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Adhesion of titanium coatings applied by cold spraying on selected metal substrates

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ABSTRACT

Purpose: Measurement of the adhesion of a Ti coating applied by cold spraying on metal substrates with different elastic modulus. An attempt to analytically describe the experimental results, considering cold gas spray parameters such as working gas, pressure p and temperature T.

Design/methodology/approach: Ti coating was sprayed on flat bars made of metal: copper, magnesium, brass, titanium, Al 7075, Al 2024 and steel with dimensions of 4x50x400 mm. All coatings were applied under the same spray conditions (p = 3.8 MPa, T = 800°C, spray distance l = 50 mm, and spray spead V = 400 mm/s). The state of plastic deformation of coatings and substrates was examined using optical methods, and the adhesion strength was measured with the POSITEST tester.

Findings: The experimental results are presented graphically. The adhesion force as a function of the relative modulus of elasticity showed a maximum. At this time, the mutual penetration depth of the coating and the substrate showed a minimum. The extremes of the relationships mentioned above occurred for points where the relative modulus of elasticity took the value one. The curve described by formula (1) was fitted to the distribution of adhesion points as a function of the relative elastic modulus. The function parameter described by formula (1) is related to the spray parameters (p, T).

Research limitations/implications: To achieve a better accuracy of the analytical description of the adhesion of coatings deposited with cold gas, tests should be carried out on a larger number of substrates. The validity of the presented interpretation should be checked by applying coatings from other materials.

Practical implications: In coating technologies, adhesion is a key concept. A coating with high adhesion strength is used primarily in regeneration and anti-corrosion protection processes. The analytical relationship between adhesion, relative modulus of elasticity and cold gas spray parameters will significantly speed up the selection of optimal spray parameters. Cold spray technology is a cost-intensive technology, so the economic element is not without significance.

Originality/value: The article presents a method for limiting the number of variables on which the quality of the applied coatings depends. The relationship between the adhesion force, the relative elastic modulus and the selected spray parameters are indicated.

Keywords: Cold spray, Adhesion, Coating, Elastic modulus, Hardness, Plastic deformation

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PROPERTIES

1. Introduction

The preparation and application of protective or regenerative coatings are crucial in determining adhesion values. The effectiveness of coatings hinges on their ability to adhere to the substrate. In cold gas spraying, coating formation relies entirely on the kinetic energy of the impacting particles [1]. To achieve it, the velocity of the particles upon impact must surpass a critical threshold, which depends on particle size and the properties of the sprayed material [2]. Typically ranging in size from 5 to 80 μm, particles are introduced into the high-pressure gas carrier system, where they are accelerated to supersonic speeds. Upon passing through the de Laval nozzle, they impact the substrate. Additionally, in the research equipment, it is possible to heat the gas to further enhance the kinetic energy of the particles [3]. The formation of a coating film results from extensive plastic deformation of impacting particles and associated phenomena at the interfaces of the particle/substrate or particle/deposit.

The adhesion mechanism involves highly intricate issues encompassing various disciplines, such as polymer and surface chemistry, physics, fracture mechanics, mechanics of materials, and other fields [4-8]. The literature also noted that adhesion is influenced by other factors, including diffusion, mechanical properties, molecular characteristics, and chemical and thermodynamic aspects [9,10]. The study primarily focuses on determining adhesion values in conjunction with the modulus of elasticity of both the substrate and coating.

2. Materials and methodology

The adhesion of the resulting coating is influenced by various factors, including but not limited to the shape and size of grains, the velocity of powdered material particles, the hardness and elastic modulus of both the substrate and coating material, the shape of the grains, the pressure of the carrier gas, the distance between the spray gun and the substrate, the speed at which it moves, the substrate temperature, the gas temperature, the substrate surface condition, the spray angle relative to the sample's normal surface, and properties such as grain hardness and elasticity modulus, among other potential variables.

Titanium was selected as the coating material, with powder grains having a spherical symmetry. The particle size distribution of the Ti powder was determined as d_{10} = 15 μm, d_{50} = 31.5 μm, and d_{90} = 59.9 μm.

The cold spray process was used to apply titanium coatings onto metal substrates. The coatings were sprayed onto metal substrates with different elastic modulus (E) values: copper, titanium, brass, magnesium, steel, Al7075, and other aluminium alloys. The specific values of the modulus of elasticity (E) can be found in Table 1. The prepared substrates took the form of flat plates measuring 4 x 50 x 400 mm and were grit-blasted immediately before the coating application.

The surface of the substrate was shot-blasted with medium corundum sand, size 30 (medium shot-blasting). As mentioned above, adhesion depends on many variables influencing its value, e.g., temperature, pressure, spray distance, spray gun speed, etc. The study investigated the relationship between individual variables influencing the adhesion value. Principal Component Analysis (PCA) was employed to reduce the number of variables, and the results are depicted in Figure 1. All coatings were applied under the same spraying conditions. An analysis of the interdependencies among the factors affecting adhesion was conducted, and their quantity was restricted to four factors, which were managed during the experiment. Based on the PCA analysis and our own experience, we chose to focus on four key factors: pressure (p), temperature (T), spray distance (l), and spray speed (V). Figure 1 shows a strong correlation between hardness (H) and the modulus of elasticity (E). Therefore, our subsequent research examined the impact of the modulus of elasticity (E) of both the coating and substrate on the adhesion force values.

Table 1.
Adhesion, nanohardness and Elastic Modulus (E) of Grit-Blasted Substrates

Substrate	H, GPa	E, GPa	Adhesion, MPa	Penetration, mm
Copper	0.25 ± 0.05	120.0 ± 8.0	49.10 ± 0.90	34.8 ± 0.7
Magnesium	0.26 ± 0.07	1.0 ± 0.1	30.54 ± 1.30	40.8 ± 0.9
Brass	0.80 ± 0.07	110.0 ± 7.5	39.92 ± 0.90	25.8 ± 0.5
Titanium	1.61 ± 0.11	150.0 ± 8.0	41.83 ± 1.00	22.9 ± 0.5
Al 7075	1.95 ± 0.13	155.0 ± 9.0	43.91 ± 1.10	40.5 ± 0.7
Al 2024	2.32 ± 0.13	175.0 ±11.0	42.39 ± 1.50	29.5 ± 0.8
Steel	4.53 ±0.14	210.0 ± 7.6	41.58 ± 1.20	33.8 ± 0.7

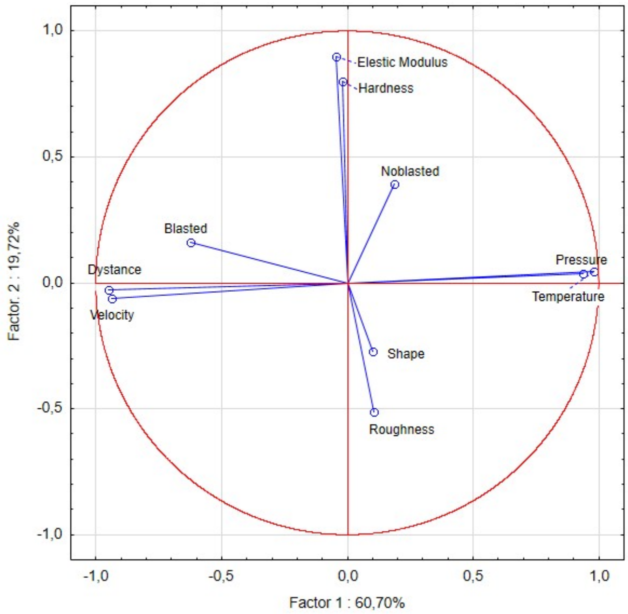


Fig. 1. Projection of variables on the plane of factors (1x2). Confidence level 80.42%

The next group in Figure 1 comprises pressure p and temperature T. The fundamentals of thermodynamics demonstrate a strong connection between p and T in closed systems. In the context of cold gas spraying, the gas is heated near the de Laval nozzle. An increase in temperature causes an increase in pressure, thus leading to an acceleration in the speed of the particles that compose the coating. Considering the available equipment and the interpretation possibilities, it was decided to control both pressure p and temperature T. Independent parameters influencing the adhesion forces include whether grit-blasting was performed on the substrate, as well as the shape of the grains and the roughness of the substrate. Confidence in the presented interpretation stands at 80.42% (PCA), calculated as the sum of two factors: 19.72% and 60.70%. In summary, the spray parameters were set as follows: pressure p = 3.8 MPa, temperature T = 800°C, spray distance l = 50 mm, and spray speed V = 400 mm/s — a mixture of 90% N_2 and 10% He was used as the working gas.

Titanium powder was deposited on the substrates using an Impact Innovations 5/8 system with a Fanuc M-20iA robot.

The adhesion of the coatings was determined as the force needed to detach a handle with a diameter of 14 mm from the tested coating. The research was carried out using a Positest AT-A. Two-component Loctite LT9466 resin bonded the samples together. The tests were repeated three times for each set of samples.

Nanohardness H and elastic modulus E were measured using the NANOVERA tester.

The visualisation of the connection between the coating and substrate was assessed using optical methods with a NIKON ECLIPSE MA 200 microscope.

3. Description of achieved results of own research

The adhesion values of the coating were analysed, considering both the elastic modulus (E) of the substrate and coating. The tests also considered mechanical bonding by measuring the degree of penetration between the substrate and coating. Table 1 displays the average adhesion and mutual penetration values obtained from the three measurements. The method for measuring the mutual penetration of the substrate and coating is illustrated in Figure 2. The same figure also demonstrates the application of a titanium coating on an Al2024 substrate and brass, serving as an example.

Figure 3 depicts adhesion and penetration (resulting from plastic deformation) as a function of the elastic modulus (E) of the substrate relative to that of the coating. The approach aids in interpreting the results, with a value of one corresponding to the E of titanium.

In Figure 3a), we can observe an increase in the coating adhesion up to a value of 49.1 MPa for copper. As the relative value of E increases, adhesion decreases, reaching 41.58 MPa for steel. The maximum adhesion is observed when the elastic modulus of the substrate is equal to that of the coating. The research confirms the work results on the adhesion of cold gas-sprayed coatings [11,12]. The bond strength depends on the properties of the substrate, both in terms of mechanical properties and surface properties.

Regarding coating materials, ductile substrates that can provide significant plastic deformation upon impact often result in higher adhesion values. Similar research results were presented by Bruera A. et al., where extreme adhesion was observed related to the type of substrate [11] or [13]. The most frequently used technique to measure its adhesion is known as Tensile Adhesion Testing (TAT) [14,15].

Comparing the results with the penetration data presented in Figure 3b), we observe that the penetration is the lowest where the adhesion is the highest. Therefore, it can be considered that the adhesion value increases for a relative E equal to 1. It means that the bond resulting from plastic deformation is strengthened. So far, although much research has been conducted in this field, the adhesion mechanism is still unclear. It is due to the complexity of the cold gas spraying process and many parameters with varying importance in the bond formation process [15-17].

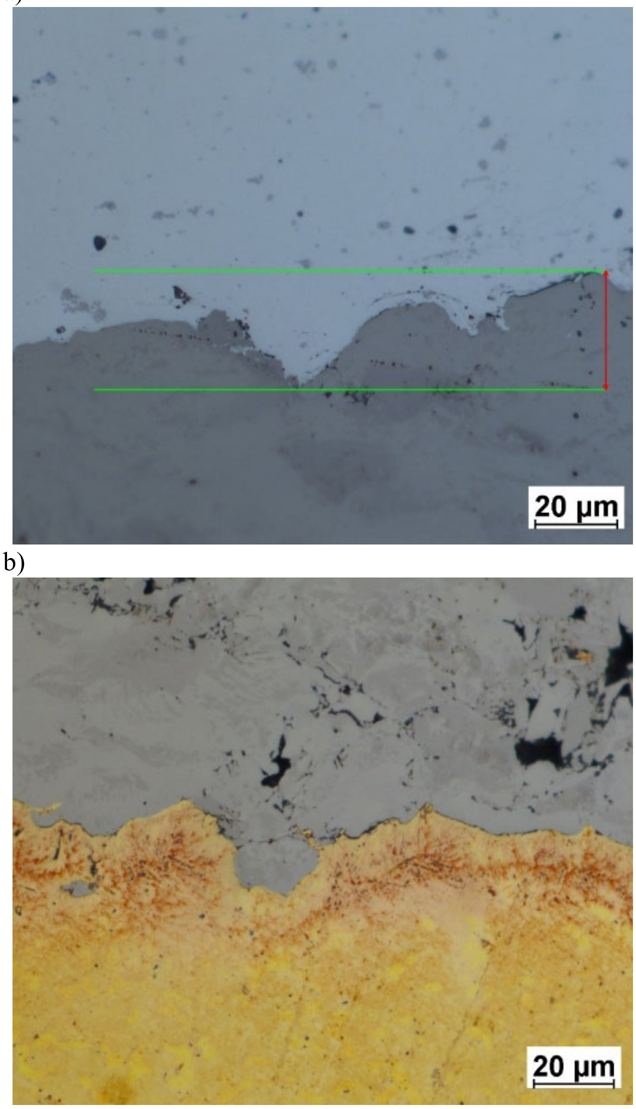
a)
b)


Fig. 2. Method of measuring penetration for an Al2024 substrate and an example of penetration on a brass substrate

An attempt was made to generalise the dependence of adhesion on the elastic modulus of both the substrate and coating. The test is limited to metal substrates and titanium coatings applied by cold gas spraying.

The shape of the adhesion curve shows the existence of a maximum depending on the E of the coating, the E of the substrate and the spray parameters, i.e., temperature T and spray pressure p.

A curve with parameters related to cold spraying was fitted to the experiment results. The essence of the attempt to analytically evaluate adhesion in cold spraying is the ability to estimate adhesion before the experiment by

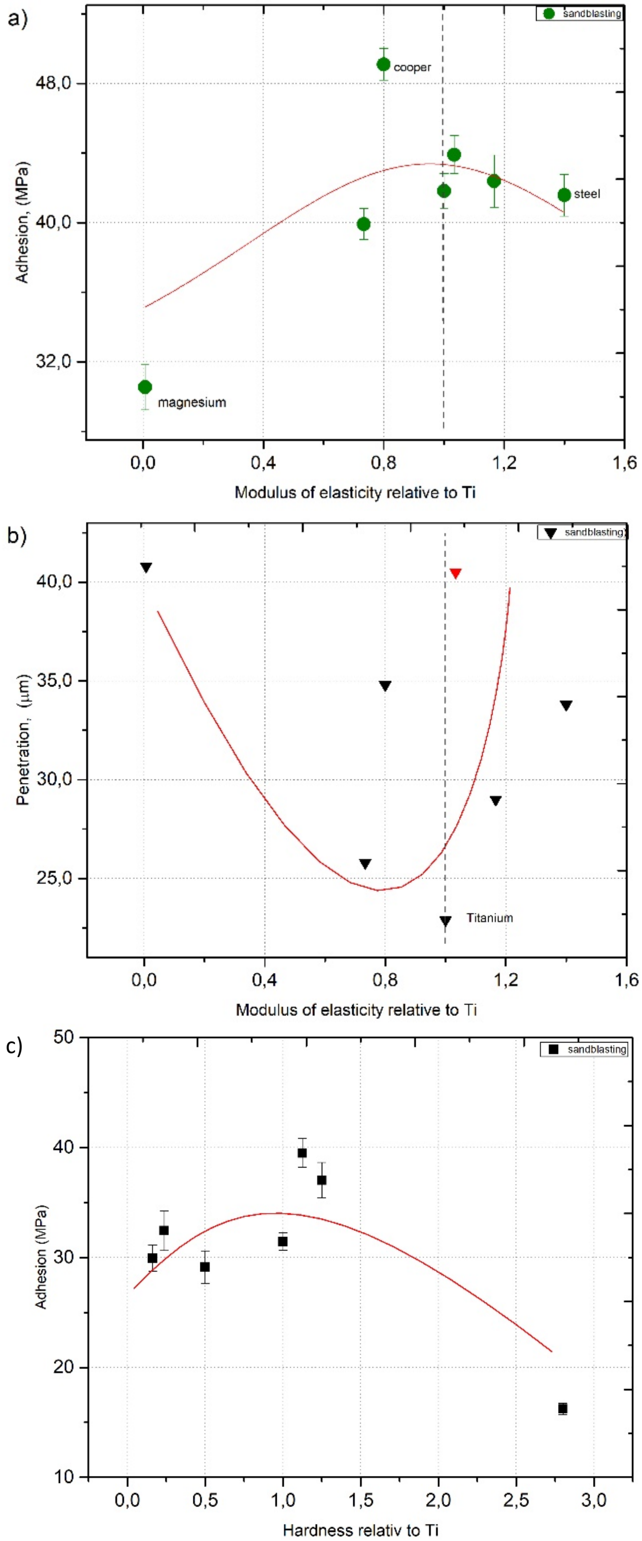


Fig. 3. The relationship between the values of adhesion and penetration vs. elastic modulus and nanohardness

selecting the appropriate values of spray parameters for the materials used. In equation (1), x represents the relative modulus of elasticity of the substrate relative to the coating. Considering the results of the PCA analysis, hardness analysis will be equally effective.

$$A(z) = a_0 + \frac{Kexp(-z)}{(1+exp(-z))^2} \tag{1}$$

$$z = \frac{x-x_c}{w} \tag{2}$$

where: a_0 – constant, ω – curve shape factors, x_c – value of the elastic modulus of the coating (centre of symmetry), x – value of the relative elastic modulus calculated in relation to the E value of the coating material (Ti). The curve factor K relates to the temperature and pressure of the cold gas spraying process.

For the adhesion data, functions (1) were fitted and marked (Fig. 3a) with a line. The K value is 80.58 ± 41.34, x_c = 0.948 ± 0.131, w = 1.082 ± 0.034. The fit is not fully satisfactory due to the large error of the K value. A rough estimate of the K function is the equation

$$K = 4*T/p \tag{3}$$

As seen from the K error, the proposed formula requires further experiments. The error value may result from the scattering of points visible in Figure 3b and is related to the penetration of titanium particles into the Al7075 substrate. The point related to penetration into copper also deviates from the course of the function.

Hardness is one of the basic factors influencing the connection quality between the metal coating and the metal substrate [14, 18-20]. The results of adhesion tests as a function of substrate hardness are presented in Figure 3c. The presented function is described by equation (1). The curves in Figure 3a and Figure 3c show extremes. The experiment was carried out at a temperature below the phase transitions, so the dominant bond is the mechanical bond. The presence of extreme adhesion was described in the work of Bruer et al., emphasising surface roughness. Fitting the function (1) allows the calculation of the function K(T, p). The function calculates T and p as cold gas spray parameters (3).

4. Conclusions

The adhesion test of a coating made of spherical titanium on metal substrates with different elastic modulus values was carried out.

1. The obtained results revealed a linear dependence of adhesion and mutual penetration on the elastic modulus of the coating.
2. Adhesion reached its maximum values when the elastic modulus of the substrate was close to that of the coating.
3. Mutual penetration related to the plasticity of materials had the lowest values when the modulus of elasticity of the substrate and coating had similar values. For these values, adhesion had the highest value.
4. The analysis of the above research leads to the conclusion that in the process of cold spraying titanium coatings on metal substrates, adhesion reaches the highest values for the nanohardness of the substrate, and the modulus of elasticity has values close to H and E of the coating material.
5. The attempt to find an analytical relationship between adhesion and the elasticity modulus E and H led to the presentation of formula (1). The analytical connection of adhesion with the modulus of elasticity (nanohardness) will make it possible to find the adhesion extreme depending on the pressure and temperature of the cold gas spraying process of metals.

Additional information

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