

Effect of Substrate Properties on the Adhesion Strength of Cold Sprayed TiO₂ on Annealed SUS304 at Low Temperature

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Abstract: Titanium dioxide is the most studied functional ceramic due to its wide range of applications, chemical stability and low cost. One of the most promising properties of TiO₂ is its photocatalytic activity. However, due to the phase transition, it is difficult to produce high-performance photocatalytic TiO₂ coatings by conventional thermal spraying. In previous studies, it was possible to produce pure TiO₂ coatings by a cold spray process. However, the details of the deposition mechanism still need to be clarified. The purpose of this study is to investigate the effect of substrate properties on the adhesion of cold-sprayed TiO₂ layers. Experiments were performed at various substrate annealing temperatures using stainless steel SUS304. Separately, tensile bond strength, substrate hardness, substrate surface oxide, and interfacial microstructure were evaluated for the bonding mechanisms involved.

Keywords: *Titanium dioxide, ceramic cold spray, adhesion strength, bonding mechanism*

1. Introduction

From a worldwide perspective of various research domains, attention has been attracted by the reduction of environmental pollutants. The industrial world and the researcher community are being challenged by the advancement of materials with the ability to guarantee safe surroundings; furthermore, photocatalysis is now a principal means of attaining satisfactory depollution standards. Moreover, competitors of this procedure gain some benefits as oxidation agents are not required. Since nanostructured TiO₂-anatase coatings have an extensive active surface and

chemical stability, and are at a comparatively reasonable cost, they are utilized as functional material [1]. The crystalline framework of TiO₂ has a major impact upon its photocatalytic performance where TiO₂ in anatase stage supplies greater photocatalytic activity than in its rutile stage. At temperatures exceeding 900°C, which is above the melting point of TiO₂ (1908°C), the anatase stage irreversibly changes into the rutile stage. At temperatures above the melting point of TiO₂, the deposition of molten or semi-molten droplets form thermal-sprayed coating, meaning that it is impossible to avert the phase transformation of TiO₂ in thermal spray procedures [2].

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Otherwise, you don't need to melt the material for cold spray. As a result, such techniques can avoid unwanted phase transitions [1]. During this procedure, small particles ranging from 1 to 50µm are stimulated by a stream of supersonic gas at a temperature below the material's melting point, leading to the production of coating formation from the solid state particles in which the bonding of microparticles, severe deformation and high-velocity impact cause material deposition. The procedure of deposition is entirely dependent upon particle kinetic energy instead of the integration of kinetic and thermal energy. Consequently, there will be no residual stress or oxidation in the course of the deposition procedure. Bonding mechanism is dependent upon converting the particles' kinetic energy in order to produce either particle-substrate or particle-particle bonding. It is essential that a particle's kinetic energy and each particle's momentum are converted into different types of energy through mechanisms; for example, plastic deformation for particle and substrate interactions involving the initial particle as well as particle-particle interactions during the building of coating, particle-particle rotation, strain, void consolidation, and eventually, heat [3-4].

Many exploratory works recently concentrated upon the impact of surface temperature and substrate preheating upon the deposition procedure in the case where cold spraying was applied. According to Fukumoto et al. [2], a long spraying time and high gas temperature could cause the substrate temperature to increase, thereby enhancing the effectiveness of the deposition. Furthermore, Legoux et al. [1] observed that the substrate temperature is increased by substrate preheating, causing coating formation and particle deformation. Shuo Yin et al. [5] observed that with sufficiently long spraying time, the substrate surface temperature can reach its maximum and substrate preheating perform its optimal functions. Moreover, Watanabe et al. [6] stated that substrate heating eases thermal stress, thereby resulting in improved coating adhesion. It was shown by Arabgol et al.[7] that the application of substrate preheating and lower thermal effusivity substrates can lead to a considerably enhanced quality of cold-sprayed deposits up to a millimetre thick. Nevertheless, all of the exploratory work aforementioned concentrated upon the impact of substrate

preheating upon the cold-sprayed deposition procedure, utilizing feedstock materials such as aluminum and copper. This procedure has effectively sprayed this ductile material as a result of its own plastic deformation. Otherwise, it has been regarded as being difficult for brittle substances like ceramics to be deposited by the cold-spray procedure [2]. This study indicates how TiO₂ was cold-sprayed upon annealed substrate and the coating's adhesion strength associated with substrate properties was considered, involving properties such as surface oxidation and hardness upon stainless steel substrate.

2. Methodology

2.1 Cold spray process

We applied a commercially available cold-spray technique (CGT KINETIKS 4000; Cold Gas Technology, Ampfing, Germany) to all of the coating experiments. High-pressure nitrogen gas is used not only for the process itself, but also for the powder carrier gas. A De-Laval custom-made 24TC nozzle was used to heat and accelerate the process gas and to inject the feedstock powders into the spray nozzle through a high-pressure powder feeding technique having a calibrated powder feeder rate. We oversaw the gas pressure and temperature and maintained the system by a sensor. Table 1 shows the cold spray conditions.

Table 1: Cold spray conditions.

Powder	TiO ₂ : 20µm
Substrate	SUS 304
Substrate temperature	RT, 100°C, 200°C, 300°C, 400°C
Working gas	Nitrogen
Gas pressure	3 MPa
Gas temperature	500°C
Spray distance, mm	20
Traverse speed, mm/s	10

2.2 Material

As a feedstock, we applied TiO₂ powder (TAYCA, Okayama, Japan) containing pure anatase crystalline structure. Figure 1 illustrates the morphology of powder particles. The Microtrac Particle Analyzer measures the average size of a powder particle as 20µm. For a substrate, we utilized stainless steel SUS304 having a dimension of Ø25mm x 10mm. We used an electric furnace to preheat the grit-blasted substrate to four different temperatures: 100°C, 200°C, 300°C and 400°C respectively, the increment being 15°C/5 minutes, and after a five-minute soaking it was cooled in the furnace to room temperature.

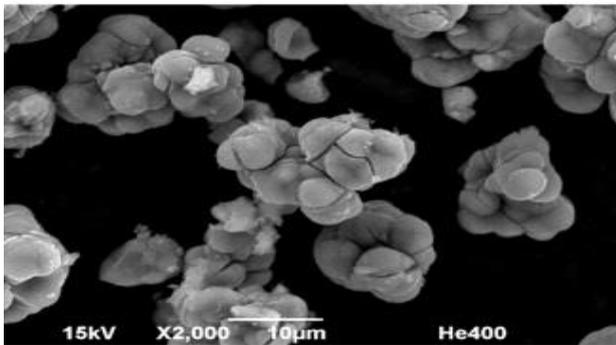


Figure 1. TiO₂ powder

2.3 Coating evaluations

Scanning electron microscope (SEM:JSM-6390, JEOL, Tokyo, Japan) was used to observe the cross-sectional microstructure of the coating.

Based on JIS H 8402, a test piece of Ø25mm x 10mm was used to evaluate the coating film adhesion strength, and the breaking load value measured with a universal tester (Autograph AGS-J 10kN Shimadzu Corporation) was divided by the cylindrical coating film, expressed as a value range. A strong epoxy-based adhesive bonded the pin and the coating (Huntsman Advanced Materials Company:

Aralkyl standard). A strength test was performed after the adhesive had cured for 24 hours. Adhesion strength was determined by averaging 5 samples for each spray condition.

2.4 Substrate evaluations

The substrates' surface oxidation for SUS 304 were under five different conditions. An X-ray Photoelectron Spectroscopy (XPS: Quantera SXM-CI, ULVAC-Phi,Inc.) was used to measure room temperatures and temperatures of 100°C, 200°C, 300°C and 400°C. The substrates were rinsed with acetone before testing.

An HMV-G micro Vickers hardness tester (Shimadzu Corporation) was used to measure the microhardness of the substrates. The measurement showed a hardness of HV 0.01 and the test load on the cross section was 98.07mN. We acquired the micro-hardness value by an average of five points per substrate conditions for SUS304.

3. Results and Discussion

3.1 Influence of annealed substrates on adhesion strength

Figure 2 illustrates the adhesion strength for titanium dioxide coating on annealed stainless steel SUS304. It showed an increasing trend from 0.36MPa to 1.55MPa with an increasing substrate temperature from 100°C to 400°C. This figure shows that the substrate pre-heating improves the adhesion strength in hard material such as SUS304. The EDX mapping in figure 3 showed a small part of ferum substrate is embedded on the TiO₂ coating.

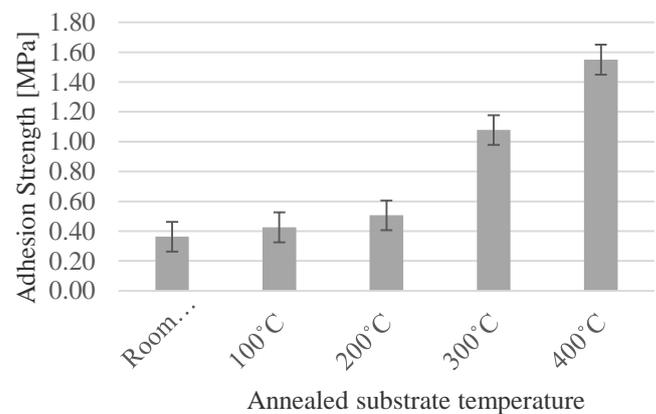


Figure 2. Coating strength of the TiO₂ on annealed SUS304.

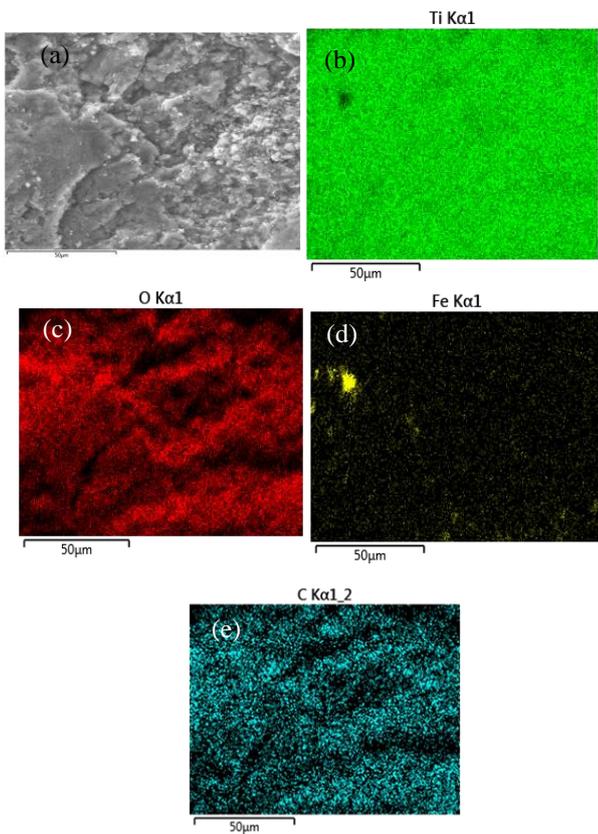


Figure 3. EDX elemental mapping of TiO_2 /annealed SUS304 fracture coating (a) SEM (b) Titanium (c) Oxygen (d) Ferum (e) Carbon.

3.2 Titanium dioxide coating microstructure on annealed SUS304

Figure 4 depicts the TiO_2 coating cross-section area on stainless steel 304 for various substrate temperatures. Almost every figure depicted a dense coating with a thickness in the range of 200 μm to 300 μm , showing that a critical velocity has been reached. We can categorise the cold-spray procedure into two stages, and the coating formation in this procedure is shown in the schematic diagrams in Figure 5. The first step, adhesion or formation of an interface between the substrate and the particle.

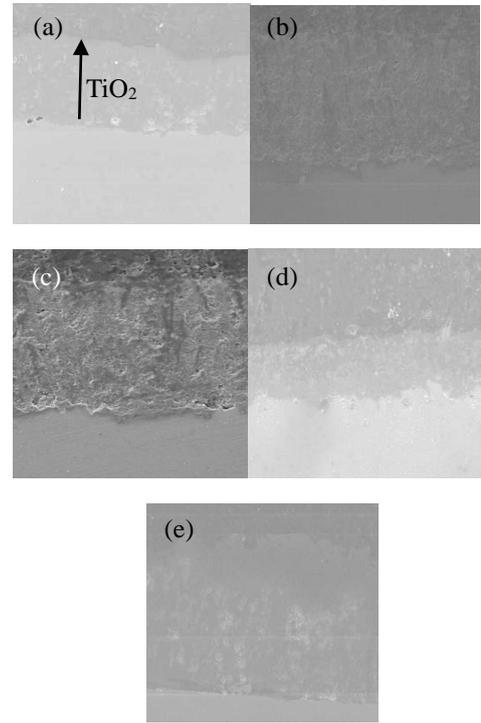


Figure 4. Cross-sectional microstructure of titanium dioxide coating on SUS304 (a) RT (b) annealed at 100°C (c) annealed at 200°C (d) annealed at 300°C (e) annealed at 400°C.

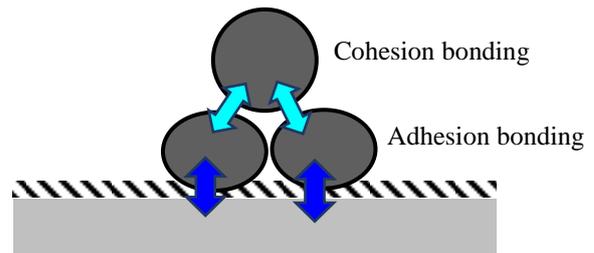


Figure 5. Schematic diagram of coating formation in cold spray

The annealed substrates can apparently implement this stage, which forms the first coating layer, particularly for hard material, SUS 304 to bond with the substrate. The cohesion between the particles and coating growth upon the first layer is the second stage.

The annealed temperature substrate in this study was below the process gas temperature. It appears that the substrate conditions like temperature had minimal impact on the cohesion procedure.

It is necessary for the entire particle's kinetic energy to be changed into heat and to strain energy to the substrate or coating if a particle is to adhere. This needs an inelastic procedure such as: plastic deformation of substrates or particles, grain deformation, particle rotation, void consolidation and suchlike. The coating is built by using momentum and kinetic energy from the incoming high-velocity particles as they affect deposit particles.

3.3 Vickers Microhardness

A small change from 297HV to 329.8HV with an increase in substrate temperature was shown by SUS 304 in figure 6. Changes in stainless steel substrate hardness are less conspicuous, probably because re-crystallization within stainless steel should happen at slightly over 500°C being 0.4 times the melting point, with the surface temperatures being less than these typical temperatures. As hard substrate but coating adhesion strength showed an increased trend, therefore substrate deformation that may lead to mechanical interlocking or metallurgical bonding mechanism seems difficult to occurs.

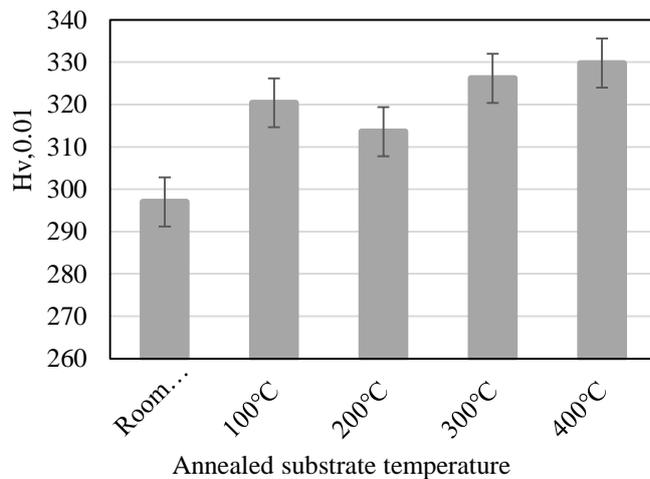


Figure 6. Annealed hardness of SUS 304.

3.4 Depth profile of the oxide layer

An atomic concentration upon the substrate which was annealed from room temperature to 400°C through depth

direction analysis by utilising XPS for stainless steel is indicated in figure 7 below. The measurement indicated the variation in oxygen content increment by depth direction analysis according to the material. In the case of hard material, SUS304, the oxygen content increased with depth direction analysis of annealed substrate from room temperature to 400°C. This indicates a thicker in the oxide layer thickness.

Coating adhesion strength showed an increasing trend and it have a good agreement with oxide thickness. Based on the result, 3 elements present in the oxide; Ferum, Oxygen and Chromium. Which element influence directly toward coating adhesion strength and how it bonding mechanism is still unclear and further investigation is needed.

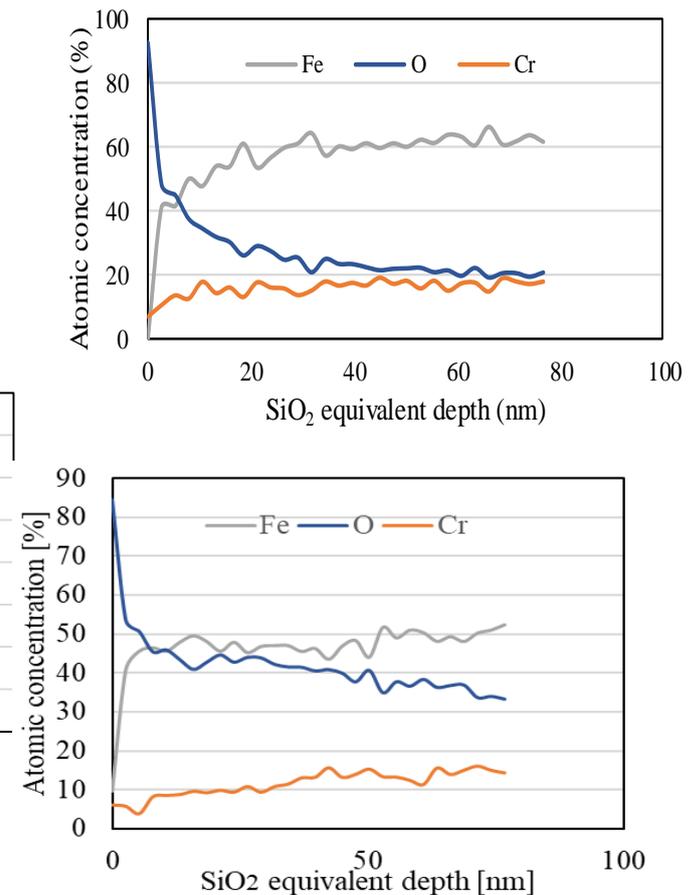


Figure 7. Depth profile analysis of SUS 304 (a) room temperature (b) annealed at 400°C.

4. Conclusion

We examined the impact of substrate properties upon cold-sprayed TiO₂'s adhesion strength on stainless steel and through annealed substrate properties in an electric furnace, ranging from room temperature to 400°C respectively. We summarize the outcomes attained in this study as follows:

1. Substrate hardness properties: there was a tendency for SUS 304 are less conspicuous, probably as a result of negligible recrystallisation in stainless steel occurring at a temperature of slightly over 500°C.

2. Adhesion coating strength tendency which increased from 0.36MPa to 1.55MPa, as the substrate temperature also increased. This may contribute by element presents in oxide on substrate surface but further investigation is needed to confirm the trend.

5. Acknowledgement

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