed air/ m ³ h ⁻¹	Oxygen/Fuel ratio	Spray distance/ mm
Jet Kote	Hydrogen 26 Propane 3 Ethylene 5	18 21 20	- - -	1 7 4	250
Top Gun	Hydrogen 26 Propane 3 Ethylene 5	13 15 14	- - -	0.5 5 3	250
DJ 260	Hydrogen 38	13	21	0.5 ⁽¹⁾	230 – 250
DJ 270	Propane 4 Ethylene 7	15 15	22 22	5 3 ⁽¹⁾	230 – 250
JP-5000	Kerosene (1h ⁻¹) 21	54	-	4 ⁽²⁾	350– 380

Table 6: Standard parameters for various HVOF systems [23].

Oxy-acetylene Flame Torch Techniques

Oxyacetylene flame is ordinarily deployed for flame cutting and/or joining but they have now found additional use for surface modification [7,10]. Incidentally, some researchers [5,6] have reported the use of novel low energy techniques such as flame torch melting using oxy-acetylene gas mixture, and tungsten inert gas (TIG) torch melting for surface modification of substrate properties. [28] reported the use of oxyacetylene to evaluate the potential of Tantalum carbide for ultra-high temperature application. Similarly, [29] reported the use of oxyacetylene flame torch technique for depositing Zn-Ni composite on Q235 steel to determine the corrosion behavior of the coating in seawater and the result show a deposition thickness of about 300um thickness. [30] also deposited Ni-Al and NiO-Al composites on mild steel, stainless steel and aluminum alloys, and the result exhibited very low porosity, high surface hardness, and erosion resistance at a substantially lower cost than equivalent coatings using pre-prepared alloy powders. The oxyacetylene flame technique has generated wear resistance quite comparable to the conventional high energy beam processes. Additionally, convectional high beam/laser technique is costlier, difficult to design and fabricate using indigenous capability as compared with oxy-acetylene flame torch melting technique. While oxyacetylene gas mixture flame torch melting offers potentials for low technology low energy surface modification of substrate properties, the dynamics of the technique is not fully understood.

The oxyacetylene flame is available in three different options; the oxidizing flame, the reducing flame and the neutral flame which depended on oxygen- acetylene ratio (for 1:1 of oxygen to acetylene is neutral, more oxygen to acetylene is oxidizing and more acetylene to oxygen is reducing); and knowledge is not available on which of these options is most appropriate for surface modification. With any fuel gas, oxygen is needed for ignition; the proportion of which influences the “flame quality” in respect of temperature, output and speed. Acetylene attains the absolutely highest flame temperature of 3,160 °C at a mixture ratio of 1:1.1 to 1:1.5(studylib.net, docplayer.net, twi-global.com). All other fuel gases need more oxygen (up to a ratio of 1:4.5) to achieve maximum performance (studylib.net). Of all fuel gases, the oxygen requirements of acetylene are the lowest, and due to the variable oxyacetylene flame and easily inter-changeable torch tips, any desired heat output can be set, enabling optimal and economical treatment of the workpiece.

More so, the relative influence of the pressure of the gas mixture on the surface modification process has not been determined. Other than these, the dependence of the surface modification process on the distance of the torch from the substrate surface known as stand-off distance (SOD) is equally not known. The few reported works in this area hardly address these issues; rather they are essentially exploratory works [31]. In essence, in spite of the potential offered by oxyacetylene flame torch melting, there are still some unresolved issues about the dynamics of the process. Further, surface modification using oxy-acetylene flame as currently operates is prone to contamination from undesirable reaction of the molten pool with suspended particles in the vicinity of the pool. Therefore, it is quite necessary to incorporate self-shielding in oxy-acetylene flame torch for surface modification in order to avoid melt pool contamination and prevents the production of defective claddings. Presently, the few reported works on the process has not fully addressed the shielding for the prevention of contamination. It is postulated that oxy-acetylene flame torch system capable of self-shielding has the potential for expanding the deployment of oxy-acetylene flame for surface modification.

Friction Stir Processing

Friction stir processing (FSP) is a method of changing the properties of a metal through intense, localized plastic deformation and is a variation of Friction Stir Welding (FSW). Unlike the conventional arc melting process, FSP is a non-arc process for surface modification. It was developed as a solid state joining process at The Welding Institute (TWI), UK in 1991 for the joining of aluminum alloys that are difficult to fusion weld. FSP is an emerging surface-modification technique that can be deployed to eliminate local resolidification defects and refine microstructures. This result in improved strength, ductility and fatigue, enhanced corrosion resistance, improved formability and other properties [32].

FSP involves plunging a rapidly rotating non-consumable tool comprising a profiled pin and larger diameter shoulder into the surface and then traversing the tool across the surface as shown in Figure 12. Large surface areas can be traversed rapidly by using the appropriate tool design accompanied by rastering. Frictional heating and extreme deformation occurs causing plasticised material (constrained by the shoulder) to flow around the tool and consolidate in the tool's wake. FSP zones can be produced to depths of 0.5 to 50 mm, with a gradual transition from a fine-grained, thermodynamically worked microstructure to the underlying original microstructure.

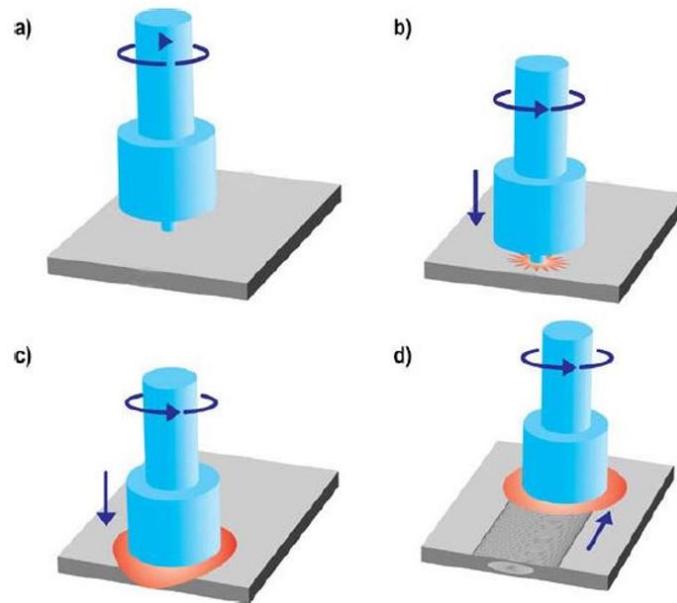


Figure 12: Friction stir processing schematic diagram [36].

The schematic diagram in Figure 12(a) illustrated the rotating tool before contact with the plate; (b) showed tool pin having contact with the plate, creating heat; (c) presented shoulder making contact, restricting further penetration while expanding the hot zone and (d) showed the plate moves relative to the rotating tool, creating a fully recrystallized, fine grain microstructure.

The precursor of this technique, friction stir welding is used to join multiple pieces of metal without creating the heat affected zone typical of fusion welding.⁸FSP is used to transform a heterogeneous microstructure to a more homogeneous, refined microstructure. Initially, FSP was used for making surface composites in aluminum and magnesium based alloys and in the last decade, surface composites including steel and titanium based alloys have also been reported [33]. Literature [32] has reported the deployment of the process to surface modified Al, Cu, Fe, and Ni-based alloys with measurable improvement in property characteristics.

FSP as a surface modification technique confers such benefits as: doubling of strength of cast nickel-aluminium-bronze; 5 folds increase in ductility of Al alloy A356; increase in fatigue life via surface fusion of interface layers; more than 10 folds increase in the corrosion resistance of Cu-Mn alloy, depending on the microstructure; and bonding of 25 mm thick 2519 Al plate to 85° at room temperature without surface cracking. The technique is utilized in shipbuilding and offshore, aerospace, automotive, railway rolling stock, general fabrication, robotics, and computers industries [35].

Modeling and Computational Simulation of Surface Modification Process

Modeling and computational simulation of surface modification process are emerging for more understanding of the process mechanism and applications. Researchers had critically compared the theoretical values and experimentation values of some techniques in this area to develop model for industrial applications. Modeling and simulations have been widely used to

investigate the importance of various relative parameters that influence surface coating, minimizes the experimental cost and gives insight into the physical processes using either analytical or numerical methods. Analytical methods provide an effective study of materials source effect whereas numerical solutions focus on the effect of material properties. This has actually assisted researchers in the field to predict experimental values through theoretical approach which has shown close convergence with experimental characterisation. The application of this has been widely used in industries for modifying materials surface using modeling and computational simulation approach to achieve the same result as experimentation methods.

Israr (2013) developed a combination of Cellular Automata (CA) and Boundary Element Method (BEM) to simulate pitting corrosion growth under certain environment. The conceptual framework for the study was underpinned by the assumption that pitting corrosion can be simplified to electrochemical corrosion cell and the distribution of potential around this corrosion cell can then be simulated by BEM. The result show that certain pits induced highly varying stress concentration as it grows which was in conformity with experimentation.

[36] introduces an effective and feasible computer-aided modeling/simulation methodology to study and analyse the anti-corrosion performance in regular and nano coatings. The nano- coating technology applies the non-chromate, effective slip-resistant, scratch-resistant, and anti-abrasion coatings to improve material performance. According to this work, the effective lifecycle of nanocoating is significantly longer than regular surface coatings, and the anti-corrosion performance of nanocoating is more durable and reliable than regular coatings with no contamination to the environment. The computer-aided modeling, computational simulation, and prototype testing methodology introduced in the study helps to understand the anti-corrosion mechanism and superior performance of nanocoating in rust prevention. Both computational and prototype testing in this research show close results in anti-corrosion performance which validates the credibility and feasibility of this research methodology.

Trends and Direction in Surface Modification of Metallic Materials

Surface modification over the years has progressed from the conventional thermochemical and conversion coating processes to advanced deposition techniques of high beam energy deposition and sol-gel techniques. The process has been extended to a wide range of materials specification with substantial improvement in surface characteristics. Yet there is a continuous demand for better quality surface features particularly at the nanoscale as obtained in the electronic industries and biomedical application. Therefore, there are continuous incentives for researchers to further explore ways in expanding the horizon of the various surface modification techniques while addressing the inherent challenges associated with each of the process options although depending on the application. Arising from these are new research frontiers in surface modification most especially in liquid phase surface melting processes typically represented by electron beam and laser surface modification processes. While thermochemical processes still find application in several industries, high energy beam process such as electron beam and laser surface melting appears to be fast becoming the standard in the metal industries. Therefore, emerging research efforts in surface modification for metallic materials are majorly being focused on understanding wholesomely the mechanisms underpinning the process dynamics. Some of these emerging research trends include interface structure and morphology in high beam surface modification, development of amorphous coating, optimization of process parameters and integration of other techniques to high beam surface modification such as laser assisted cold spray process. New research frontiers are equally emerging from modeling and simulation of surface modification process for greater insight into the mechanism of surface modification.

Furthermore, high energy beam processes are capital intensive and requires great expertise and competence; and thus, the widespread application of the processes are limited by skill and economics particularly in low income economies. Therefore, researchers are also interested in evaluating the adoption of cheap low energy process such as oxy-acetylene flame torch for surface modification. Research questions in this process include providing answers to what type of flame is required for what type of materials? What is the SOD for defect free oxy-acetylene coating on materials? What is the nature of shielding for protection of the

surface and what is the means of delivering the shielding gas and in what ratio? For instance, optimization parameters for the surface modification of mild steel via oxy-acetylene flame torch are currently being evaluated by the authors. Preliminary results show that the fuel-air ratio is significant parameter in initiating the liquid phase melting of the preplaced powder at a higher ratio than the fuel but significant contamination does occur. This suggests there is need for shielding to protect the molten region from contamination which otherwise results in defective coatings.

Conclusion

The extensive spectrum of the processes for the altering of the surface chemistry, crystal/microstructure and topography of metallic materials for improved surface functionalities has been presented. The progression of surface modification from thermal spray through high energy beam and low energy processes such as the oxy-acetylene technique for surface modification has been reviewed. The extensive treatment of these processes has exposed the complexity of the processes in terms of process dynamics, materials application and limitation of each of the processes. The application areas have equally been presented. It emerged from this review that because of the peculiarity of each process and materials susceptibility, these processes cannot be applied across the materials spectrum. Each process appears fit for specific class of materials but high energy beam processes of electron beam and/or laser melting and their hybrids appears to have universal appeal in the surface modification industry. Therefore, further development in the surface modification industry would be focused on addressing the challenges associated with high energy beam melting processes such as incidence of cracks, elimination of sharp interface between the substrate and the clad material, optimization of process parameters. There is also an emerging interest in the adaptation of the very basic oxy-acetylene flame melting technique for surface modification. However, the challenge in this is to develop a system that is capable of self-shielding to prevent melt pool contamination; and this is the focus of an on-going research by the authors.

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