

Article

Effect of Cold-Spray Conditions Using a Nitrogen Propellant Gas on AISI 316L Stainless Steel-Coating Microstructures

Shinichiro Adachi * and Nobuhiro Ueda

Research Division of Metal Finishing and Analysis, Osaka Research Institute of Industrial Science and Technology, Ayumino 2-7-1, Izumi 594-1157, Japan; ueda@tri-osaka.jp

* Correspondence: shinadachi@tri-osaka.jp; Tel.: +81-725-51-2648; Fax: +81-725-51-2749

Received: 7 March 2017; Accepted: 24 June 2017; Published: 28 June 2017

Abstract: Cold-spray techniques have been a significant development for depositing metal coatings in recent years. In cold-spray processes, inexpensive nitrogen gas is widely used as the propellant gas in many industries. However, it is difficult to produce austenitic stainless steel coatings with dense microstructures with cold-spray techniques when using nitrogen propellant gas because of work hardening. In this study, the effects of cold-spray conditions using a nitrogen propellant gas on AISI 316L stainless steel coatings were examined. It was found that a higher nitrogen propellant gas temperature and pressure produce coatings with dense microstructures. The measured AISI 316L coating hardness values suggest that AISI 316L particles sprayed at temperatures of 700 and 800 °C soften due to the heat, allowing uniform deformation on the substrate and consequently forming dense coating microstructures. In addition, AISI 316L powder with particle diameters of 5–20 µm resulted in a denser coating microstructure than powder with particle diameters of 10–45 and 20–53 µm. Finally, the standoff distance between the nozzle and the substrate also affected the AISI 316L coating microstructures; a standoff distance of 40 mm produced the densest microstructure.

Keywords: cold-spraying; AISI 316L stainless steel; microstructure; porosity; hardness

1. Introduction

Conventional thermal spraying uses high-temperature flames, such as combustion gas, arc, or plasma flames. The metal materials being sprayed are subjected to one of these high-temperature flames and sprayed onto a substrate. The sprayed material then fuses completely and becomes stacked on the substrate to produce coatings. The problem with thermal spraying of metal materials is that the sprayed metal coatings immediately react to form oxide layers during the spraying process. These oxide layers in metal coatings deteriorate their properties, i.e., mechanical strength as well as wear and corrosion resistance.

The recent advent of cold-spray techniques has been a great development for the deposition of metal coatings [1]. A cold-spray gas is used at temperatures below the melting point of the sprayed metals; these sprayed metal materials are therefore in a solid state during cold spraying. As a result, cold-sprayed metal coatings are not fused particles stacked to form a coating, as with thermal-sprayed coatings, but rather solid particles stacked on the substrate by plastic deformation. As a result, cold-sprayed coatings contain little oxide.

For cold-spray processes, it was previously reported that the use of helium propellant gas was superior to that of nitrogen in terms of the deposition efficiency of Cu powder [2]. Thus, it is preferable to use helium for producing a dense coating. However, helium gas is expensive, and thus inexpensive nitrogen gas is still widely used in many industries. Copper and aluminum have been reported to successfully form dense coatings with the use of nitrogen propellant gas [3]. However,

it is difficult to produce cold-sprayed austenitic stainless steel coatings using nitrogen propellant gas. Austenitic stainless steel exhibits work hardening and resists plastic deformation, but when the sprayed particles are stacked on the substrate, the sprayed particle velocity with nitrogen propellant gas is significantly lower than with helium propellant gas at the same gas temperature [4–7]. As a result, the stacked stainless steel particles on the substrate do not deform completely, resulting in many voids between the stacked particles.

It has also been reported that cold-sprayed 316L stainless steel coatings using nitrogen propellant gas exhibited a porous microstructure as opposed to coatings using helium propellant gas, whereas the use of a heat treatment up to 800 °C enabled the same coating microstructures to be dense [8]. In addition, stainless steel 316L powder mixed with Co-Cr powder has been cold-sprayed using nitrogen propellant gas, and heat treatments were found to cause densification and porosity reduction of the coating microstructures [9]. We have previously investigated low-temperature plasma nitriding for AISI 316L coatings using a cold-spray technique to enhance the wear resistance while maintaining the corrosion resistance [10]. In that work, cold-sprayed AISI 316L coatings using nitrogen propellant gas also exhibited porous microstructures; subsequently, laser annealing was performed. As a result, the pores and cracks in the coatings disappeared completely. Furthermore, by using an optimized rectangular divergent cold-spray nozzle, sprayed stainless steel 316L coatings were fabricated successfully as dense microstructures when using nitrogen propellant gas [11].

A porous microstructure significantly deteriorates the corrosion resistance, wear resistance, and mechanical strength of sprayed coatings. As explained above, it seems to be challenging to achieve as-sprayed AISI 316L coatings, using nitrogen as the propellant gas, that are amenable to industrial applications without subsequent heating treatments, the addition of other metals, or modifications to the cold-spray nozzle.

Some papers investigating the cold-spray conditions for AISI 316L coatings have previously been published [4,12–14]. However, those papers discussed individual cold-spray conditions and did not consider all cold-spray conditions as a whole. Indeed, there seems to be a lack of consideration of the effects of combining various spray conditions on coating microstructures. In the current paper, we discuss the integration of various cold-spray conditions, such as the propellant gas temperature and pressure, sprayed particle diameter, and standoff distance from the nozzle to the substrate, while also including measurements of the coating hardness. As the result, various cold-spray conditions were optimized to achieve a dense AISI 316L stainless steel-coating microstructure.

2. Experimental Procedure

The substrate used was an AISI 316L stainless steel plate with dimensions of 25 mm × 55 mm × 5 mm, and the spraying materials were AISI 316L stainless steel powders with particle diameters of 5–20, 10–45, and 20–53 µm, as shown in the scanning electron microscope (SEM) images in Figure 1. Cold spraying was performed with a CGT Kinetics 4000 (Winterthur, Switzerland) system with nitrogen as the propellant gas, using the cold spray parameter values listed in Table 1. The sprayed-coating thickness was approximately 400 µm.

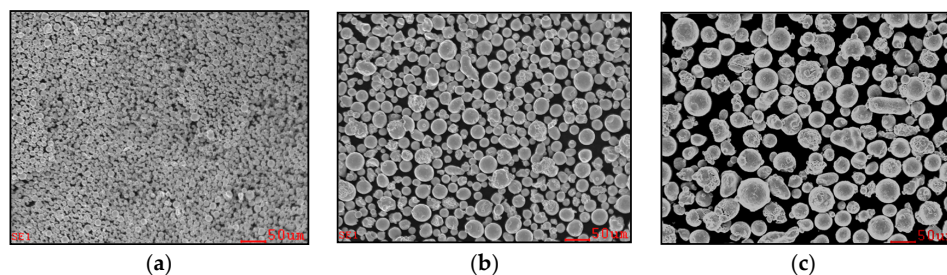


Figure 1. Cold-sprayed AISI 316L powders with various particle diameters: (a) 5–20 µm, (b) 10–45 µm, and (c) 20–53 µm.

Table 1. Cold-spraying conditions.

Nitrogen Propellant Gas		Standoff Distance from the Nozzle to the Substrate (mm)	Spray Nozzle Traverse Speed (mm/s)	AISI 316L Powder Diameters (μm)
Temperature ($^{\circ}\text{C}$)	Pressure (MPa)			
500, 600, 700, 800	2.5, 3, 3.5	10, 15, 40	150, 250	5–20, 10–45, 20–53

Cross-sections of the cold-sprayed AISI 316L coatings were polished and observed using an optical microscope. The porosities of the cold-sprayed AISI 316L coatings were measured using commercially available image analysis software for photographs of the AISI 316L coating cross-sections.

The hardness values of the AISI 316L coating cross-sections at approximately the through-thickness center were measured using a Vickers tester (HVM-2000; Shimadzu, Kyoto, Japan) at a test load of 0.098 N. The Vickers test for each sample was repeated eight times, and the lowest and highest values were excluded.

3. Results and Discussion

3.1. Effects of Nitrogen Propellant Gas Temperature and Pressure

The effects of the nitrogen propellant gas temperature and pressure on cold-sprayed AISI 316L coatings were investigated. The cold-spray conditions were: cold-sprayed AISI 316L powder particle diameters of 10–45 μm , standoff distance from the nozzle to the substrate of 15 mm, and spray nozzle traverse speed of 150 mm/s.

Figure 2 shows the microstructures of the cross sections of the cold-sprayed AISI 316L coatings at various propellant gas temperatures and pressures. When the propellant gas pressure was 2.5 MPa, the spray-coating microstructures showed significant numbers of pores and cracks at all gas temperatures; the porosities of those coatings were 11.9%–18.7%. At propellant gas pressures of 3 and 3.5 MPa, the densities of the AISI 316L coating microstructures increased with the increasing gas temperature. The porosities of the AISI 316L coatings with a gas pressure of 3 MPa were 3.6%–17.9%, while those with a gas pressure of 3.5 MPa were 1.9%–22%. The cold-sprayed AISI 316L particles at a propellant gas pressure of 2.5 MPa were considered not to reach high enough velocities to induce plastic deformation on the substrate during the coating process due to the insufficient propellant gas flow. On the other hand, the AISI 316L particles at 3 and 3.5 MPa would be accelerated by the high-pressure propellant gas flow. As a result, the particles can reach high enough velocities to become considerably deformed on the substrate.

The propellant gas temperature also had a great influence on the AISI 316L coating microstructures. Figure 3 shows the porosities of the AISI 316L coatings as a function of gas temperature. At a propellant gas temperature of 500 $^{\circ}\text{C}$, the AISI 316L coatings exhibited porous structures, even at gas pressures of 3 and 3.5 MPa. The porosities of the AISI 316L coatings at a gas temperature of 800 $^{\circ}\text{C}$ and pressures of 3 and 3.5 MPa were low at 3.6% and 1.9%, respectively, indicating dense microstructures. These results indicate that, when the cold-sprayed AISI 316L particles reach sufficient velocity at a certain high temperature, plastic deformation of the sprayed particles on the substrate can easily occur. The densest coating structures with the fewest cracks and pores were obtained at a gas temperature of 800 $^{\circ}\text{C}$ and pressure of 3.5 MPa. Thus, the cold-sprayed AISI 316L coatings were found to require high-pressure and temperature propellant gas conditions in order to produce dense microstructures.

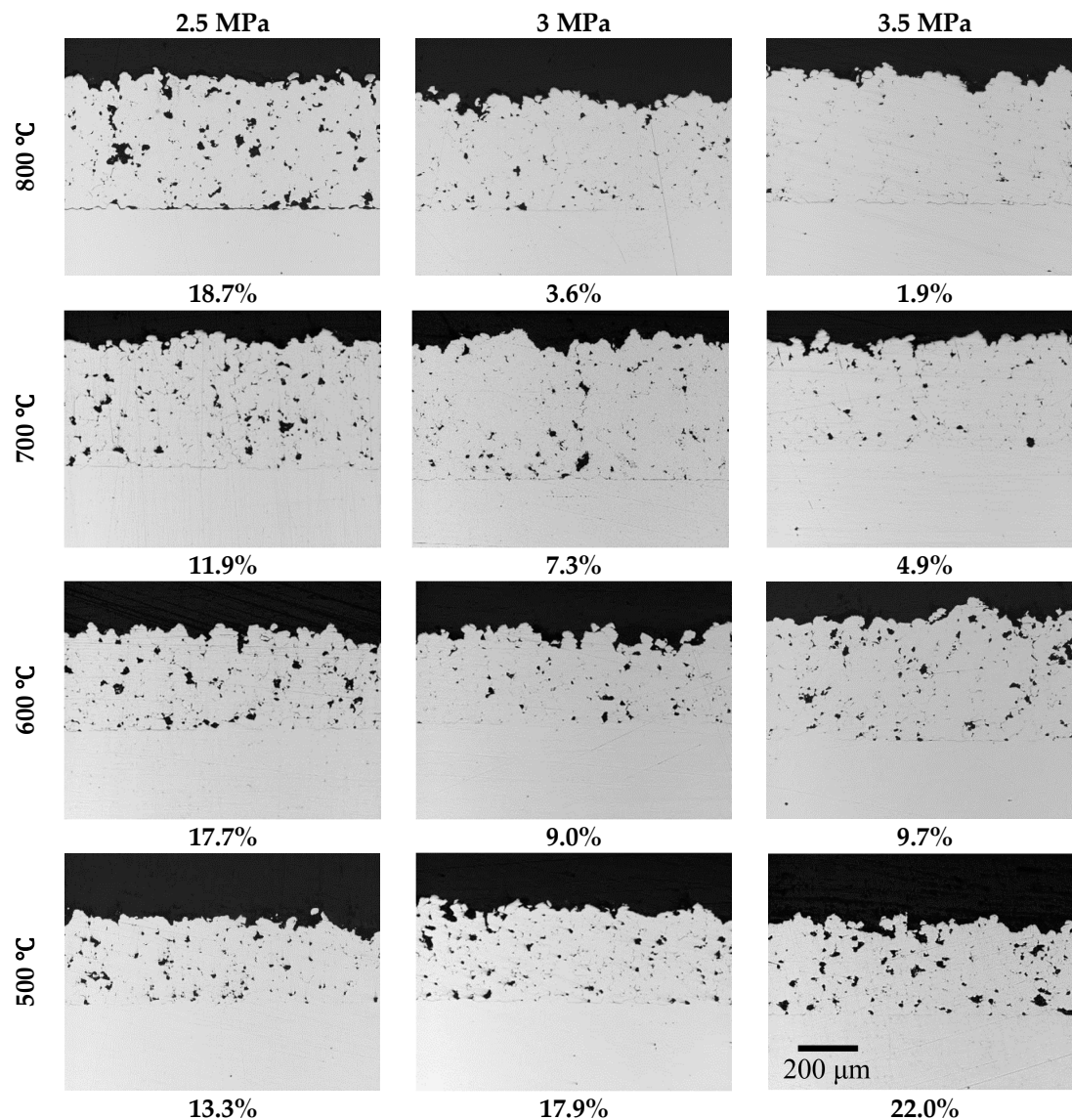


Figure 2. Cold-sprayed AISI 316L coating cross-sectional microstructures using various nitrogen propellant gas temperatures and pressures; the used AISI 316L powder had particle diameters of 10–45 μm .

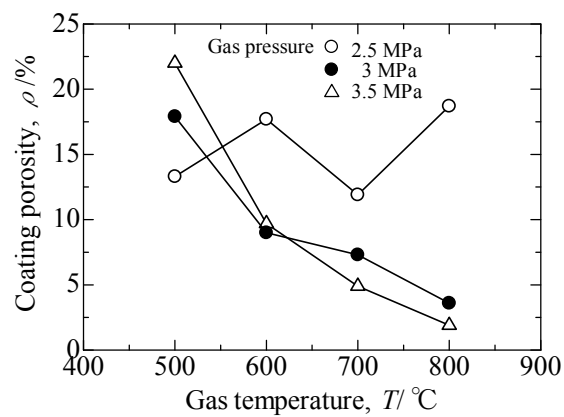


Figure 3. Porosities of cold-sprayed AISI 316L coatings with various nitrogen propellant gas temperatures and pressures using AISI 316L powder with particle diameters of 10–45 μm .

Villa et al. reported that the cold-spray conditions of cold-sprayed 316L coating on an Al alloy substrate optimized for a dense microstructure were the highest propellant gas temperature and pressure in a cold gas spray system, and the gas temperature had a larger influence on the coating microstructure than the gas pressure [13]. Using an AISI 316L stainless steel substrate, the results obtained here also show that the highest propellant gas temperature and pressure were optimal. However, our results indicate that the propellant gas pressure had a significant impact on the coating porosity. Since the Al alloy is a soft material, it could deform easily when impacted by cold-sprayed AISI 316L particles. The AISI 316L stainless steel substrate, on the other hand, would be expected to have higher resistance to deformation. Accordingly, the propellant gas pressure of 2.5 MPa did not result in the critical velocity needed to deposit dense coatings.

The Vickers hardness of cross sections of the AISI 316L coatings with various propellant gas temperatures at the gas pressure of 3.5 MPa is shown in Figure 4. The average hardness remained constant at about 400 HV regardless of the gas temperatures. The measured hardness of 400 HV is relatively high compared to that of normal AISI 316L stainless steel, indicating that work hardening occurred. The lower and upper hardness limits at 700 and 800 °C occurred over a narrow range compared to those at 500 and 600 °C. The standard deviations of the hardness also suggest that the variation in hardness at temperatures of 700 and 800 °C was small compared to that at 500 and 600 °C. The latter indicates that the AISI 316L particles sprayed at 700 and 800 °C were softened by the higher temperature and deformed uniformly on the substrate. Figure 3 showed that the coating porosity decreased with increasing gas temperature at the gas pressure of 3.5 MPa. As mentioned, an increase in propellant gas temperature leads to greater velocity and allows greater compaction of coatings [12]. Thus, the sprayed AISI 316L particles at high gas temperatures deformed sufficiently on the substrate due to the synergetic effects of the softening of sprayed AISI 316L particles and higher compaction. Consequently, the AISI 316L coatings formed a dense microstructure.

Figure 5 shows the Vickers hardness of cross sections of AISI 316L coatings with various propellant gas pressures at 800 °C. The coating hardness seems to be constant irrespective of the used gas pressure. In Figure 3, the coating porosity decreased with an increase in gas pressure. It thus seems that the velocity of the sprayed AISI 316L particles increased with an increase in gas pressure, achieving limited coating porosity due to sufficient deformation of the sprayed AISI 316L particles on the substrate. However, the hardness of these AISI 316L coatings did not show any appreciative variation, which means that the sprayed AISI 316L particles were processed at almost identical rates at any gas pressure. Therefore, the AISI 316L coating porosity was considered to be significantly affected by slight changes in the deformation of the sprayed AISI 316L particles.

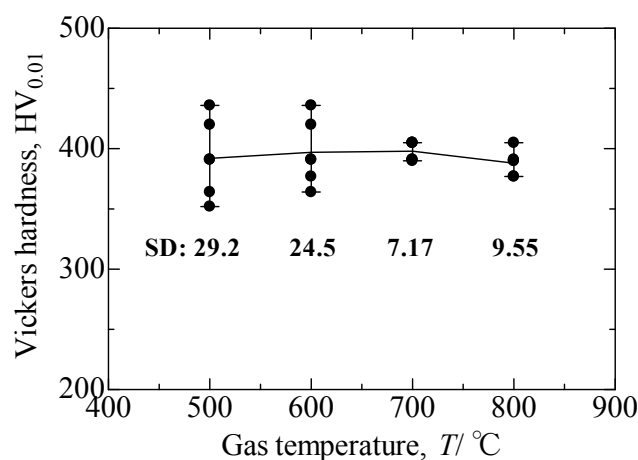


Figure 4. Vickers hardness of cross sections of cold-sprayed AISI 316L coatings with various nitrogen propellant gas temperatures at 3.5 MPa using AISI 316L powder with particle diameters of 10–45 μm .

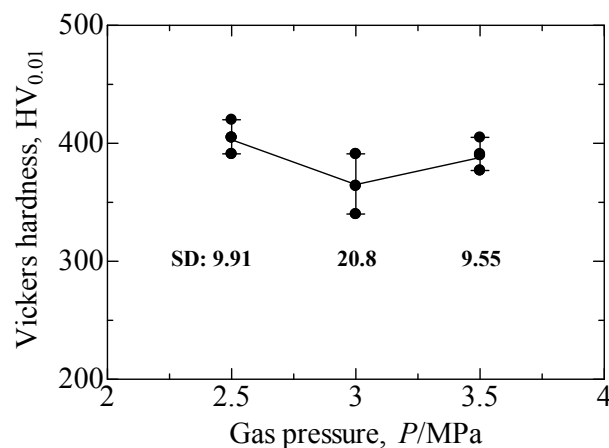


Figure 5. Vickers hardness of cross sections of cold-sprayed AISI 316L coatings with various nitrogen propellant gas pressures at 800 °C using AISI 316L powder with particle diameters of 10–45 μm .

3.2. Effects of Cold-Sprayed AISI 316L Powder Diameter

The effects of the particle diameter of cold-sprayed AISI 316L powders on the coating microstructures were also examined. The AISI 316L powder diameters were increased to 20–53 μm from the prior diameters of 10–45 μm ; that is, the mean particle diameter was enlarged by approximately 10 μm .

The cold-spray conditions were a nitrogen propellant gas temperature of 800 °C and pressures of 2.5, 3 and 3.5 MPa. The nozzle standoff distance from the substrate was 15 mm, and the spray nozzle traverse speed was 150 mm/s; these conditions were the same as those reported in the previous Section 3.1.

Figure 6 shows the resulting AISI 316L coating microstructures, and their corresponding porosities are shown in Figure 7. The porosities were 29.8% at 2.5 MPa, 11.5% at 3 MPa and 6.9% at 3.5 MPa. Thus, the AISI 316L coatings with particle diameters of 20–53 μm exhibited a porous microstructure comparable to that of the AISI 316L coatings with particle diameters of 10–45 μm in Figure 2.

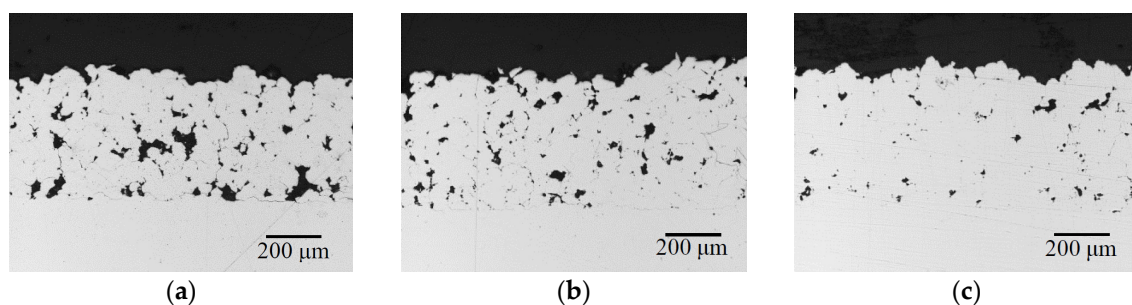


Figure 6. Cold-sprayed AISI 316L coating cross-sectional microstructures with various nitrogen propellant gas pressures at 800 °C using AISI 316L powder with particle diameters of 20–53 μm : (a) porosities of 29.8% at 2.5 MPa (b) 11.5% at 3 MPa and (c) 6.9% at 3.5 MPa.

Figure 8 shows the Vickers hardness of cross-sections of the AISI 316L coatings. The hardness of the coatings, as in Figure 5, did not show any apparent correlation with the gas pressure. In addition, no clear difference in average hardness exists between the AISI 316L powders with particle diameters of 20–53 μm in Figure 8 and 10–45 μm in Figure 5. However, the hardness values with particle diameters of 20–53 μm exhibited larger standard deviations than those with particle diameters of 10–45 μm . The sprayed AISI 316L particles with diameters of 20–53 μm may not have deformed uniformly on the substrate due to their relatively large volume, and the varying processing rate of the sprayed particles resulted in a wide range of coating hardness. That is, the sprayed AISI 316L

particles with diameters of 20–53 μm deformed only slightly compared to the particles with diameters of 10–45 μm . The larger particles may require high deformation strain to induce sufficient plastic deformation on the substrate; the AISI 316L coatings with diameters of 20–53 μm therefore formed a porous microstructure.

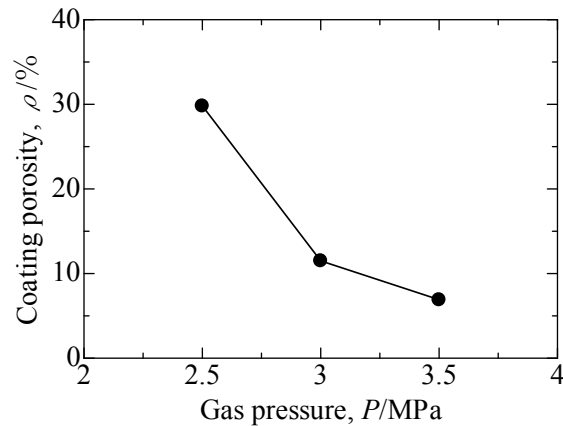


Figure 7. Porosities of cold-sprayed AISI 316L coatings with various nitrogen propellant gas pressures at 800 °C using AISI 316L powder with particle diameters of 20–53 μm .

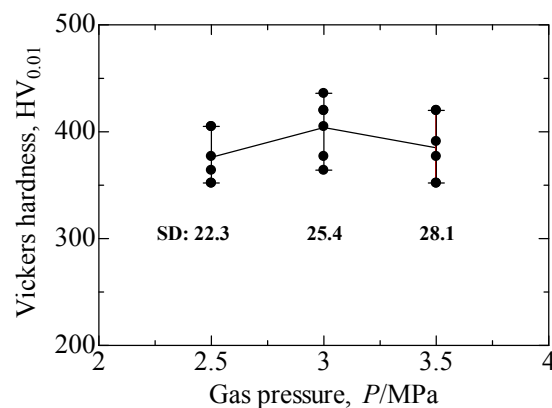


Figure 8. Vickers hardness of cross sections of cold-sprayed AISI 316L coatings with various nitrogen propellant gas pressures at 800 °C using AISI 316L powder with particle diameters of 20–53 μm .

3.3. Effects of the Nozzle Standoff Distance from the Substrate

The effect of the nozzle standoff distance from the substrate was also examined. The spray distance was varied from 10 to 40 mm, while the nitrogen propellant gas temperature and pressure were 700 °C and 3 MPa, respectively. The used cold-sprayed AISI 316L powder diameters were 5–20 and 10–45 μm , and the spray nozzle traverse speed was 250 mm/s.

Figure 9 shows the cold-sprayed AISI 316L coating microstructures as a function of standoff distance. In Figure 9a, the porosity of the AISI 316L coating with powder particle diameters of 10–45 μm and a standoff distance of 40 mm is 6.4%. Compared to the microstructure with a standoff distance of 15 mm shown in Figure 2, the AISI 316L coating with a 40 mm standoff distance was less porous and exhibited a denser microstructure. For the AISI 316L coating with powder particle diameters of 5–20 μm , the coating porosities with standoff distances of 10 and 40 mm (shown in Figure 9b,c, respectively), were 4.2% and 2.1%, respectively. These results suggest that a standoff distance of 40 mm resulted in a denser coating microstructure than a distance of 10 mm. A standoff distance of 40 mm could therefore produce a dense coating microstructure, irrespective of the sprayed AISI 316L powder particle diameter.

It has previously been reported that when the nozzle standoff distance is small, a bow shock forms between the spray jet and the substrate, resulting in porous cold-sprayed coating microstructures [15]. In this work, when the standoff distance was 10 or 15 mm, a bow shock may have caused the porosity of the resulting AISI 316L coating microstructures. Thus, a standoff distance of 40 mm is preferred for producing a dense AISI 316L coating microstructure.

Previously, Sova et al. reported that higher nozzle traverse speeds during single-track cold spraying of 316L stainless steel increase the deposition efficiency [14]. The nozzle traverse speed used here was 250 mm/s, which was higher than the value of 150 mm/s used in the previous Sections 3.1 and 3.2. The possibility therefore exists that the low porosities of the AISI 316L coatings with 700 °C and 3 MPa in Figure 9 compared to that of 7.3% in Figure 2 partially resulted from the higher traverse speed.

In addition, it was confirmed that the AISI 316L coating using a powder with particle diameters of 5–20 µm formed a denser microstructure than the coatings with powder particle diameters of 10–45 and 20–53 µm. These results also suggest that a finer powder had a beneficial effect on the densification of the coating microstructures.

We should note here that the AISI 316L coatings shown in Figure 9a,b exhibit flat surfaces because their surfaces were polished after cold spraying. Therefore, the surface morphologies of the coatings in Figure 9 are unrelated to the cold-spray conditions.

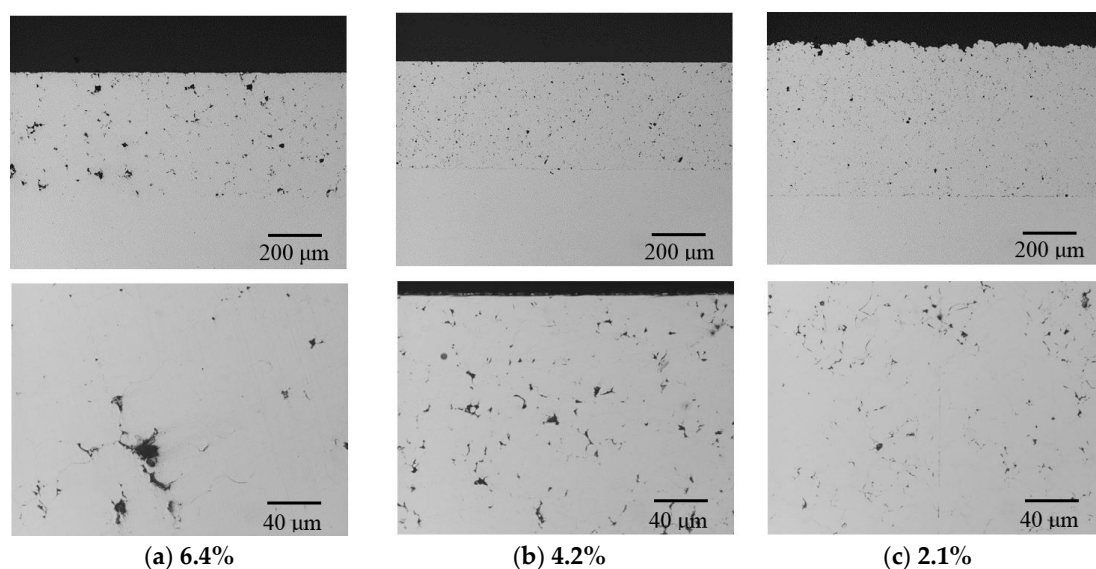


Figure 9. Cold-sprayed AISI 316L coating cross-sectional microstructures with nitrogen propellant gas temperature of 700 °C, pressure of 3 MPa, and spray nozzle traverse speed of 250 mm/s: (a) the porosity is 6.4%, AISI 316L powder with particle diameters of 10–45 µm and standoff distance of 40 mm, (b) the porosity is 4.2%, AISI 316L powder with particle diameters of 5–20 µm and standoff distance of 10 mm, and (c) the porosity is 2.1%, AISI 316L powder with particle diameters of 5–20 µm and standoff distance of 40 mm.

4. Conclusions

The effects of the cold-spray conditions such as nitrogen propellant gas temperature and pressure, sprayed AISI 316L powder particle diameter, and nozzle standoff distance from the substrate on the microstructures and Vickers hardness values of AISI 316L coatings were examined. It was found that dense AISI 316L coatings were produced at a propellant gas temperature of 800 °C and gas pressures of 3 and 3.5 MPa due to sufficient deformation of the sprayed AISI 316L particles on the substrate. In addition, the AISI 316L coating hardness indicated that the sprayed particles at nitrogen propellant gas temperatures of 700 °C and 800 °C were softened by the heating and deformed

uniformly on the substrate. The particle diameter of the cold-sprayed AISI 316L powder also affected the coating microstructure: AISI 316L coating powder with particle diameters of 5–20 μm resulted in denser structures than with particle diameters of 10–45 and 20–53 μm . Finally, the nozzle standoff distance from the substrate also affected the AISI 316L coating microstructure: a standoff distance of 40 mm was optimal to form a dense coating microstructure.

Acknowledgments: This work was supported financially by KAKENHI (25420747).

Author Contributions: Shinichiro Adachi conceived and designed the experiments, fabricated samples, measured porosities and hardness, and wrote this paper owing to an advice and support by Nobuhiro Ueda.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Schmidt, T.; Gartner, F.; Kreye, H. New Developments in Cold Spray Based on Higher Gas and Particle Temperatures. *J. Therm. Spray Technol.* **2006**, *15*, 488–494. [[CrossRef](#)]
- Ning, X.-J.; Jang, J.-H.; Kim, H.-J. The Effects of Powder Properties on In-flight Particle Velocity and Deposition Process during Low Pressure Cold Spray Process. *Appl. Surf. Sci.* **2007**, *253*, 7449–7455. [[CrossRef](#)]
- Schmidt, T.; Assadi, H.; Gartner, F.; Richter, H.; Stoltenhoff, T.; Kreye, H.; Klassen, T. From Particle Acceleration to Impact and Bonding in Cold Spraying. *J. Therm. Spray Technol.* **2009**, *18*, 794–808. [[CrossRef](#)]
- Spencer, K.; Zhang, M.-X. Optimization of Stainless Steel Cold Spray Coatings Using Mixed Particle Size Distributions. *Surf. Coat. Technol.* **2011**, *205*, 5135–5140. [[CrossRef](#)]
- Papayrin, A.; Kosarev, V.; Klinkov, S.; Alkimov, A.; Fomin, V. *Cold Spray Technology*; Papayrin, A., Ed.; Elsevier: Amsterdam, The Netherlands, 2007; p. 262.
- Sova, A.; Grigoriev, S.; Okunkova, A.; Smurov, I. Cold Spray Deposition of 316L Stainless Steel Coatings on Aluminium Surface with Following Laser Post-treatment. *Surf. Coat. Technol.* **2013**, *235*, 283–289. [[CrossRef](#)]
- Maestracci, R.; Sova, A.; Jeandina, M.; Malhaire, J.-M.; Movchan, I.; Bertrand, P.; Smurov, I. Deposition of Composite Coatings by Cold Spray Using Stainless Steel 316L, Copper and Tribaloy T-700 Powder Mixtures. *Surf. Coat. Technol.* **2016**, *287*, 1–8. [[CrossRef](#)]
- AL-Mangour, B.; Vo, P.; Mongrain, R.; Irissou, E.; Yue, S. Effect of Heat Treatment on the Microstructure and Mechanical Properties of Stainless Steel 316L Coatings Produced by Cold Spray for Biomedical Applications. *J. Therm. Spray Technol.* **2014**, *23*, 641–652. [[CrossRef](#)]
- AL-Mangour, B.; Mongrain, R.; Irissou, E.; Yue, S. Improving the Strength and Corrosion Resistance of 316L Stainless Steel for Biomedical Applications Using Cold Spray. *Surf. Coat. Technol.* **2013**, *216*, 297–307. [[CrossRef](#)]
- Adachi, S.; Ueda, N. Formation of Expanded Austenite on a Cold-Sprayed AISI 316L Coating by Low-Temperature Plasma Nitriding. *J. Therm. Spray Technol.* **2015**, *24*, 1399–1407. [[CrossRef](#)]
- Varadaraajan, V.; Mohanty, P. Design and Optimization of Rectangular Cold Spray Nozzle: Radial Injection Angle, Expansion Ratio and Traverse Speed. *Surf. Coat. Technol.* **2017**, *316*, 246–254. [[CrossRef](#)]
- Li, W.-Y.; Liao, H.; Douchy, G.; Coddet, C. Optimal Design of a Cold Spray Nozzle by Numerical Analysis of Particle Velocity and Experimental Validation with 316L Stainless Steel Powder. *Mater. Des.* **2007**, *28*, 2129–2137. [[CrossRef](#)]
- Villa, M.; Dosta, S.; Guilemany, J.M. Optimization of 316L Stainless Steel Coatings on Light Alloys using Cold Gas Spray. *Surf. Coat. Technol.* **2013**, *235*, 220–225. [[CrossRef](#)]
- Kotoban, D.; Grigoriev, S.; Okunkova, A.; Sova, A. Influence of a Shape of Single Track on Deposition Efficiency of 316L Stainless Steel Powder in Cold Spray. *Surf. Coat. Technol.* **2017**, *309*, 951–958. [[CrossRef](#)]
- Pattison, J.; Celotto, S.; Khan, A.; O'Neill, W. Standoff Distance and Bow Shock Phenomena in the Cold Spray Process. *Surf. Coat. Technol.* **2008**, *202*, 1443–1454. [[CrossRef](#)]

