Plasma Spraying with Wire Feeding: A Facile Route to Enhance the Coating/Substrate Interfacial Metallurgical Bonding

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Abstract: Thermal spray coatings are widely used in many applications, and the adhesion effect at the coating/substrate interface plays an important role during the service life. The thermal spraying coating and substrate is primarily combined by a mechanical seizure effect. In this work, a strategy to generate interfacial metallurgical bonding is proposed. Plasma spraying with wire feeding was adopted to increase the size of sprayed particles, and metallurgical bonding was clearly formed between deposited particles and the substrate (304 stainless-steel and 7075 aluminum alloy). Interface reaction can be found at both NiAl/7075 and NiAl/304 interfaces. Typical Al-Al3Ni eutectic phase with higher microhardness was formed at NiAl/7075 interface. The adhesive strength of the coatings was significantly improved to 82.67 ± 3.96 MPa and 64.45 ± 2.84 MPa, respectively, for NiAl coating on 304 and 7075 substrates through tensile adhesion tests (TAT) without surface roughening pretreatment. This technique shows a promising aspect of the application of thermal spray coatings.

Keywords: plasma spraying; interface structure; nickel alloys; metallurgical bonding

1. Introduction

Thermal spraying technology has been widely used in many industrial applications, such as aerospace, automobile manufacturing and chemical industry. High-performance coating can protect the component surface from wearing, corrosion, erosion, oxidation, etc. The adhesive strength between the thermally sprayed coating and the substrate plays a key role during its service life. Normally, the mechanical anchor effect is believed to be a result of the clamping between rapidly cooling particles and the surface irregularities, namely the average roughness Ra and skewedness of the surface R∆q [1,2], as shown in Figure 1a. However, the strength of mechanical bonding is quite limited compared to the metallurgical bonding. Atmospheric plasma sprayed (APS) NiAl coatings were reported to have higher bonding strength (24 MPa) on polished magnesium alloy substrate than sand-blasting substrate (19 MPa), which proved a stronger metallurgical bonding at the interface than with a mixed bonding mechanism [3]. Another drawback of mechanical bonding is in some applications like thermal barrier coatings on single crystal substrate, the surface roughening process (e.g., grit blasting) probably leads to an undesirable recrystallization phenomenon during the service life of the coating [4].

Metallurgical bonding happens when high temperature spraying particles are impinged on substrate with a relatively low melting point [5,6]. Several methods have been applied to improve metallurgical bonding at the coating/substrate interface, including raising the spraying particle temperature, preheating the substrate surface and improving the interface contact condition. Normally, high melting point coating materials were chosen, and the spraying particles were usually melted or semi-melted during the thermal spraying process. High melting point Mo coating was prepared on Fe substrate, and the intermetallic compound Fe2Mo was found at the interface [7]. Another recent report indicated that NiCr powder wrapped in an Mo shell achieved a higher particle temperature, therefore
promoting the interfacial bonding of the coating. The tensile strength of NiCr based coating was significantly improved, rising from 30.5 MPa to 61.2 MPa [8]. Surface pre-heating was mentioned to induce metallurgical bonding at interface. Surface contamination would be removed by heating; the thermal resistance and activation energy would also decrease during the process [9–11]. Other surface pretreatments are focused on the improvement of the interface contact condition. Preplaced brazing flux was reported to promote metallurgical bonding, as it could remove surface oxide when molten particles impinged onto the surface [12]. This phenomenon requires further confirmation, but does demonstrate that a clean surface is quite beneficial.

![Schematic of bonding mechanism of thermal sprayed coating: (a) mechanical anchor, (b) metallurgical bonding.](image)

Figure 1. Schematic of bonding mechanism of thermal sprayed coating: (a) mechanical anchor, (b) metallurgical bonding.

Obviously, the coating’s adhesive strength would be greatly improved once metallurgical bonding has taken place at the coating/substrate interface. This type of bonding can be regarded as a localized cold-welding between sprayed particles and the substrate, because the sprayed coating is formed by the accumulation of the successive impingement and flattening of molten particles. However, the phenomenon of metallurgical bonding induced by thermal spraying has been sporadically reported until now.

2. Materials and Methods

2.1. Governing Model

It is naturally thought that when the molten particle results in the melting of a substrate surface, metallurgical bonding will take place at interface. The actual heat transfer process from a single molten particle to substrate can be seen as a one-dimensional heat transfer process [13], which can be simplified since the particle’s flattening is quite rapid, lasting only a few μs. Assuming that the heat flux during the heat transfer from the flattened splat to the substrate is relatively stable in a short duration, the rise of the substrate surface temperature can be calculated following the Equation (1) [12]; likewise with a very short pulse laser heating on the substrate surface.

\[
T - T_s = \frac{2q\sqrt{t}}{\pi ks\rho cs} \tag{1}
\]

where \( T \) (K) and \( T_s \) (K) are the surface temperatures before and after the heat input, \( q \) (J·s\(^{-1}\)) is the heat flux to the substrate, which can be regarded as the energy density absorbed by substrate, \( t \) (s) is the heat transfer time, \( k_s \) (W·m\(^{-1}\)·K\(^{-1}\)), \( \rho_s \) (kg·m\(^{-3}\)) and \( c_s \) (J·kg\(^{-1}\)·K\(^{-1}\)) are the thermal conductivity, density and specific heat capacity of the substrate, respectively.
Assuming a steady state heat transfer process takes place from the flattened splat to the substrate within a short duration, the heat flux \( q \) is given by Equation (2).

\[
q = \frac{Q}{A_1} = \frac{m_p \cdot (T_p - T_s)}{A_1} = \frac{\rho_p \cdot 4 \cdot \pi \cdot r^2 \cdot c_p \cdot (T_p - T_s)}{\pi \cdot r^2 \cdot c_p} \cdot \frac{T_p - T_s}{2} = \frac{4 \cdot \rho_p \cdot c_p \cdot T_p - T_s}{\pi \cdot r^2 \cdot c_p} \cdot \frac{T_p - T_s}{2} \quad (2)
\]

where \( Q \) (J) is the heat the substrate received, \( A_1 \) (m²) is the area of the interface that is equal to the area of the flattened splat, \( T_p \) (K), \( T_s \) (K) are the temperature of particles and the substrate, respectively, and \( \rho_p \) (kg·m⁻³), \( c_p \) (J·kg⁻¹·K⁻¹) are the thermal conductivity and density of molten particle, respectively. \( \xi = \frac{R}{r} \) is the flattening ratio of the sprayed particle, which is mainly determined by particle velocity, where \( R \) (m) is the radius of the flattened particle and \( r \) (m) is the radius of the particle [14].

The Equation (3), which combines Equations (1) and (2), shows the threshold of substrate melting induced by the heat transfer from a flattened particle.

\[
\frac{T_p - T_s}{T_m - T_s} = \frac{3}{8} \cdot \frac{\pi \cdot r^2 \cdot c_p \cdot T_p - T_s}{\rho_p \cdot c_p} \cdot \frac{\xi^2 \cdot \sqrt{I}}{r} \quad (3)
\]

where \( T_m \) (K) is the melting point of the substrate, in this work, 304 stainless steel and 7075 aluminum alloy were chosen as substrates, and Ni5Al wire was selected as a spraying material. As can be seen from the formula, the substrate surface melts when the particles’ diameter and temperature rise. The flattening rate \( \xi = 4 \) [15] for a thermally sprayed nickel-based particle was used in the calculation. It has to be pointed out that the latent heat of the substrate is not considered in the calculation. Once the substrate reaches its melting point, extra energy has to be added to initiate the liquid formation. The corresponding diagrams following Equation (3) are illustrated in Figure 2. It was shown that the temperature of the substrate surface is mainly determined by both the temperature and the diameter of the sprayed particle. When the sprayed particle reaches its melting point, it will vaporize, and less energy will be carried to the substrate surface. Therefore, the more efficient way of melting substrate surface is to increase the particle’s diameter.

Figure 2. Surface melting criteria induced by the heat transfer of flattened particle: (a) 7075 substrate, (b) 304 substrate.

Usually, thermal spraying technology uses powder as feedstock, whose size is larger than 100 μm in rare cases. Moreover, in the traditional powder spraying process, all the particles were heated and accelerated only at their flight journey in the spraying jet. Herein we proposed a different approach, using wire as feedstock instead of powder. When the wire was fed into the plasma jet, the wire tip could be instantly heated and melted by the high-temperature plasma jet. The molten wire tip was then broken into pieces by the jet. The molten droplet was subsequently re-heated in its flight journey until the
final impingement on the substrate. In this way, even higher particle temperature can be obtained using a relatively low power input.

The criteria of substrate surface melting and metallurgical bonding can be roughly determined from Figure 2. Three curves in the diagram show different cases with different heat transfer duration supposed, which roughly indicate different interface heat transfer conditions.

2.2. Plasma Wire Spraying and Coating/Splat Preparation

In this paper, Ni5Al wire with a diameter of 1.6 mm was used as feeding wire. 304 stainless steel and 7075 aluminum alloy were used as substrates. Prior to spraying, all the substrate surfaces were machined and grounded by 800# SiC sandpaper in order to reduce the influence of surface roughness to minimum. The roughness of the surface was tested by laser confocal scanning microscopy (OLS4100, Olympus, Tokyo, Japan).

The coating’s preparation and particle collection were carried out using Metco 3M plasma spraying system with a homemade wire feeding nozzle. This proprietary method has already been patented (CN110919017A) [16]. As shown in Figure 3, the wire was fed perpendicularly into the plasma jet. Therefore, it could be delivered into the higher temperature zone of the plasma jet, producing droplets with higher temperatures. A large amount of pre-experiments have been conducted to determine the best wire feeding speed. When the feed speed is too fast, the wire will not be fully melted, and the drops will be scattered; sometimes this may even damage the nozzle. When it is too slow, the particles stream will incline to the feed-in direction. The proper feeding speed was determined depending upon spraying parameters to ensure a concentrated particle stream. The spraying parameters are shown in Table 1. The view of the equipment and experiment process are shown in Figure 4.

![Figure 3. Schematic of plasma spraying with wire feeding.](image)

| Coating Materials | Voltage /V | Current /A | Power /kW | Ar /L·min⁻¹ | H₂ /L·min⁻¹ | Distance /mm | Wire Feed Rate /m·min⁻¹ |
|-------------------|------------|------------|-----------|-------------|-------------|--------------|-------------------------|
| Ni5Al             | 64         | 350        | 22.4      | 50          | 8           | 100          | 3.5                     |

Table 1. Plasma spraying parameters.
During the process of particle collection, the droplets were sprayed into the water. The diameters of the collected particles were measured using an imaging analysis method. The morphology and composition of the particles were then observed by SEM (JSM-7100F, JEOL, Tokyo, Japan).

The cross-sections of coatings and splats were observed by SEM, and the composition were characterized by the quantitative electron probe microanalysis (EPMA1720, Shimadzu, Kyoto, Japan). The composition of the substrates is shown in Table 2. The adhesive strength of coatings will be mentioned in the following Section 2.4.

|           | Al  | Si  | Fe  | Mg  | Cu  | Mn  | Cr  | Zn  | Ti  | Ni  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 7075 substrate | 92.982 | 0.506 | 0.111 | 0.841 | 0.291 | 0.099 | 0.051 | 0.135 | 0.017 | -   |
| 304 substrate | -   | 0.511 | 69.841 | -   | -   | 1.300 | 17.954 | -   | -   | 7.646 |

2.3. Particles Temperature Measurement

The particle temperature was measured by a homemade device based on the entropy method. The schematic of the equipment is shown in Figure 5. A small test tube filled with water with an internal diameter of 6 mm was put in the center of a chamber with thermal insulation cotton surrounding it. The position of the chamber was adjusted to make sure the surface of water to the nozzle was equal to the spray distance. A fire-resistant graphite plate with a hole of 4 mm diameter and a water-cooled cover plate with a 3 mm diameter hole was placed in front of the test tube to shelter the plasma from heat damage. A stainless steel plate with a 1 mm hole was put underneath to screen the central particles. All these shielding cages were aligned concentrically so that the particles could fly directly into the water and the center particles in the plasma jet could be well collected. Two thermal couples were applied to measure the temperature of water and the body of the tube. The general view of the equipment is shown in Figure 6.
The temperature increment of both the water and the glass tube induced by the collected particles was recorded. The particle temperature was then determined by the following Equations (4)–(7) [17].

\[ \Delta Q_1 + \Delta Q_2 = \Delta Q_3 + \Delta Q_4 \]  

(4)

where \( \Delta Q_1 \) (J) is the enthalpy change of water, \( \Delta Q_2 \) (J) is the enthalpy change of glass tube, \( \Delta Q_3 \) (J) is the enthalpy change of the particles and \( \Delta Q_4 \) (J) is the heat caused by the plasma jet.
The enthalpy change of water and glass were determined through Equations (5) and (6):

\[
\Delta Q_1 = c_{p1} \cdot m_1 \cdot (T_1 - T_0)
\]

\[
\Delta Q_2 = c_{p2} \cdot m_2 \cdot (T_2 - T_0)
\]

where \( c_{p1} \) (J·kg\(^{-1}\)·K\(^{-1}\)) is the specific heat capacity of water, \( c_{p2} \) (J·kg\(^{-1}\)·K\(^{-1}\)) is the specific heat capacity of glass, \( T_0 \) (K) is the temperature of water and glass before heat input, \( T_1 \) (K) is the temperature of water after heat input, \( T_2 \) (K) is the temperature of glass after heat input, \( m_1 \) (kg) is the mass of water and \( m_2 \) (kg) is the mass of glass.

The influence of the plasma jet (\( \Delta Q_4 \)) was determined by a pre-experiment using the same process parameter but exempting wire feeding.

The average temperature of the particles can be determined by estimating the enthalpy change of particles \( \Delta Q_3 \), which can be determined by Equation (7).

\[
\Delta Q_3 = m_3 \cdot \left( L + c_{pm} \cdot (T - T_m) + c_{ps} \cdot (T_m - T_1) \right)
\]

where \( m_3 \) (kg) is mass of particles, \( L \) (J·kg\(^{-1}\)) is latent heat of fusion, \( c_{pm} \) (J·kg\(^{-1}\)·K\(^{-1}\)) is the specific heat capacity of liquid metal, \( c_{ps} \) (J·kg\(^{-1}\)·K\(^{-1}\)) is the specific heat capacity of solid metal, \( T \) (K) is temperature of particles and \( T_m \) (K) is the melting point of the particles.

2.4. Adhesive Strength Testing

The tensile adhesion test (TAT) was applied to measure the coating’s adhesive strength. This adhesion test is believed to be the most widely used method to test thermal spray coatings [18]. The bonding strength of sprayed coatings on both the 7075 aluminum alloy substrate and 304 stainless steel substrate was tested. In order to eliminate the influence of surface roughness as much as possible, all the substrate surfaces were grounded by 800 # SiC sandpaper. The adhesive strength of the thermal spray coatings was measured according to ASTM C633-08. The thickness of the coating was higher than 400 µm to avoid the penetration of adhesive epoxy. The FM1000 film (Cytec Inc., Cytec, Princeton, NJ, USA) was applied to glue the sprayed samples to the tensile rods. During the tensile test, the load was applied continuously at a loading speed of 1 mm/min until fracture occurred. The bond strength was calculated by Equation (8).

\[
S = \frac{F}{A}
\]

where \( S \) (MPa) is the bonding strength of the coating, \( F \) (N) is the load at which the sample is broken and \( A \) (m\(^2\)) is the surface area of the coating.

2.5. Nano Indentation Hardness Test of Coatings

Nanoindentation is widely used for thin film characterization. It is a powerful quantitative method for obtaining mechanical properties from very small volumes. It can determine not only the elastic modulus and microhardness values, but also other properties such as fracture toughness, creep, yield stress and friction coefficient at the nanometer scale [19,20].

The microhardness on the cross-section of the coatings was determined by nanoindentation hardness test (G200, Agilent, Santa Clara, CA, USA). Since the area was quite small, the depression depth was set at 1000 nm. At least three points were tested for each phase.

3. Results and Discussion

3.1. Surface Roughness of 304 and 7075 Substrate Prior to Coating Deposition

The substrate surface roughness \( Ra \) was 0.038 ± 0.001 µm and 0.331 ± 0.023 µm the for 304 and 7075 substrates, respectively, which could hardly cause a mechanical bonding [1,2].
The difference of roughness between the 304 and 7075 substrates was probably due to their different hardness. The surface morphology is shown in Figure 7. The relevant data is shown in Table 3.

![Figure 7](image_url)

**Figure 7.** Surface morphology of the substrates pre-treated by mechanical grinding using 800 # SiC sandpaper: (a) 2D photo and tested lines of 304 substrate, (b) 3D surface topography of 304 substrate, (c) Surface profiles of line 1–3, (d) 2D photo and tested lines of 7075 substrate, (e) 3D surface topography of 7075 substrate, (f) Surface profiles of line 4–6.

**Table 3.** Surface roughness of the substrate prior to coating deposition.

| Substrate | Ra (μm)         | RΔq          |
|-----------|----------------|--------------|
| 304       | 0.038 ± 0.001  | 5.979 ± 0.325|
| 7075      | 0.331 ± 0.023  | 31.269 ± 2.070|

3.2. Particle Temperature and Size Distribution

Using the enthalpy change method, the average temperature of the particles was calculated. The temperature measured curve is shown in Figure 8. Two groups of experiments were applied. Group A was the experience group with feeding wire and group B was the control group applied with the same parameter without feeding wire. The corresponding data is shown in Table 4.
The initial heat flux is thought to be higher in the real condition, so the substrate surface could be more easily melted, and the critical particle size could be smaller than that predicted. The thermal contact resistance at interface would also vary depending on the splat-substrate contact condition. For a simplistic consideration, only a steady heat transfer model was adopted here. The temperature difference between flattened particles and a substrate decreases. Moreover, the cooling of splat is a transient process, and the heat flux tends to fall when the temperature difference between flattened particles and a substrate decreases. Therefore, the thermal contact resistance at interface would also vary depending on the splat-substrate contact condition.

The size distribution and the morphology of all the sprayed particles is shown in Figure 9. As can be seen, the temperature rises when the hot particles and plasma jet are impinged into the system. The temperature of water raises dramatically as the heat of particles transfer into the water directly. The heat then transfers from the water to the glass tube, and they finally reached the thermal equilibrium. As the calculation indicates that \( \Delta Q_3 = 27.33 \text{ J} \), the final result of the temperature of sprayed particle was about 2130 K.

The average size of the sprayed particles (\( D_{50} \)) was 129.29 μm. Naturally, a larger molten particle would experience a longer cooling time when it impacted on the substrate. Supposing that the heat transfer time is about 10–20 μs, the mainstream particles’ temperature is 2130 K; the critical particle diameter that induces a substrate surface melting is 150 μm and 180 μm for 7075 aluminum alloy and 304 for stainless steel, respectively (Figure 2a,b). This implies that a large number of sprayed particles would exceed the threshold mentioned above and would potentially induce the substrate melting.

It has to be pointed out that the real heat transfer process would be much more complicated. The cooling of splat is a transient process, and the heat flux tends to fall when the temperature difference between flattened particles and a substrate decreases. Moreover, the thermal contact resistance at interface would also vary depending on the splat-substrate contact condition. For a simplistic consideration, only a steady heat transfer model was adopted here. The initial heat flux is thought to be higher in the real condition, so the substrate surface could be more easily melted, and the critical particle size could be smaller than that one predicted.

One interesting finding is that all the spherical particles had a portion of ‘tail’, as can be seen from Figure 9b. The EDS analysis showed that the ‘tail’ was mainly Al₂O₃, as shown in Figure 10. It is believed that the aluminum could be oxidized in a higher priority and act as a deoxidizing agent during the spraying process, therefore ensuring a pure nickel impinged on the substrate surface. This phenomenon also leads to the formation of oxide in the coatings, which will be mentioned later.
This means that the actual bonding strength of the coating should be much higher, but it can hardly be tested owing to the insufficient strength of the glue. It should be mentioned that the bonding strength of coating on 7075 substrate was 64.45 ± 2.84 MPa; all the samples fractured in the epoxy film (Figure 11c,d). While on the 304 stainless substrate, the bonding strength of the coating was 82.67 ± 3.96 MPa; most of the fractured zone was on the glue, and a small part of area was found at the coating/substrate interface (Figure 11a,b). The bonding strength of the sprayed NiAl coating was much higher than coating that relied on pure mechanical bonding effect, i.e., arc sprayed NiAl coating with sand-blasting surface pre-treatment [23,24]. As for the NiAl coating deposited by a high-velocity oxy-fuel (HVOF) process and APS spraying, the most reported adhesive strength of coating was 30–60 MPa [25,26]. The recent reports are summarized in Table 5.

Figure 9. Particle size distribution and morphology: (a) Particle size distribution, (b) Particle morphology.

Figure 10. EDS area scan of Ni5Al sphered particles: (a) Original SEM photo, (b) Map of oxygen, (c) Map of aluminum, (d) Map of Nickel.
that in the condition without surface roughing treatments, the bonding strength of the sprayed NiAl coating was much higher than coating that relied on pure mechanical bonding effect, i.e., arc sprayed NiAl coating with sand-blasting surface pretreatment [23,24].

As for the NiAl coating deposited by a high-velocity oxygen-fuel (HVOF) process and APS spraying, the most reported adhesive strength of coating was 30–60 MPa [25,26]. The recent reports are summarized in Table 5.

**Figure 11.** Adhesive surfaces after tensile adhesion test (TAT): (a,b) NiAl coatings on 7075 substrates, (c,d) NiAl coatings on 304 substrates.

**Table 5.** Reported bonding strengths, spraying and pre-treating methods in other studies.

| Substrate                  | Spraying Method | Surface Pre-Treatment | Testing Method | Average Adhesion Strength (MPa) | Ref. |
|----------------------------|-----------------|-----------------------|----------------|--------------------------------|------|
| 1 Al-Mg Alloy              | Arc-wire        | Sand-blasting         | TAT            | 39.8                           | [23] |
| 2 6061-T6 Alloy            | Arc-wire        | Sand-blasting         | TAT            | 55.6                           | [24] |
| 3 Superalloys (Hastelloy X, Inconel X750, Incoloy 800) | APS              | Cathodic Cleaning     | TAT            | 32.4                           | [25] |
| 4 Superalloys (Hastelloy X, Inconel X750, Incoloy 800) | HVOF             | Sand-blasting         | TAT            | 42.62                          | [26] |

3.4. **Cross-Sectional Observation on Interface**

The plasma spray coating has the typical lamellar-look structure. Some black zones inside the NiAl coatings are the oxide that formed during the particle flight.

The surface melting of 7075 substrate can be easily observed, since the melting point of 7075 aluminum alloy is relatively lower. As shown in Figure 12a,b, the substrate and the coating were fused locally at the interface and the phenomenon of metallurgical reaction can be characterized. The result of quantitative electron probe microanalysis (EPMA) was shown in Table 6, which showed a typical Ni-Al intermetallic compound with the atomic ratio of 1:4 of Ni and Al. A further EDS test was applied in smaller scale, and the atom ratio of the granular structure was close to Al$_3$Ni intermetallics, as reported in [27] and as shown in Figure 12c. It was reported that Al-Al$_3$Ni intermetallics can be formed by the Al–Ni eutectic reaction [28], which provided a more efficient inter-phase load transfer.
and lower microcracking probability \cite{29,30}. This may account for the higher interfacial bonding strength. The phase transformation reaction was reported as below \cite{27}:

\[
Al + Al_3Ni = \text{eutectic liquid (640 °C)}
\]  

(9)

Figure 12. Metallurgical bonding at NiAl/7075 interface: (a) Cross section of plasma wire sprayed NiAl coating on 7075 substrate, (b) Magnified observation of the square zone of (a), (c) Further enlarged observation of the eutectic phase.

Table 6. Atom ratio (Avg. at. %) of NiAl coating, 7075 substrate and the inter-phase in Figure 12b.

|         | Al   | Ni  |
|---------|------|-----|
| NiAl coating | 15.313 | 84.687 |
| Inter-phase  | 79.126 | 19.047 |
| 7075 substrate | 98.165 | - |

The melting area at the interface of 304 substrate was difficult to characterize, probably due to the higher melting point (about 1700 K) of 304 stainless steel. As the particle temperature was about 2130 K, the melting of the 304 substrate was much shallower, so the cross-section of NiAl coating on 304 substrate was etched (20 mL $H_2O$, 20 mL HCl, 4 g CuSO$_4$). As shown in Figure 13b, a small crater was formed at the interface due to substrate melting. The crater is similar to a welding molten pool. The grain of the 304 substrate can be observed after etching. The EDS line scan proved the melting and mixing at the interface (Figure 13c). The composition was not homogeneous in the area since the melting, mixing and reaction process happened in a very short period. As iron and nickel are soluble in any proportion, no specific compound was found at the interface. The compositions of points tested in Figure 13b are shown in Table 7; points 1–3 had the composition that combined NiAl and iron, which further proved that an interface reaction had taken place.

Figure 13. NiAl/304 interface: (a) Plasma wire sprayed NiAl coating on 304 substrate, (b) Magnified observation of the square zone of (a), (c) EDS line scan across the interface.
Table 7. Compositions (wt. %) of points at NiAl/304 interface.

|   | Al  | Cr   | Fe   | Ni  |
|---|-----|------|------|-----|
| 1 | 0.72| 14.89| 58.10| 26.29|
| 2 | 0.21| 17.17| 69.43| 13.18|
| 3 | 0.19| 16.92| 67.37| 15.52|
| 4 | 5.94| 0.32 | 1.41 | 92.33|
| 5 | 0.10| 19.57| 72.78| 7.54 |

3.5. Microhardness of the Reaction Zone/Phase

The result of microhardness test was shown in Table 8. At least 3 spots were tested in each area. The results on both the 304 and 7075 substrates could be influenced by adjacent areas, since metallurgical bonding areas were small. As the NiAl/7075 interface has a relatively larger bonding area, the result could be more accurate. The spots at NiAl/7075 interface are shown in Figure 14.

Table 8. Microhardness (GPa) of the relevant spots.

| NiAl Coating on 7075 Substrate | NiAl Coating on 304 Substrate |
|-------------------------------|-------------------------------|
| Coating Interfacial Zone Substrate | Coating Reaction Zone Substrate |
| 3.187 | 4.643 | 1.179 | 2.852 | 1.905 | 3.100 |
| 3.338 | 4.600 | 1.117 | 3.010 | 2.805 | 3.255 |
| 3.373 | 5.120 | 1.228 | 2.981 | 2.564 | 2.982 |

Figure 14. Microhardness testing spots at NiAl/7075 interface.

As can be seen in Table 8, the microhardness of the interfacial zone of NiAl coating on the 7075 substrate was higher than both the coating and the substrate. The Al₃Ni phase was reported to have a hardness of 594.73 HV in sintered matrix composite [28], which is much higher than the 7075 aluminum alloy and Ni₅Al materials. The hardness of the
diffusion area between the NiAl and 304 substrates was not as significant as the coating and the substrate, although it still formed a strong bonding at the interface.

4. Conclusions
1. A strategy was proposed to form metallurgical bonding between the thermal spray coating and metallic substrate. In this work, enlarged spraying particles with high temperatures could potentially melt the substrate surface to form metallurgical bonding at the interface, which can greatly enhance the bonding strength of the coatings.
2. The process method was proposed and conducted by experiments. Using plasma spraying with wire feeding, coating with much higher bonding strength was successively obtained on both the 304 stainless-steel and 7075 aluminum alloy substrates (82.67 ± 3.96 MPa and 64.45 ± 2.84 MPa respectively), with the exception of grit blasting surface pretreatment, while conventional grit blasting pre-treatment is of necessity for the thermal spraying coatings. During the TAT test, the fracture occurred inside the glue.
3. Interface reaction was found at both the NiAl/7075 and NiAl/304 interfaces, which may account for the higher interfacial bonding strength. While a typical Al-Al₃Ni eutectic phase was formed at the NiAl/7075 interface, no specific compound was formed at the interface of Ni-304 steel.

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References
1. Wang, Y.; Li, C.J.; Ohmori, A. Influence of substrate roughness on the bonding mechanisms of high velocity oxy-fuel sprayed coatings. Thin Solid Film. 2005, 485, 141–147. [CrossRef]
2. Bahbou, F.; Nylen, P. Relationship between surface topography parameters and adhesion strength for plasma spraying. In Proceedings of the Thermal Spray connects (ITSC 2005): Explore its surfacing potential!, The Material Information Society, Basel, Switzerland, 2–4 May 2005; pp. 1027–1031.
3. Parco, M.; Zhao, L.; Zwick, J.; Bobzin, K.; Lugscheider, E. Investigation of particle flattening behaviour and bonding mechanisms of APS sprayed coatings on magnesium alloys. Surf. Coat. Technol. 2007, 201, 6290–6296. [CrossRef]
4. Wang, H.; Liu, Y.; Ning, X.; Wang, Q.; Wang, F.; Chen, D. Oxidation of Ni-based single crystal after grit-blasting during exposure at high temperature. Mater. High Temp. 2017, 34, 215–221. [CrossRef]
5. Kubatik, T.F.; Pala, Z.; Neufuss, K.; Vilémová, M.; Mušálek, R.; Stoulil, J.; Slepčička, P.; Chráska, T. Metallurgical bond between magnesium AZ91 alloy and aluminium plasma sprayed coatings. Surf. Coat. Technol. 2015, 282, 163–170. [CrossRef]
6. Jia, D.; Yi, P.; Liu, Y.; Sun, J.; Yue, S.; Zhao, Q. Effect of laser textured groove wall interface on molybdenum coating diffusion and metallurgical bonding. Surf. Coat. Technol. 2021, 405, 126561. [CrossRef]
7. Matejicek, J.; Sampath, S. Intrinsic residual stresses in single splats produced by thermal spray processes. Acta Mater. 2001, 49, 1993–1999. [CrossRef]
8. Tian, J.J.; Yao, S.W.; Luo, X.T.; Li, C.X.; Li, C.J. An effective approach for creating metallurgical selfbonding in plasma-spraying of NiCr-Mo coating by designing shell-core-structured powders. Acta Mater. 2016, 110, 19–30. [CrossRef]
9. Jiang, X.; Wan, Y.; Herman, H.; Sampath, S. Role of condensates and adsorbates on substrate surface on fragmentation of impinging molten droplets during thermal spray. Thin Solid Film. 2001, 385, 132–141. [CrossRef]
10. Mcdonald, A.; Moreau, C.; Chandra, S. Effect of substrate oxidation on spreading of plasma-sprayed nickel on stainless steel. *Surf. Coat. Technol.* 2007, 202, 23–33. [CrossRef]

11. Yang, K.; Fukumoto, M.; Yasui, T.; Yamada, M. Role of substrate temperature on microstructure formation in plasma-sprayed splats. *Surf. Coat. Technol.* 2013, 214, 138–143. [CrossRef]

12. Lugscheider, E.; Dicks, R.; Kowalsky, K.; Cook, D.; Nassenstein, K.; Verpoort, C. A materials system and method of its application for the wear protection of aluminium engine cylinder bore surfaces. In Proceedings of the 2004 International Thermal Spray Conference, Osaka, Japan, 10–12 May 2004.

13. Wang, S.P.; Wang, G.X.; Matthys, E.F. Melting and resolidification of a substrate in contact with a molten metal: Operational maps. *Int. J. Heat Mass Transf.* 1998, 41, 1177–1188. [CrossRef]

14. Fauchais, P.L.; Heberlein, J.V.R.; Boulos, M.I. Powders, Wires, Cords, and Rods. In *Thermal Spray Fundamentals*; Springer: New York, NY, USA, 2014.

15. Kromer, R.; Cormier, J.; Costil, S. Role of powder granulometry and substrate topography in adhesion strength of thermal spray coatings. *J. Therm. Spray Technol.* 2016, 25, 933–945. [CrossRef]

16. Li, H.; Wei, Y.; Qu, H.; Lin, J.; Fu, H. Method and Device for Preparing Apherical Metal Powder by Hot Wire Assisted Plasma Arc. China CN110919017A, 27 March 2020.

17. Merz, R.; Prinz, F.B.; Ramaswami, K.; Terk, M.; Weiss, L.E. Shape deposition manufacturing. In Proceedings of the 1994 International Solid Freeform Fabrication Symposium, Austin, TX, USA, 1 August 1994; pp. 1–8.

18. Ang, A.S.M.; Berndt, C.C. A review of testing methods for thermal spray coatings. *Int. Mater. Rev.* 2014, 59, 1743280414Y.0000000029. [CrossRef]

19. Mann, A.B. *Surfaces and Interfaces for Biomaterials*, 1st ed.; Woodhead Publishing: Cambridge, UK, 2005.

20. Sasmai, S.; Anoop, M.B. *Nanotechnology in Eco-Efficient Construction*, 2nd ed.; Woodhead Publishing: Cambridge, UK, 2019.

21. Mcdonald, A.; Moreau, C.; Chandra, S. Estimating the Thermal Contact Resistance between Plasma-Sprayed Molybdenum and Metal Surfaces. In Proceedings of the 3rd International Conference on Spray Deposition and Melt Atomization, Bremen, Germany, 4–6 September 2006.

22. Ageorges, H.; Fauchais, P. Oxidation of stainless steel particles with and without an alumina shell during their flight in a plasma jet. *High Temp. Mater. Processes* 2000, 16, 6. [CrossRef]

23. Wang, B.; Wang, L.; Feng, Z.W.; Cheng, Y.X.; Zhang, C.G. Effect of processing parameters on adhesion strength of arc sprayed NiAl coating. *Therm. Spray Technol.* 2014, 6, 50–55.

24. Wang, J.X.; Liu, J.S.; Zang, L.Y.; Sun, J.F.; Wang, Z.P. Microstructure and mechanical properties of twin-wire arc sprayed Ni-Al composite coatings on 6061-T6 aluminum alloy sheet. *Int. J. Miner. Metall. Mater.* 2014, 21, 469–478. [CrossRef]

25. Raimonda, L.; Olegas, Č.; Jelena, Š.; Darius, Z.; Rimvydas, S.; Regina, K.; Valentin, A. The effect of Al-Mg substrate preparation on the adhesion strength of plasma sprayed Ni-Al coatings. *Surf. Coat. Technol.* 2017, 316, 93–103.

26. Mahesh, R.A.; Jayaganthan, R.; Prakash, S. Microstructural characterization and hardness evaluation of HVOF sprayed Ni–5Al coatings on Ni- and Fe-based superalloys. *J. Mater. Processing Technol.* 2009, 209, 3501–3510. [CrossRef]

27. Cai, X.; Feng, P. Reaction mechanism and oxidation resistance at 700–900 °C of high porosity NiAl intermetallic. *Corros. Sci.* 2021, 191, 109731. [CrossRef]

28. Gxowa-Penxa, Z.; Daswa, P.; Modiba, R.; Mathabathe, M.N.; Bolokang, A.S. Development and characterization of Al–Al3Ni–Sn metal matrix composite. *Mater. Chem. Phys.* 2021, 259, 124027. [CrossRef]

29. Martín, J.W.; Doherty, R.D.; Cantor, B. *Stability of Microstructure in Metallic Systems*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1997; pp. xv–xvi.

30. Yu, W.; Hao, Q.; Fan, L.; Li, J. Eutectic solidification microstructure of an Al–4Ni–2Mn alloy. *J. Alloy. Compd.* 2016, 688, 798–803. [CrossRef]