On the role of substrate temperature into bonding mechanism of cold sprayed Titanium Dioxide

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Abstract. Metal oxide, Titanium dioxide, TiO₂ draw a huge attention due to its wide range of applications, chemical stability and low cost. TiO₂ coatings have potential applications in biomedical implants or as photo-catalytic functional systems. Cold spraying is a process where small particles ranging from 1 to 50μm are stimulated by a stream of supersonic gas at a temperature below material melting point and leading to the coating formed in solid state particles. The aim of the present study was to investigate the influenced of once heated substrate properties on bonding mechanism of cold sprayed Titanium dioxide, TiO₂. In this study, tensile adhesion strength, substrate hardness, oxide thickness, oxide composition and interfacial microstructure were evaluated for the coatings. The results of this study indicated that coating adhesion strength reveal a decreased trend from 1.35MPa to 0.49MPa when once heated substrate temperature is increased. Influenced of oxide thickness also will be discussed here as factor that contributed to bonding mechanism between TiO₂ and copper substrate.

1.Introduction

Cold spray that is also named as cold gas dynamic spray has drawn growing attention because of the specific ‘cold’ feature. In this process, powder particles are accelerated by a supersonic gas stream at a temperature that is lower than the melting point of the material, resulting in a coating formation from particles in a solid state. As a consequence, the cold sprayed coating can effectively eliminate the influence of thermal stress, severe oxidation, thermal phase transformation and other common problems associated with traditional thermal spray processes and distortion [1]. Therefore, cold spray has been broadly implemented for the fabrication of coatings for different applications, as well as a technology of additive manufacturing [2]. Presently, the most applicable theory of bonding mechanism in cold spray of metal is considered as the mechanical interlocking and metallurgical bonding. As a non-chemical reaction, the mechanical interlocking is formed due to intense plastic deformation of material under high-speed collision process [3,4]. The metallurgical bonding is considered a consequence from chemical reaction at the oxide-free interface between particles or particle/substrate [5-7]. Both of them are assumed to make a plastic deformation for both particle and substrate. Based on the bonding mechanisms, it is difficult to fabricate ceramic coating through cold spray process due to lack of its ductility. However, our group succeeded to fabricate Titanium dioxide (TiO₂) thick coating through cold spray process and its deposition mechanism were discussed [8-12].
Nanostructured TiO₂-anatase coatings draw a huge attention due to have an extensive active surface and chemical stability, and are at a comparatively reasonable cost, they are utilized as functional material. 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 impossible to avert the phase transformation of TiO₂ in thermal spray procedures [13] Otherwise, it is not necessary to melt the material in order to apply cold spraying. Consequently, such technology can avert the unwanted phase transformation [14]. It was enabled to fabricate TiO₂ ceramic coating by cold spray, the details of bonding mechanism have not been clarified yet. Our previous study described that the possibility of chemical bonding between the fractured agglomerated particles and the substrate [15]. K.Schmidt et al claim the plastic deformation of the substrate lead to a large continuous contact zone between TiO₂ particle and substrate and induced to a durable bonding[16]. M.Gardon et al reveal that titanium sub-oxide coating provided a necessary surface geometry and composition that favored the deposition of anatase particles, bonded by chemical interactions with the substrate [13]. Nevertheless, the role of substrate properties toward the bonding mechanism has not been discussed yet. The substrate properties such as hardness, roughness and oxide formation can be controlled by heat treatment of the substrate. The importance of substrate temperature on the cold spraying of metallic coating has already been reported, but the details of the mechanism even in the metal materials has not been clarified [17]. In this study, the effect of once heated pure copper substrate properties from room temperature to 400°C were carefully investigated toward the bonding mechanism of cold sprayed TiO₂.

2. Methodology

2.1 Cold spray process

We applied a commercially available cold-spray apparatus (CGT KINETIKS 4000; Cold Gas Technology, Ampfing, Germany) to all of the coating experiments. We utilized high-pressure nitrogen gas for the powder carrier gases as well as for the procedure itself. A De-Laval 24TC nozzle was used to accelerate the process gas and to inject the feedstock powders. In order to investigate the influence of the substrate conditions, we used same spray conditions for all experiments. Table 1 shows the cold spray conditions and figure 1 shows a schematic diagram of cold spray process.

| Working gas | Nitrogen |
|------------|----------|
| Gas pressure | 3 MPa |
| Gas temperature | 500°C |
| Spray distance, mm | 20 |
| Traverse speed, mm/s | 10 |
2.2 Materials

As a feedstock, we applied TiO$_2$ powder (TAYCA, Okayama, Japan) which has been succeeded to fabricate thick coatings by cold spray in our previous studies [8-12]. Figure 2 shows the morphology of the TiO$_2$ powder particles. The average particle size ($D_{50}$) is 7μm measured by a particle size analyser (SALD). For a substrate, we utilized pure copper, C1020 having a dimension of Ø25mm x 10mm. We used an electric furnace in air environment 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. The substrates were rinsed with acetone before they were sprayed.

![Diagram of Cold spray process](image1)

**Figure 1.** Schematic diagram of Cold spray process

![Morphology of TiO$_2$ feedstock powder](image2)

**Figure 2.** Morphology of the TiO$_2$ feedstock powder
2.3 Coating evaluations
A scanning electron microscope (SEM: JSM-6390, JEOL, Tokyo, Japan) was used to observe the coating’s cross-sectional microstructures.

2.4 Adhesion Strength
In accordance with JIS H 8402, specimens of dimensions of Ø25mm x 10mm assessed the coating’s adhesion strength which was given as the fracture load’s value as measured by a universal testing machine (Auto graph AGS-J 10kN Shimadzu) and subsequently divided by the cylindrical coating area. The epoxy-based strong adhesive bonded the pin and coating (Huntsman Advanced Materials Company: Aralkyl Standard). We conducted the strength test subsequent to curing the glue for a period of 24h. We acquired the adhesion strength with an average of five specimens for each of the spray conditions.

2.5 Substrate evaluations
An X-ray Photoelectron Spectroscopy (XPS: Quantera SXM-CI, ULVAC-Phi,Inc.) was used to measure compositional and chemical state analysis for 5 different substrates. The substrate conditions are room temperatures and once heated temperatures of 100˚C, 200˚C, 300˚C and 400˚C. We used an HMV-G micro-Vickers hardness tester (Shimadzu) to measure the substrates’ micro-hardness. We acquired the micro-hardness value by an average of five points per substrate conditions.

3. Results

3.1 Interfacial coating microstructure
Figure 3 depicts the TiO₂ coating cross-section area on pure copper, C1020 for various substrate temperatures. Almost every figure depicted a dense coating with a thickness in the range of 200μm to 300μm, showing that a critical velocity has been reached. Figure 2(a) to 2(e) show some degree of porosity was observed in pure copper substrate as well as crack between the coating at substrate especially on once heated substrate at 300˚C and 400˚C, shown by figure 2(d) and 2(e). We can categorize the cold-spray procedure into two stages. The adhesion or interface formation between substrate and particle is the first stage. The once-heated substrates can apparently implement this stage, which forms the first coating layer. The cohesion between the particles and coating growth upon the first layer is the second stage. The once-heated 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.

![Figure 3. Cross section microstructure of TiO₂ coatings on different once heated substrate temperature : (a) RT, (b) 100˚C, (c) 200˚C (d) 300˚C (e) 400˚C](image-url)
3.2 Adhesion strength

Figure 4 shows the adhesion strength of the coatings deposited onto different substrate conditions. The coatings which are sprayed upon the substrate at a temperature of 400°C in the course of specimen preparation peel off automatically; consequently, at this temperature the evaluation was not succeeded. The result indicates that the adhesion strength showed a reduced trend from 1.35MPa to 0.49MPa. Therefore, increasing the once heated temperature reduce the adhesion strength of cold-sprayed TiO\textsubscript{2} coatings on the copper substrate. Figure 5 shows fracture picture of cold sprayed TiO\textsubscript{2} coating onto once heated C1020 substrates after adhesion strength testing. It is confirmed the interface fracture occur between coating and substrate for pure copper substrates in all conditions as reveal by figure 5 (a) to 5(d).

![Figure 4](image)

**Figure 4.** Adhesion strength of cold sprayed TiO\textsubscript{2} coating onto once heated C1020 substrates

| Once heated substrate temperature | Adhesion strength [MPa] |
|----------------------------------|-------------------------|
| Room temperature                 | 1.59                    |
| 100°C                            | 1.28                    |
| 200°C                            | 0.75                    |
| 300°C                            | 0.59                    |
| 400°C                            | NA                      |

**Figure 5.** Fracture picture of cold sprayed TiO\textsubscript{2} coating onto once heated C1020 substrates after adhesion strength testing of (a) room temperature (b) 100°C (c) 200°C and (d) 300°C
3.3 Substrate hardness

Substrate hardness for room and once heated conditions are depicted in Figure 6. The hardness from room temperature to 300 °C was almost similar. On the other hand, the substrate once heated with 400°C exhibited lower hardness compared with other substrates. Thermal re-crystallization could cause the apparent reduction of the hardness. It is known that re-crystallization temperature about 0.4 times the melting point (copper is 1080 °C). Grains become coarser when they are heated to this temperature, and slow cooling in the furnace enables the alloy to develop larger grains, thereby supporting the reduction of hardness.

![Figure 6](image_url)

**Figure 6.** Once heated pure Copper hardness from room temperature to 400°C

3.4 Oxide thickness

Figure 7(a) to (e) shows the concentration as a function of depth of oxygen and copper in the substrates. Oxygen atomic concentration in the deepest part of the oxide layer, in the substrates, C1020, increases significantly as the annealing temperature increases from room temperature to 400°C. This indicate that the oxide layer of pure copper grows thicker as the annealing temperature of substrate increases where oxide thickness for pure copper at room temperature is approximately 20nm and increased to more than 90nm of annealed temperature 400°C.

![Figure 7](image_url)
(b) 100°C

(c) 200°C

(d) 300°C

Atomic concentration [%]

SiO₂ equivalent depth [nm]

Cu

O
3.6 Oxide composition

Result of through depth direction analysis by utilizing XPS for substrates is indicated in figure 8(a) and (b). Oxide layer formed on pure copper shown in figure 8(a) and (b) is Cu$_2$O for once heated substrate temperature 100°C and 200°C, while CuO for once heated substrate temperature 300°C and 400°C. The peak for Cu 2p3/2 in this study is 932.5 eV, indicated the presence of Cu$_2$O. The O1s peaks shown in figure 8 (b) are 530.3, 531.3 eV indicated the presence of Cu$_2$O and CuO and hydroxide species physically adsorbed on the Cu surface. The peak at 529.3 eV was the CuO sub-peak, when the Cu substrate contained two oxidized states, each Cu peak and corresponding O peak were detected [18].
Figure 8. XPS spectra of (a) Cu 2p3/2 and (b) O1s for C1020 from room temperature to 400°C

4. Discussion

Cold-sprayed TiO₂ coatings on the pure copper, (C1020) substrates revealed a decreased trend in adhesion strength from 1.35MPa to 0.49MPa for room temperature substrate to once heated substrate of 400°C. The adhesion strength value represent the adhesion bonding occurring between the first layer of TiO₂ coating and the surface of copper substrate. Referring to factors that we studied; substrate hardness, oxide thickness and oxide composition, some of these factors may pronounce to bonding mechanism of cold-sprayed TiO₂ onto pure copper substrate. Once heated substrate of pure copper from room temperature to 400°C revealed a decreasing trend of hardness due to re-crystallization effect by the heat treatment. In this situation, substrate become softer and easier to deform due to kinetic impact energy of the sprayed particles. If the main deposition factor is the mechanical anchoring, softer substrate should have an advantage for the adhesion strength. Nevertheless, the adhesion strength was decreased at higher heated temperature. It means that the mechanical anchoring is not the main bonding mechanism between the cold-sprayed TiO₂ coating and the copper substrate.

According to K.H.Ko et al the increasing of quantity of high oxidation state in copper feedstock can produce large amounts of rebounding particles which do not accumulate but tamping of the surface of the coating[18]. This condition maybe one of the explanation due to thicker oxide thickness at once heated substrate of 400°C and SEM images of picture 2(e) reveal a crack between particle/substrate. Thick oxide formation on the copper substrate prevented the bonding between the particle and the substrate. Figure 7(a) to (e) shown depth profile analysis of pure copper, C1020 result from X-Ray photoelectron spectroscopy. Oxide thickness is increased from 20nm on surface of room temperature C1020 to more than 90nm on surface of once heated 400°C. According to W.Ya Li et.al stated that the increasing of oxide film thickness, it will need more kinetic energy to break up and extrude the oxide film, thus a higher particle velocity is needed for bonding. In other words, the effective bonding area is decreased under the same particle impact conditions [19]. It could explain the decreased trend of adhesion strength of once heated substrate of pure copper from room temperature to 400°C, because the particle velocity was constant in all condition. Therefore, a chemical bonding between newly- formed pure copper and cold-sprayed TiO₂ particle can be the main factor on this process.
There is another possibility for the chemical bonding, which is cold-sprayed TiO₂ and surface oxide of copper substrate. The composition of copper oxide films that coexist two phases, cuprous oxide, Cu₂O and cupric oxide, CuO. According to G. Papadimitriou and al claim that at temperature up to 225°C, Cu and Cu₂O is formed while above this temperature only CuO forms[20]. Both Cu₂O and CuO phases existed on our substrate and it has been supported by O1s peak shown in figure 8(b). F.-H. Lu stated for solid state reaction between CuO-TiO₂, phase diagram of the CuO-TiO₂ system, the eutectic temperature is 900°C in air, therefore the sample will react each other due to eutectic reaction[21]. Referring to our spray conditions that involved gas temperature of 500°C and pressure at 3MPa, this condition is not reached up to eutectic temperature. Therefore, the oxide composition may not be the main factor that influences the adhesion strength in cold sprayed TiO₂ onto pure copper.

The metallurgical bonding is considered a consequence from chemical reaction at the oxide-free interface between particles or particle/substrate [5-7]. According to the results we obtained in this study, chemical bonding between cold-sprayed TiO₂ particle and newly formed copper substrate is considered be the main factor. Once heated temperature of 400°C decreased the hardness due to the recrystallization, however, thick oxide layer which prevent the bonding was formed and reduced the adhesion strength. Hence the bonding mechanism between cold-sprayed TiO₂ onto pure copper substrate can be explain with the chemical reaction which is similar with the cold spraying of metallic materials. Figure 9 shown a schematic diagram of factor that influenced toward adhesion strength of TiO₂ coating on substrate.

| Room temperature | Once heated substrate 400°C |
|------------------|-----------------------------|
| Cu₂O oxide       | Cold sprayed TiO₂ particles |
|                  | CuO oxide                   |
| C1020            | Cold sprayed TiO₂ particles |

**Figure 9.** Factor that influenced toward adhesion strength of TiO₂ coating on pure copper

5. Conclusions

The present work demonstrates factors that influenced toward bonding mechanism of cold sprayed titanium dioxide, TiO₂ onto soft material, pure copper, C1020. We summarize the outcome attained in this study as follows:

1. Thick TiO₂ coatings could be deposited onto all substrate conditions, though some cracks were observed in the substrates once heated at 300°C and 400°C.

2. Increasing the heating temperature decreased the coating adhesion strength and substrate hardness. On the other hand, oxide thickness on the substrate was increased with the heating temperature.

3. CuO and Cu₂O were formed on the substrate by the heat treatment. These oxides did not contribute the chemical reaction with the cold-sprayed TiO₂ particles.

4. The major bonding mechanism is considered to be the chemical bonding between the cold-sprayed TiO₂ particle with newly-formed copper substrate.
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