Article

Nanosecond-Pulse Laser Assisted Cold Spraying of Al–Cu Aluminum Alloy

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Abstract: In this study, nanosecond-pulse laser is used in combination with cold spraying to form a hybrid solid-state forming technology: nanosecond-pulse laser assisted cold spraying. This method successfully manufactured Al–Cu high-strength aluminum alloy coatings. The nanosecond-pulse laser reduced the porosity of the coatings. The laser-induced micro-texture on the substrate surface had the ability of improving the bonding strength of the coating-substrate interface. The bonding strength was closely related to the depth of the micro-texture. The deeper micro-texture caused an unfused interface on the bottom of the texture, which produced voids and reduced the bonding strength. The nanosecond-pulse lasers can also increase the hardness of the coatings. The assistance of the nanosecond-pulse laser has proved to be an effective method to improve the quality of cold sprayed metal coatings.

Keywords: cold spray; nanosecond-pulse laser; hybrid processing; aluminum alloy

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1. Introduction

The high-strength aluminum alloy coatings manufactured by melting methods often face the issue of pores and cracks, due to the high absorptivity of H elements, high thermal expansion coefficients and element segregation [1–3]. Cold spraying (CS), a solid forming method, can avoid the melt-mentioned problems [4,5]. The CS process accelerates metal particles through high-temperature and high-pressure airflow to supersonic speed. The high-speed particles impact the substrate and deform with a high-strain rate, which makes the particles form a metallurgical bond or mechanical bond with the substrate [6,7]. The mechanisms involved with CS include adiabatic shear instability [8]. Therefore, the CS process without melting avoids pores and cracks caused by melting. This method has extremely low heat input to the substrate and can repair the thin wall structure without deforming the substrate. CS has great application potential in the fields of coating manufacturing, repairing and additive manufacturing [9,10].

However, CS also faces the problems of weak interface bonding and low deposition efficiency. In particular, the high strength of high-strength aluminum alloys leads to more serious problems. To this end, the researchers proposed the laser-assisted cold spraying (LCS) to improve interface strength and increase deposition efficiency. Bray [11] successfully realized LCS of titanium alloy coating, with depositing rate up to 45 g·min^{−1} and porosity less than 1%. Barton [12] and Li [13] successfully realized LCS of steel coating. Current LCS mostly use high-power continuous wavelength lasers, which have a large heat input and may even produce macroscopic melting phenomena, which offset the advantages of cold spraying. The nanosecond (ns) pulsed laser was able to ablate materials with low heat input due to the high energy density and extremely short pulse time [14,15]. It is possible to overcome the shortcomings of LCS if the ns pulsed laser is used to form a new

nanosecond-pulse laser assisted by the cold spraying (nLCS) technology. When the ns laser interacts with the material, it can produce local micro heating, which is beneficial to improve the plastic deformation ability of the particles and the substrate, and then the bonding strength. Moreover, the total energy of the ns laser is low, and the substrate will not be heated significantly, which reduces the heat input. The ns laser can also induce micro-textures on the substrate, and these structures are suitable to improving the bonding strength between the particles and the substrate. Kromer [7] used the ns laser to induce the microstructure to improve the processing deposition efficiency and interface bonding strength. Danlos [16] proposed the ns pulsed laser ablation and ms pulsed laser heat treatment of the 2017 aluminum alloy substrate before cold spraying. The ablation of the ns pulsed laser eliminated pollutants and the heating of the ns pulsed laser improved the coating-substrate adherence. However, the laser and cold spraying are not performed simultaneously in the above studies. The nLCS enables the laser and sprayed powder to work simultaneously in the same area, enabling laser cleaning, laser heating and particle deposition to take effect at the same time. This significantly reduces the pre-spraying treatment process and can improve efficiency. So far, there are no research reports on nLCS technology.

This research studied the structural characteristics of Al–Cu high-strength aluminum alloy coatings made by nLCS, and focused on the analysis of interface evolution and coating mechanical properties. The results proved that the performance of nLCS coating under reasonable laser parameters, the bonding strength of the interface and the strength of the coating itself were better than CS.

2. Experimental Procedure and Analysis Methods

The setup of the experimental equipment is shown in Figure 1a. The equipment is mainly composed of a nanosecond pulsed laser (MFPT-120P, Maxphotonics Co., Ltd., Shenzhen, China), a low-pressure cold spray machine ((LP-TCY-II, Beijing TianChengYu New Material Technology Co., Ltd., Beijing, China) and Robot. The spot size of the nanosecond laser beam is 50 μm , maximum power is 120 W, pulse width range is 60–300 ns, and frequency range is 10–1000 kHz. The substrate is 2219-T6 aluminum alloy with a thickness of 5 mm. The powder is Al–Cu aluminum alloy with diameter range of 15–53 μm as shown in Figure 1b. The Cu content is 0.594% by weight. The d50 of the powder was 37.9 μm . The working gas is compressed air. The process is as follows: the laser beam moves through the scanner, and the movement area is a 10 mm $\times$ 10 mm rectangle. The rectangular area overlaps with the cold spray powder spot on the substrate surface, and the robot drives the scanner and the spraying head moves along the planed path together. The processing parameters are shown in Table 1. The parameters produced the laser-induced textures with different depths on the surface of the substrate.

Table 1. Processing parameters.

No.	Laser Pulse Frequency KHz	Laser Pulse Width ns	Scanning Speed mm/s	Hatching Space mm	Gas Pressure PSI	Gas Temperature $^{\circ}\text{C}$
0	-	-	-	-	-	-
1	150	100	500	0.05	250	325
2	100	100	300	0.05		
3	100	300	500	0.05		
4	100	100	100	0.05

Figure 1. (a) Experiment setup of the nanosecond-pulse laser assisted cold spraying; (b) the SEM image of powder; (c) the tensile testing sample size; (d) analysis locations for porosity and hardness, the white box for porosity, the dot line for hardness.

After the processing is completed, the metallographic sample of the cross-section and the tensile sample were cut by electrical discharge method. The metallographic samples were grinded by emery paper, polished by anti-scuffing paste, and then etched by 0.5% hydrofluoric acid. The observation surfaces of the metallographic samples were analyzed by optical microscope. The shape of the tensile specimen is shown in Figure 1b. The two end faces of the circular specimen were bonded to two clamping sticks with E7 glue as shown in Figure 2c. The specimens were tested on the tensile mechanics machine at room temperature with a load speed of $3 \text{ mm} \cdot \text{min}^{-1}$. The tensile results were the average of three specimens. The tensile fracture was analyzed by scan electron microscope (MIRA3 TESCAN, Brno, Czech Republic). The locations of Vickers micro hardness measurements are shown in the Figure 1d. The Vickers hardness was tested using a load of 100 g for 15 s. Image-pro-plus code was used to analyze the porosity of the metallographic samples. Porosity was defined as the percentage of void area. The porosity analysis location on the metallographic samples was shown in Figure 1d.

Figure 2. Microstructures of the sample #0 without laser assisting. (a) Interface; (b) coating near to interface; (c) coating away from interface; (d) substrate.

3. Results and Discussion

3.1. Microstructures

Figure 2 shows the microstructure of the pure CS sample with a straight interface. Due to the plastic deformation caused by the particle impact, the grains and dendrites of the coating are mostly flat. The yellow arrow points to the grains with big size. The size of the grains and dendrites near the interface is smaller than those far away from the interface. This is because the microstructure at the interface was impacted by more subsequent particles. The more impact times made a greater degree of plastic deformation. Figure 3 shows the microstructures of the nLCS samples. The ns laser made wavy interfaces between the coatings and the substrates, which is the surface micro-texture formed by the ns laser ablating aluminum alloy. As the sample number increases, the depth of the laser-induced texture becomes deeper, from 19 μm for sample #1 to 74.5 μm for sample #4. The dendrite size of the coatings at the interfaces of samples #1–#3 is close to that of the coatings away from the interfaces, which is different from pure cold spraying. The dendrite size of the coating at the interface of sample #4 is significantly smaller than that of other areas. It is also smaller than the microstructure at the interface of other samples, indicating that the degree of plastic deformation is greater. Due to the high momentum of the impact force, the peak of the wave texture of #4 base metal also has severe plastic deformation. Its peak is flattened, while the deformation degree of other samples is not obvious. Too high a peak means lower material stiffness and easy deformation. At the same time, there are large-scale pores in the trough of the #4 interface texture. Obviously, high-speed particles were not enough to enter such a deep area.

Figure 3. Microstructures of the samples with ns laser assisting. (a) Sample #1; (b) sample #2; (c) sample #3; (d) sample #4.

3.2. Defects

According to the microstructure analysis, the main processing defect of the sample is voids. Figure 4 shows the porosity of different areas of the samples. In general, the porosity of the nLCS coatings is lower than that of pure cold spraying, and the porosity of sample #1 is the lowest. The coating near the interface has a low porosity, which is due to the compaction effect of the particles that have been deposited by subsequent particle impacts. With the increase of the sample number, the porosity of the interface gradually increases, and the porosity of the interface of #3 and #4 samples is greater than 3%. The reason for the increased porosity is that the laser-induced texture grooves are deeper and the groove bottom is narrow, which prevents particles from reaching the bottom of the groove, which induces more pores at the interface.

Figure 4. Porosity percentage of interfaces and coatings.

3.3. Mechanical Properties

Figure 5a shows the hardness plots of the samples. For all samples, the hardness of the coating and interface is higher than the substrate. The interface hardness of the nLCS samples reaches its peak, and as the coating position moves away from the interface, the hardness decreases and tends to a stable value. The fine microstructure at the interface contributed to the improvement of the hardness. The compaction of the subsequent particles not only refined the grains but also generated compressive stress, which are all suitable to improving the hardness. Sample #4 has the highest interface hardness due to the finest microstructure. The deep micro-texture of sample #4 made the particles produce greater plastic deformation, and finally induced recrystallization and reduced the grain size. This involves deformation hardening due to dislocation movements and dislocation generation within the grains [17]. The interface hardness of the pure CS sample is close to that of other positions, which indicates that the compaction effect is limited when there is no laser assisting. The coating hardness out of the interface at the nLCS samples is higher than that at the pure CS sample, indicating that the ns laser is beneficial to improve the coating hardness.

Figure 5. (a) Micro hardness, (b) bonding tensile strength of interface.

Figure 5b shows the bonding strength histogram of the interfaces. The bonding strength of sample #0 is 34.5 MPa, while the strength of sample #1–#3 exceeds 40 MPa. The strength of #4 sample is only 28.9 MPa. Figure 6 is the tensile fracture of typical samples. The morphology of sample #0 illustrates the extruded particles, and the surface of the particles is smooth, indicating that most of the interface is mechanically bonded. Sample #1 retains the periodic micro-textured morphology, indicating that the fracture location is at the contact interface. Obvious dimples are visible, indicating that metallurgical bonding occurs in some areas of the interface. The micro-texture morphology in sample #4 almost disappeared because of the irregular interface morphology caused by excessive interface voids. There are obvious micro cracks in the fracture, indicating that the degree of particle

deformation is huge and exceeds the plastic deformation threshold, causing cracks, which is not conducive to strength. Obviously, the metallurgical bonding in sample #1 is beneficial to improve its interface strength. The interfacial pores and cracks lead to the decrease of the bonding strength of sample #4.

Figure 6. Fracture morphology. (a) Sample #0, (b) sample #1, (c) sample #4.

4. Conclusions

Nanosecond pulsed laser and cold spraying were combined to successfully fabricate Al-Cu aluminum alloy coating with low defect rate. The coating hardness and the bonding strength of the substrate-coating interface were higher than the traditional cold spray. The increase in interface strength was mainly due to the texture structure induced by the nanosecond pulsed laser on the surface of the substrate. In addition, the micro heating effect of the nanosecond pulsed laser improved the performance of the coating. The texture depth had an important effect on the performance. When the texture depth was less than 38 µm, the coating and interface performance will improve significantly. After the texture depth exceeded 38 µm, the impact particles were not easy to fill the texture, which led to the increase of interface porosity and reduced the interface strength.

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References

1. Ma, C.; Chen, L.; Cao, C.; Li, X. Nanoparticle-induced unusual melting and solidification behaviours of metals. *Nat. Commun.* **2017**, *8*, 14178. [[CrossRef](#)] [[PubMed](#)]
2. Talbot, D.E. *The Effects of Hydrogen in Aluminium and Its Alloys*; CRC Press: Boca Raton, FL, USA, 2004.

3. Soysal, T.; Kou, S. Role of liquid backfilling in reducing solidification cracking in aluminium welds. *Sci. Technol. Weld. Join.* **2020**, *25*, 415–421. [[CrossRef](#)]
4. Assadi, H.; Kreye, H.; Gärtner, F.; Klassen, T. Cold spraying—A materials perspective. *Acta Mater.* **2016**, *116*, 382–407. [[CrossRef](#)]
5. Dykhuizen, R.C.; Smith, M.F. Gas dynamic principles of cold spray. *J. Therm. Spray Technol.* **1998**, *7*, 205–212. [[CrossRef](#)]
6. Schmidt, T.; Gärtner, F.; Assadi, H.; Kreye, H. Development of a generalized parameter window for cold spray deposition. *Acta Mater.* **2006**, *54*, 729–742. [[CrossRef](#)]
7. Kromer, R.; Danlos, Y.; Aubignat, E.; Verdy, C.; Costil, S. Coating deposition and adhesion enhancements by laser surface texturing—metallic particles on different classes of substrates in cold spraying process. *Mater. Manuf. Process.* **2017**, *32*, 1642–1652. [[CrossRef](#)]
8. Assadi, H.; Gärtner, F.; Stoltenhoff, T.; Kreye, H. Bonding mechanism in cold gas spraying. *Acta Mater.* **2003**, *51*, 4379–4394. [[CrossRef](#)]
9. Yin, S.; Cavaliere, P.; Aldwell, B.; Jenkins, R.; Liao, H.; Li, W.; Lupoi, R. Cold spray additive manufacturing and repair: Fundamentals and applications. *Addit. Manuf.* **2018**, *21*, 628–650. [[CrossRef](#)]
10. Gärtner, F.; Stoltenhoff, T.; Schmidt, T.; Kreye, H. The cold spray process and its potential for industrial applications. *J. Therm. Spray Technol.* **2006**, *15*, 223–232. [[CrossRef](#)]
11. Bray, M.; Cockburn, A.; O'Neill, W. The laser-assisted cold spray process and deposit characterisation. *Surf. Coat. Technol.* **2009**, *203*, 2851–2857. [[CrossRef](#)]
12. Barton, D.J.; Bhattiprolu, V.S.; Thompson, G.B.; Brewer, L. Laser assisted cold spray of AISI 4340 steel. *Surf. Coat. Technol.* **2020**, *400*, 126218. [[CrossRef](#)]
13. Li, B.; Yao, J.; Zhang, Q.; Li, Z.; Yang, L. Microstructure and tribological performance of tungsten carbide reinforced stainless steel composite coatings by supersonic laser deposition. *Surf. Coat. Technol.* **2015**, *275*, 58–68. [[CrossRef](#)]
14. Torrisi, L.; Gammino, S.; Andò, L.; Nassisi, V.; Doria, D.; Pedone, A. Comparison of nanosecond laser ablation at 1064 and 308 nm wavelength. *Appl. Surf. Sci.* **2003**, *210*, 262–273. [[CrossRef](#)]
15. Chichkov, B.N.; Momma, C.; Nolte, S.; von Alvensleben, F.; Tünnermann, A. Femtosecond, picosecond and nanosecond laser ablation of solids. *Appl. Phys. A* **1996**, *63*, 109–115. [[CrossRef](#)]
16. Danlos, Y.; Costil, S.; Guo, X.; Liao, H.; Coddet, C. Ablation laser and heating laser combined to cold spraying. *Surf. Coat. Technol.* **2010**, *205*, 1055–1059. [[CrossRef](#)]
17. Lee, H.; Shin, H.; Lee, S.; Ko, K. Effect of gas pressure on Al coatings by cold gas dynamic spray. *Mater. Lett.* **2008**, *62*, 1579–1581. [[CrossRef](#)]