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Research Article

Fabrication of Low-Cost Superhydrophobic Coating on Low-Carbon Steel Using Liquid Flame Spray

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ABSTRACT

A nano-engineered superhydrophobic coating was fabricated using a two-step and low-cost method employing a liquid oxy-acetylene flame spray mechanism on mild A516 steel. Oxygen and acetylene were used as flammable gases. Nanostructured coating is obtained by flame spraying aluminum nitrate solved in ethanol on the substrate. To lower the surface energy, Perfluorodecyltriethoxysilane [PFDTES] and silicone elastomer were used. Results revealed that the wettability of the surface strongly depends on the precursor concentration so that at 3.5% concentration of aluminum nitrate in ethanol, maximum contact angle [157°] occurs. The distance between the substrate and nozzle is another key parameter to control and it directly affects the contact angle. Sandpaper abrasion test showed outstanding mechanical durability so that the coating maintained in hydrophobicity range under the load of 100 grams of weight and moving 10 cm on sandpaper 1000 grit for 8 cycles. The parameters affecting the process were thoroughly analyzed according to the applied liquid flame spray mechanism and the appropriate performance range of each was obtained that According to the experiments, the precursor flowrate and the distance between the substrate and nozzle should be repectively 0.9-1.9 ml/min and 14-22 cm.

1. INRODUCTION

Fabrication of superhydrophobic surfaces by thermal spray methods due to their durability has drawn much attention in the past decades [1]. The most widely used thermal methods include flame spray [2, 3, 4, 5, 6], plasma spray [7, 8], arc spray [9], HVOF [high velocity oxygen fuel] spray [10], and VPS [vacuum plasma spray] [11]. Liquid flame spray pyrolysis [LFS] is a thermal spray method that can produce metal oxide powders from highly volatile gaseous metal chlorides that are decomposed in flame to form nano-oxide powder. The production of nano-engineered superhydrophobic coatings by the LFS method can be done in two different ways; the direct use of nano-powder homogenized in the solvent which is recommended to use with micro-powder, due to its low mechanical durability [6], or simultaneous production of nano-powder during the process .

Regarding the direct use of nano-powder during thermal coating methods, In previous studies, rutile and anatase titanium nanoparticles have been used and the mechanical and photocatalytic properties of the coatings have been investigated [7, 8]. Among the various thermal methods, mostly plasma spray and flame spray have been used for this purpose [6, 7, 8]. Titanium nanoparticles change at about 900k from anatase structure to rutile. Coatings produced by the direct use of nano-powder, less emphasis is placed on the super hydrophobicity and mostly titanium-coated properties based on hydrophilicity have been studied. Dimension and structure of the produced nano powder are a function of temperature, so that at different temperatures, the rutile or anatase structure may be produced and as a result the dimensions of the sedimentary grains on the coating will vary [8].

Regarding the production of nano-particles during coating process, the liquid flame spray method has been used to produce different nanoparticles, e.g. titanium [5, 12, 13, 14], aluminum [4, 15, 16], zirconium [17], and silica [2, 13, 18], from ceramics. To produce nano powder simultaneously during the process, liquid feedstock containing metal chlorides sprayed into high-temperature flame and after solvent evaporation, particles of the desired element settled on the surface under a complex process that occurs. In this process liquid precursor evaporates in the flame and form nanoparticles in the gas phase. The solvent material burns into the fire and then the evaporated precursor decomposes into the vapor of the product material. Next, nucleation occurs and after that, coagulation and sintering take place on the nucleation molecules. As the temperature of the flame decreases along the fire stream, sintering turns into aggregation and finally agglomeration [2]. In many studies, titanium and aluminum nanoparticles have been produced by the LFS process and validated using X-ray diffraction analysis. Many parameters in the LFS process affect the diameter of the produced nano powder e.g. injection flow rate If the injection rate increases, the observations indicate an increase in the average diameter of the formed nano powders. Previous work results revealed that if 14% of the total steel surface is covered by nano powder, it still has super hydrophilic properties [5].

Generally, studies have used oxygen and hydrogen gases to create a flame, and only a limited number of them have used other gases such as acetylene or propane [6]. Using acetylene instead of hydrogen has some advantages. First, acetylene produces a higher flame temperature than hydrogen. The acetylene flame will have a maximum temperature of about 3100°C, while hydrogen will eventually create a temperature of 2800°C. Hydrogen is a more dangerous gas and more complicated and expensive equipment is needed to work with. These reasons make acetylene a more suitable and applicable option for liquid flame spray instead of hydrogen .

A good way to increase the adhesion of a nano-coating to the surface is using a hybrid micro and nano powder at the same time [6]. The increase in adhesion appears to be due to an increase in the momentum of the colloidal particles which contains micro-particles surrounded by nano-particles moving toward the steel surface, which results in higher intensity and consequently an increase in mechanical strength so that the produced nano powders surround the microparticles and move rapidly. The results were compared with those which used only nano powder, in which case the adhesion was up to 9 times higher [6]. Affecting parameters generally include [14]: Precursor injection flow rate, Distance between the substrate and the torch, Movement speed of the sample and Concentration of solute in the solvent.

As the flow rate of injecting liquid increases, the production rate of the nano powder increases. If the injection flow increases, the concentration of the solution should be reduced to prevent the small particles from joining and becoming bullet-shaped.

As the distance between the substrate and the flame increases, the solution with a higher concentrate should be used, respectively. On the other hand, as the distance decreases, there is not enough time for liquid flame spray to take place so nano powder production process can't occur perfectly. Based on the working mechanism and all of the affecting parameters, the optimum distance between the substrate and the torch can be detected.

As the substrate moves faster in front of the flame, the nano powder settles less on the surface and eventually exhibits less super hydrophobicity [14, 19].

The solvent is one of the most effective parameters in the LFS process. Two of the most widely used solvents are ethanol and isopropanol that ethanol is hygroscopic and isopropanol is not. Due to the higher percentage of water in ethanol in comparison with isopropanol at the same concentration, it delays the opportunity for evaporation and reassembly, so using isopropanol as a solvent seems to lead to a much more nano powder production [19]. The interaction between the parameters should be observed more closely. Imagine if the injection flow rate increases, in order to keep the production rate of nano powder constant, the concentration of the solution must be decreased. In this case of increasing the injection flow rate, it is practically similar to the situation where the solute percentage has increased, which causes the flame to be longer and wider, and as a result, the maximum temperature of the flame is moved forward and the solution has more opportunity to evaporate. This means that despite the decrease in the concentration of the solution, there might be no difference in the amount of nano powder produced [19]. Reducing the energy level of super hydrophilic surfaces is done by low-energy substances such as silicon elastomers [20] and epoxy resins [21, 22, 23, 24, 25], polypropylene [26], silane derivatives [27, 28, 29] and some low-energy acids. Typical cured epoxies have surface energy around 45 dyne/cm [30] while silicon rubber which is used as lowering surface energy material has surface energy about 19-22 dyne/cm [31].

2.METHODOLOGY

Low-Carbon Steel [A516 Gr 60] is used as a working substrate and superhydrophobic coating was fabricated using a two-step and low-cost method employing a liquid oxy-acetylene flame spray mechanism. First, the substrate polished by 400-2000 sandpapers from rough to soft ones, then the samples are washed and cleaned in acetone using ultrasonic to clean all the impurities off the surface. Steel samples with 7 mm thickness and 20 mm× 30 mm size is used as shown in Figure 1.

Figure 1. *Low-carbon steel samples.*

The mechanism used for the liquid flame spray process is a simple set up cosisting: oxygen and acetylene capsule, two Volcano manometers, Volcano cutting head Eniso 5172, syringe pump, 1 ml insulin syringe and connector hoses. All the components and the operating system showed in Figure 2.

Figure 2. *1: Oxygen cylinder, 2: Oxygen manometer, 3: Acetylene cylinder, 4: Acetylene manometer, 5: Cutting Head, 6: Nozzle, 7: Hoses, 8: Operating mechanism.*

In this work both mentioned methods to fabricate superhydrophobic coatings are used but mainly emphasized on the method which the nano powder produced simultaneously due to more stability and low-cost of the fabricated coating. Nanostructured coating is obtained by flame spraying aluminum nitrate solved in ethanol on the substrate.

As mentioned before, some have used water-soluble salt of various metals with LFS and by the means of XRD test, they assured that during the thermal process, nano-powder has been produced, e.g. [2, 4, 9]. Moreover, another reason that can guarantee the formation of nano-powder is that the final surface after the LFS process shows excellent superhydrophilicity. In this work the $Al(No_3)_3$ is used as basic metal salt with melting temperature of 73°C and melting temperature of nano-powder 660°C. As you know the maximum temperature of acetylene can be 3100°C and varying along the fire stream. So, if the injection takes place at the optimal position, aluminum nano-powder will extract and settle on the surface.

In this process there are parameters to be optimized, e.g. solvent density, solution injection flowrate, oxygen and acetylene flowrate, nozzle geometry, distance between the injection position and nozzle tip, distance between the substrate and nozzle and the speed of moving substrate in front of the flame.

2.1. Parameters Optimization

Based on the experiments the gas pressure on oxygen and acetylene considered 4 bar and 1 bar, respectively. Figure 3 shows the flame morphology at different Flow rates of oxygen while acetylene flow rates is kept constant.

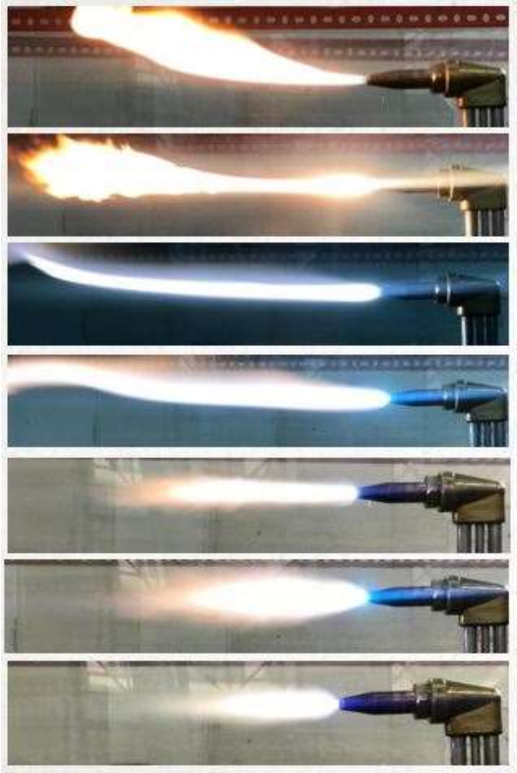

Figure 3. *Flame morphology.*

In general, to optimize the distance between the substrate and the nozzle, thermal process was implemented at different distances and analyzed the appropriate distance according to the properties of the produced coating and through experimental measures. The evidence showed that for distances greater than 22 cm between the substrate and the nozzle, the adhesion of nano powders on the surface decreases, so that the sandpaper wear tests also showed a decrease in mechanical resistance with increasing distance.

At distances less than 14 cm, the direct impact of the flame on steel quickly caused the formation of iron oxide on the sample, which prevents proper adhesion between the produced nanoparticles and the steel. Therefore, to carry out the tests of this method and avoid the mentioned problems, the distance between the substrate and the nozzle is set in the range of 14 to 22 cm.

To optimize the injection flow rate of precursor material into the flame by keeping the previous parameters constant, the experiments were performed again at different flow rates and according to the experimental observations and the thermodynamic properties of the produced coatings, we suggest the optimal range for the injection flow rate. To inject the precursor into the flame, we used a system including a syringe pump with ability to adjust the flow rate. The most ideal situation occurs when the precursor solution penetrates the center of the flame without scattering. Thus, according to observations, when the injection flow rate is less than 0.9 ml/min, the solution does not penetrate the flame, and due to the very high speed of the flame, it is completely scattered before entering it.

On the other hand, in flow rates higher than 1.9 ml/min, the injected precursor solution started moving away from the center of the flame, while the amount of material consumption was higher in this case, and the amount of nano powder production did not increase, because the solution injected into the flame is not given enough time to produce nano powder. According to the optimization that was done for different parameters, the tests of this method were designed and implemented in the range of the table below.

Table 1. *Range of test parameters of liquid flame spray method.*

Oxygen and acetylene pressure $[Bar]$	Precursor solution	Distance between the substrate and nozzle (Cm)	Precursor flowrate $(ml/\min)$
4, 1	Aluminum nitrate dissolved in ethanol	$14 < L < 22$	$0.9 < Q < 1.9$

Based on the suitable range of parameters, several methods were designed to fabricate superhydrophobic coating. The LFS parameters and the contact angle of the manufactured samples are listed in Table 2.

Results revealed that the wettability of the surface strongly depends on the precursor concentration so that at 3.5% concentration of aluminum nitrate in ethanol, maximum contact angle [157°] occurs.

2.2. Results and Discussion

In order to reduce the energy of the surfaces produced by liquid flame spray, various low energy materials were used.

Table 2. *Coating specifications.*

	Precursor flowrate $(ml/\min)$	Distance between the substrate and nozzle [Cm]	Method of lowering surface energy	Contact angle
Aluminum nitrate 3.5% in isopropanol	1.15	22	RTV/Powersil552	133±3°
Aluminum nitrate 3.5% in ethanol	1.5	20	RTV/Powersil552	138±3°
	1.15	22	FAS-17	150±3°
	1.15	17	FAS-17	157±3°

It should be noted that the silicone elastomer used in this section is Powersil RTV1-552. Both static and dynamic contact angles were taken by Jikan CAG-20 contact angle goniometer device and analyzed in ImageJ software. Static Contact angle of the produced coating showed in Figure 4.

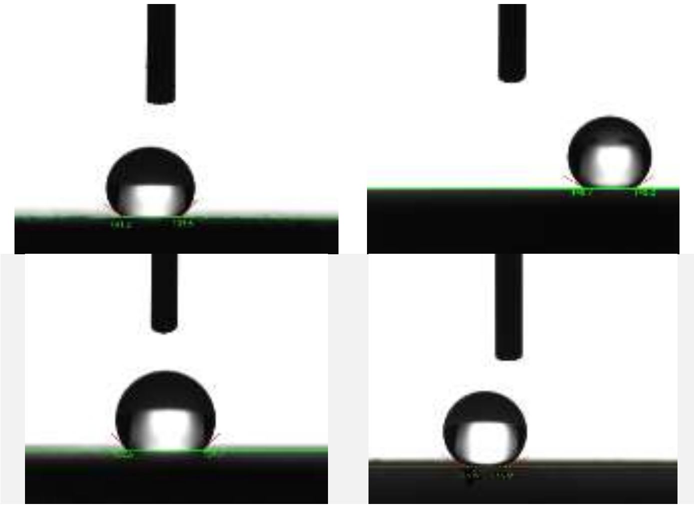

Figure 4. *Static contact angle.*

The best contact angle of the coating made by this method was 157°, advancing and receding contact angles of 159° and 154° respectively and hysteresis less than 5°. To produce this coating, 3.5% aluminum nitrate in ethanol precursor injected with a flow rate of 1.15 [ml/min] at a distance of 0.5 cm from the nozzle head into the fire stream. The distance between the sample and the nozzle kept 17 cm and the whole process of LFS completed in 180 seconds. The lowering surface energy step completed by immersing in FAS-17 solution and drying at 250° C in oven. Figure 5 indicates dynamic contact angles measured by Jikan CAG-20 goniometer.

Figure 5. *Dynamic contact angles* $\theta_{advancing}$ & $\theta_{receding}$.

The coatings produced by this method before applying the low-energy material are super hydrophilic with a contact angle of less than 5°, with a very high mechanical resistance to wear, so that even after washing with very rough items, They have kept their super hydrophilic state.

The abrasion test mechanism is shown in Figure 6. Prepared sample after the LFS method pushed on 1000 grit SiC sandpaper with a weight of 100 gr which provides 1.56 kPa of applied pressure. The sample moved 80 Cm in one direction. This test showed high mechanical durability of the super hydrophilic coating so that the coating still maintained its super hydrophilic properties and contact angle maintained less than 5°.

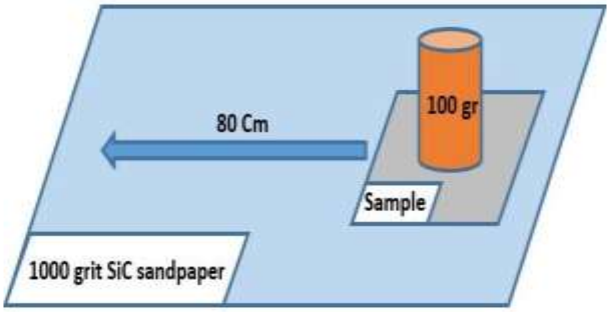

Figure 6. *Abrasion test on superhydrophilic coating.*

In this research, the effective parameters were optimized for this mechanism and the performance range was presented.

3. CONCLUSION

The main idea of the considered mechanism for LFS was lowering the cost of production and as a result, the produced coatings will be prone to use in large industries. In this work, oxy-acetylene flame used instead of oxy-hydrogen which is more dangerous gas than acetylene and even so cheaper and simpler equipment for the implementation of the oxy-acetylene liquid flame spray process is needed.

Considering the number of effective parameters and the complexity of the LFS process, it needs more research and development on parameters optimization and also considering the gap in the literature of working gases in this method, other gases that are economically more affordable and less dangerous, such as Butane and propane can also be considered. As mentioned before, one of the most influential parameters in the liquid flame spray process is the flame morphology, which directly affects the amount of nano powder production and momentum of the produced particles towards the surface. Therefore, the issue of designing and manufacturing special nozzles aiming to simultaneously control the morphology of the flame and the integrated injection system on it, can be investigated.

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DECLARATIONS

Ethical Approval. The authors declare that there are no animal studies in this work.

Conflict of Interest. The authors declare that they have no conflict of interest.

Author Contributions. First author gave the first idea of investigation, concept and modeling. The methodology and computations have been done by both authors.

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Data availability. There is no data set used.

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