Bond Strength, Hardness, and Microstructure Analysis of Stellite Coating Applied on 410 Steel Surface Using Flame Spray, Plasma Spray, and High-Velocity Oxyfuel Spray Process

Nail Widya Satya, Sunoto Mudiantoro, and Winarto Winarto*
Metallurgy and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia

*winarto@metal.ui.ac.id

Abstract. Three thermal spray methods often used in industry are flame spray, plasma spray, and high-velocity oxyfuel (HVOF) spray. This research is intended to compare the properties of those methods in depositing Stellite coating on 410 martensitic stainless steel. The results showed that both plasma spray and HVOF coating show an even deposition, which could not be achieved by a flame spray method. Those three coatings meet manufacture minimum bond strength requirements. The highest bond strength and hardness were provided by the HVOF process with a value of 33.1 MPa and 719 HV, respectively. According to bond strength and standard hardness deviation, the HVOF process gives the most homogeneous coating. Substrate hardness just below the coating interface after flame spray, plasma spray, and HVOF process are raised by 236%, 56%, and 65% each from the specification. HVOF coating has the best cross section compared to others. Smallest porosity percentage, porosity size, and average interface unbonding is got by the HVOF process, with a value of 0.2%, 7.2 μm, and 31%, respectively. Coating microstructure after etching shows phases related to heat input during application. The dendritic structure is observed on flame spray and plasma spray coating after etching but not on HVOF coating. Oxides and carbides of both cobalt and chrome are formed in the coating.

Keywords: Stellite; 410 Steel; Flame Spray; Plasma Spray; HVOF

1. Introduction
Thermal spray is often applied to increase abrasion resistance. Stellite is a commonly used material in the thermal spray process as it has excellent resistance against abrasion, oxidation, and corrosion at elevated temperatures. This resistance is gained from cobalt content as its primary alloy. The service temperature of a Stellite coating is around 538°C to 843°C. Three thermal spray methods often used in industry are flame spray, plasma spray, and HVOF. Flame spray generally used in a small industry because of its simple system and relatively cheap equipment. Plasma spray and HVOF equipment usually owed by a bigger shop or industry as the price is quite high. In this research, the property of these three methods in depositing Stellite coating on 410 martensitic stainless steel will be compared. It can give some idea to engineer to choose the suitable thermal spray methods based on the coating produced.
Recent researches in thermal spray focus on advance technology involving self-made equipment, whereas basic knowledge is still needed by the beginners new to thermal spray. This research is performed using industrial equipment and powder available in the market. Coating application and characterization methods used can be easily emulated by practitioners or researchers for a different type of base material, powder, method, or parameter. Coating color gradation after etching rarely observed in other studies even though it can provide valuable information about heat input of the spraying process.

2. Experimental method
The substrate used is 410 stainless steel classified as martensitic. This steel has 142 HV hardness. The specimen is cut to a dimension of 20x20x10 mm. Two types of Stellite, i.e., Stellite 1 and Stellite 6, are used as a coating. Substrate and powder chemical composition can be seen in Table 1.

Table 1. Substrate and powder chemical composition (in % weight).

| Element | Co | Fe  | Cr | Mn | Si | Ni | C | S   | Mo | W | Nb |
|---------|----|-----|----|----|----|----|---|-----|----|---|----|
| S S 410 | 0.018 | 85.2 | 13.3 | 0.487 | 0.451 | 0.199 | 0.105 | <0.005 | 0.069 | <0.02 | 0.014 |
| Stellite 6 | 63 | 1.5 | 28 | - | 1 | 1.5 | 1 | - | - | 4 | - |
| Stellite 1 | 50.5 | 2 | 30 | - | 1.1 | 1.5 | 2.4 | - | - | 12.5 | - |

Before the coating application, the substrate surface is blasted with 96 psi pressure to an average roughness of 9.2 μm using Oerlikon Metco Metcolite C grit. This grit is composed of 94 wt% Al₂O₃, 3.5 wt% TiO₂, and 2.5 wt% other compounds. The blasting particle has a size of ~2 +0.6 mm with 1.92 g/cm³ density. Stellite 6 powder used is a CoCrW alloy Praxair CO-106-1. This powder has a size of -45 +15 μm with 4.41 g/cm³ density. The powder has 23.4 MPa minimum bond strength and 285-361 HV average hardness. Besides Stellite 6, Stellite 1 with brand Dura-Metal DM H ST 1 is used for the HVOF process. This powder has a size of -53 +20 μm, 4.7 g/cm³ density, and 694 HV hardness.

Flame spray process is performed using SUPERJET-S Eutalloy equipment. Oxygen and acetylene gas sets are 60 psi and 15 psi, respectively. Both gas valves are regulated manually until the oxidation flame, as well as the setting of the powder deposition rate. Besides, the coating is applied from a 25-30 mm distance. The gas used in the system is argon, hydrogen, and air. The coating is applied from a 100–125 mm distance with a 3.5 kg/hour rate. The plasma spray parameter can be seen in Table 2.

Table 2. Plasma spray parameter.

| Argon Pressure (Psig) | Argon Flowmeter (FMR) | Hydrogen Pressure (Psig) | Hydrogen Flowmeter (FMR) | Ampere | Voltage (V) | Carrier Gas (SCFH) | Vibrator (psi) |
|-----------------------|-----------------------|--------------------------|--------------------------|--------|-------------|-------------------|--------------|
| 70                    | 150                   | 70                       | 20                       | 500    | 72          | 37                | 25           |

HVOF process is performed using Diamond Jet DJC Control Unit, 9MP-DJ Closed Loop Powder Feed Unit, water-cooled DJ Spray Gun, and ABB IRB 2600 robot. A robot is used since the manual application is impossible due to the high gas pressure of the system. The gas used in the system is oxygen, hydrogen, and air. The coating is applied from a 250 mm distance with a 2.5 kg/hour rate and gas rate of 3,000 m/s. The spray parameter can be seen in Table 3.

Table 3. HVOF spray parameter.

| Oxygen Pressure (Psig) | Oxygen Flowmeter (FMR) | Hydrogen Pressure (Psig) | Hydrogen Flowmeter (FMR) | Air Pressure (Psig) | Air Flowmeter (FMR) | Oxygen Flowmeter (SCFH) | Hydrogen Flowmeter (SCFH) | Air Flowmeter (SCFH) |
|------------------------|------------------------|--------------------------|--------------------------|---------------------|---------------------|-------------------------|-------------------------|-----------------------|
| 170                    | 140                    | 100                      | 26                       | 57.5                | 37                  | 398.35                  | 1345.49                 | 663                   |
All coating process is applied from 90° angle or perpendicular to the substrate surface. The preheat of 100°C is applied to the substrate surface before the coating application. Specifically, for flame spray process, preheat variation of 100°C, 200°C, 300°C, and without preheat is used. Figure 1 shows the thermal spray application for each method.

Characterization is conducted to know and compare properties for each process variation. Coating properties to be observed are bond strength, hardness, microstructure, morphology, and chemical composition. In figures that follow, some abbreviations are used, i.e., FS for flame spray, PS for plasma spray, NP for without preheat, P for preheating, S-1 for Stellite 1 coating, S-6 for Stellite 6 coating, and S for 410 stainless steel substrate.

The bond test is performed using a universal testing machine to know the bond strength of each specimen. Microstructure examination before and after etching is carried out using an optical microscope to analyze the coating structure and make measurements such as porosity, unbonded interface, and coating thickness. Vickers hardness test was performed from the specimen cross section to measure the hardness of the coating and substrate. SEM and EDS test was used to check morphology and identify elements present, respectively.

3. Results and discussion
3.1. Coating
The result for some coating applied can be seen in Figure 2. All specimens are in as-sprayed condition.

![Figure 1](image1.png)  
**Figure 1.** Thermal spray application (a) flame spray (b) plasma spray (c) HVOF spray.

![Figure 2](image2.png)  
**Figure 2.** Coating result (a) flame spray without preheat (b) flame spray 100°C preheat (c) flame spray 200°C preheat (d) flame spray 300°C preheat (e) plasma spray (f) HVOF spray.
In Figure 2 (a), it can be seen that adhesion between coating and substrate is not excellent. As preheat temperature is increased, as shown in Figure 2(b), (c), and (d), even coating started to be formed. In Figure 2(d), some vesicles are formed on the surface. In general, flame spray coating in Figure 2(a)-(d) shows greenish color. Figure 2(e) and (f) from plasma spray and HVOF show even coating deposition. HVOF coating has brighter color than plasma spray that probably caused by lower temperature in the HVOF process and higher tungsten content in Stellite 1, which in this case plasma spray is applied using Stellite 6 while HVOF is applied using Stellite 1.

3.2. Bond test
The bond test is performed on 19 specimens consisted of 4 flame spray specimens, three plasma spray specimens, 4 HVOF specimens with Stellite 6 coating, and 8 HVOF specimens with Stellite 1 coating. In the flame spray process, higher preheat temperature leads to higher bond strength with the highest value of 36.5 MPa. The average bond strength for the plasma spray process is 27.4 MPa, with a 59% standard deviation. HVOF spray process has an average bond strength of 35.9 MPa and 33.1 MPa for Stellite 1 and Stellite 6, respectively. The result can be caused by higher tungsten and less cobalt in Stellite 1, where tungsten has more significant Young modulus than cobalt resulted in higher strength. The standard deviation for the HVOF process is around 33%. Based on this value, HVOF produces the most homogeneous coating. The three methods satisfy manufacture minimum bond strength specification of 23.4 MPa.

3.3. Hardness test
The indenter is positioned in the middle of the coating thickness. The highest average hardness is obtained by HVOF spray Stellite 1 with a value of 719 HV with an 8% standard deviation. Apart from the process itself, the high hardness may be caused by the addition of 8.5% tungsten compared to Stellite 6, where tungsten is harder than cobalt. The second hardest coating is got from the flame spray process of Stellite 6 with a value of 459 HV with an 11% standard deviation. Different from the bond test, preheat variation relatively not influence coating hardness. Plasma spray of Stellite 6 produces 356 HV hardness with a 12% standard deviation. Same as the bond test result, based on standard deviation, HVOF has the most homogeneous coating.

In addition to coating hardness, substrate hardness is also examined with an indentation point located about 50 μm below coating. Average substrate hardness of 477 HV, 222 HV, and 234 HV are obtained from the flame spray, plasma spray, and HVOF, respectively. Compared with 410 steel, substrate hardness after application of the flame spray, plasma spray, and HVOF each are raised by 236%, 56%, and 65%. Increase for plasma spray and HVOF is considered normal due to the coating or cutting process. High substrate hardness for the flame spray process could be the result of contact with the oxidation flame during coating application. The hardness of 477 HV is similar to 410 steel after normalizing, which is about 522 HV [1]. Normalized 410 steel has a martensitic lath structure that resulted in a hard, low toughness material in nature [1]. Tempering is required to decrease hardness and increase toughness [1].

3.4. Metallographic examination
The microstructure of a thermal spray coating generally consisted of structure built up of splats, oxide, inter-lamellar pores, and interface voids [2]. To investigate the porosity, unmelted particle, contaminant, and coating interface, the coating cross-section is first observed without etching. The microstructure without etching of the flame spray process is shown in Figure 3. It can be seen that the majority of the area is filled by porosity, especially for the specimen without preheating. The flame spray process produces the most significant amount of porosity, both in terms of quantity and size. Porosity could be caused by a lack of powder impact speed, unmelted particle side effect, wrong application angle, or shrinkage [3,4]. In the flame spray process, higher preheat temperature resulted in a less porosity generated. The existence of an unmelted particle can be caused by a lack of heat to melt the particle [5]. Splats are not visible to be formed, and part of the white structure produced is as dense as weld structure.
It can be due to direct heat input to the coating during the process so that powder in some area are entirely fused. This condition is different from plasma spray as well as HVOF, where heat is concentrated inside the gun, and in-flight period reduces the particle temperature, which eventually triggers splats formation along with the thickness of the coating.

![Figure 3. Flame spray microstructure without etching (a) without preheat, 50x magnification (b) 100°C preheat, 100x magnification (c) 200°C preheat, 100x magnification (d) 300°C preheat, 50x magnification.](image)

The microstructure without etching of the plasma spray process is shown in Figure 4. Coating cross-section is dominated by grey splats that evenly spread. Splats formation indicates a melted coating powder [3]. These flat structure also denotes that the powder particle has perfectly melted before deposition [6]. Porosity is much less compared to the flame spray coating with a more uniform thickness.

![Figure 4. Plasma spray microstructure without etching 200x magnification.](image)
Microstructure without etching of HVOF spray is shown in Figure 5. The cross-section of the HVOF spray microstructure showed a dense coating with little splats and porosity. A higher density is followed by higher hardness. The HVOF process produced the lowest porosity percentage and size with a value of 0.2% and 7.2 μm each. Besides porosity, unbonding length at the coating interface is an important criterion to be evaluated. Unbonding has a significant effect on bond strength results. The shortest unbonding is provided by the HVOF process with a value of 31%.

![Figure 5. HVOF spray microstructure without etching 200x magnification.](image)

Microstructure after etching for every process is shown in Figure 6–8. The etching is performed by dipping the specimen for 5 minutes into the solution made of 30 ml HCl 36% and 10 ml HNO₃ 65%.

![Figure 6. Flame spray microstructure after etching 100°C preheat (a) 100x magnification (b) 500x magnification (c) 500x magnification (d) 200x magnification.](image)

In Figure 6 (a), color gradations appear with brown color at coating interface, blue in the middle, and white at the top of the coating. As magnification is increased to 500x, as seen in Figure 6 (b) and 6 (c), a dendritic structure are visible inside the unmelted powder particle. The existence of this structure signifies that the etching process was done correctly. Figure 6 (d) shows an area with heat concentration after etching. By looking at this color gradation, it is understood that the areas with the highest heat will turn yellow, followed by orange, purple, blue, green, and brown as the heat gradually reduced.

Figure 7 shows the plasma spray microstructure after etching. In Figure 7 (a), it can be seen that color gradation is more evenly spread compared to flame spray result. This result indicates a more
homogeneous heat deployment. Similar to flame spray, the area near the interface has a brown color, followed by purple in the middle, and white at the top. In Figure 7 (b-d), a dendritic structure is seen to be formed. The dendritic structure formed after etching in flame spray and plasma spray are the same as found from the deposition of Stellite 6 using the cold spray in another research [7,8]. These structures are also identical to the structure produced from Stellite 6 welding [9].

Figure 7. Plasma spray microstructure after etching (a) 200x magnification (b) 1,000x magnification (c) 1,000x magnification (d) 1,000x magnification.

HVOF spray microstructure after etching is shown in Figure 8. A white and brown area seen signifies a low heat input during coating application. This low heat input, together with the highest system pressure from the HVOF process resulting in a dense, hard, high bond strength and low porosity coating. The dendritic structure is not found even with high magnification. It can be due to the density of the coating so that the acid solution cannot penetrate through the coating pores.

Figure 8. HVOF microstructure after etching 200x magnification.
3.5. SEM & EDS
SEM and EDS tests are performed to observe morphology, change in chemical composition, and phase of the coating. An example of the coating analyzed is shown in Figure 9. SEM result confirms the common black area at the interface to be a cavity. Based on increasing and decreasing of elements found by EDS result for three thermal spray process, oxides like CoO, Cr₂O₃, and CoCr₂O₄ may be formed within the coating [10-12]. The amount of these oxides will be greater for longer oxidation time [10]. Besides, carbides like CoC, Cr₇C₃, Co₆W₆C, or Cr₂₃C₆ also might formed [7,10,11]. In some areas, silicon oxide and the iron oxide may also be formed at the coating interface. Porosity and cavity existence at the interface could be marked by increasing carbon and oxygen content.

| Element | 1 (Wt%) | 2 (Wt%) | 3 (Wt%) |
|---------|---------|---------|---------|
| CK      | 2.8     | 3.04    | 3.31    |
| OK      | 1.2     | 2.52    | 1.57    |
| AIK     | 0       | 0.19    | 0.51    |
| SiK     | 5.72    | 6.15    | 1.83    |
| CrK     | 31.82   | 34.44   | 18.24   |
| FeK     | 1       | 1.32    | 55.15   |
| CoK     | 57.47   | 52.33   | 19.39   |

Figure 9. SEM 2,500x magnification and EDS of HVOF spray coating.

4. Conclusion
All three thermal spray processes satisfy manufacture minimum bond strength specifications. HVOF spray produces the highest bond strength and hardness with most homogeneous coating. Flame spray process could reduce substrate toughness while plasma spray and HVOF spray not. The HVOF process produced the lowest porosity percentage and size. The HVOF process also produced the shortest unbonding length. Color gradation at plasma spray structure after etching indicates a more homogeneous heat deployment than flame spray. HVOF spray microstructure after etching signifies a low heat input during coating application. Oxides and carbides are formed within coating for all three thermal spray processes.

Acknowledgment
The authors would like to acknowledge the DRPM, Universitas Indonesia, for the financial support through the PIT9 Research Grant 2019 with the contract No: NKB-0082/UN2.R3.1/HKP.05.00/2019.

References
[1] G. Chakraborty, C. Das, S. Albert, A. Bhaduri, V. T. Paul, G. Panneerselvam, and A. Dasgupta, "Study on tempering behavior of AISI 410 stainless steel," Materials Characterization, vol. 100, pp. 81–87, 2015.

[2] W. Winarto, D. Priadi, N. Sofyan, and A. Wicaksono, "Wear Resistance and Surface Hardness of Carbon Nanotube Reinforced Alumina Matrix Nanocomposite by Cold Sprayed Process," Procedia Engineering, vol. 170, pp. 108 – 112, 2017.
[3] S. Vignesh, K. Shanmugam, V. Balasubramanian, and K. Sridhar, "Identifying the optimal HVOF spray parameters to attain minimum porosity and maximum hardness in iron-based amorphous metallic coatings," *Defence Technology*, vol. 13, pp. 101-110, 2017.

[4] M. Axente and V. Geaman, "Characterization of Ni-5Al and Sprasteel Coatings Deposited by Electric Arc Wire Thermal Spraying," *Metalurgia International*, vol. XVI no. 5, pp. 89, 2011.

[5] R. Paredes, S. Amico, and A. d'Oliveira, "The effect of roughness and pre-heating of the substrate on the morphology of aluminum coatings deposited by thermal spraying," *Surface & Coatings Technology*, vol. 200, pp. 3049 – 3055, 2006.

[6] S. Saeidi, K. Voisey, and D. McCartney, "Mechanical Properties and Microstructure of VPS and HVOF CoNiCrAlY Coatings," *Journal of Thermal Spray Tech.*, vol. 20, pp. 1231–1243, 2011.

[7] B. Li, Y. Jin, J. Yao, Z. Li, Q. Zhang and X. Zhang. "Influence of laser irradiation on deposition characteristics of cold sprayed Stellite-6 coatings," *Optics and Laser Technology*, vol. 100, pp. 27–39, 2018.

[8] N. Cinca, E. López, S. Dosta and J. Guilemany, "Study of stellite-6 deposition by cold gas spraying," *Surface & Coatings Technology*, vol. 232, pp. 891–898, 2013.

[9] L. Baiamonte, M. Tului, C. Bartuli, D. Marini, A. Marino, F. Menchetti, R. Pileggi, G. Pulci and F. Marra, "Tribological and high-temperature mechanical characterization of cold sprayed and PTA-deposited Stellite coatings," *Surface & Coatings Technology*, vol. 371, pp. 322–332, 2019.

[10] R. Shoja and Razavi, "Laser Surface Treatment of Stellite 6 Coating Deposited by HVOF on 316L Alloy," *Journal of Materials Engineering and Performance*, vol. 25, pp. 2583–2595, 2016.

[11] Z. Pala, M. Bai, F. Lukac and T. Hussain, "Laser Clad and HVOF-Sprayed Stellite 6 Coating in Chlorine-Rich Environment with KCl at 700 C," *Oxidation of Metals*, vol. 88, pp. 749–771, 2017.

[12] S. Houdkova´, E. Smazalova´ and Z. Pala, "Effect of Heat Treatment on the Microstructure and Properties of HVOF-Sprayed Co-Cr-W Coating," *Journal of Thermal Spray Technology*, vol. 25, pp. 546–557, 2015.