Effect of Powder Calcination on the Cold Spray Titanium Dioxide Coating

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The agglomeration of nanoparticles is usually undesirable in the formation of powder. However, a coating process using the cold spray method only allows the usage of micrometer-sized feedstock powder in a regular powder feeder. In this study, TiO2 coatings on ceramic tiles were prepared by a cold spray process using agglomerated TiO2 powders synthesized via a simple hydrolysis method. XRD analysis showed that TiO2 powders, composed of anatase phase and calcination at 200°C to 400°C, resulted in enhanced crystallinity and crystallite size of the anatase TiO2 powders. SEM micrographs revealed that the obtained powders were in spherical-like agglomerates with the tertiary particles having diameters of 5–20 µm. TEM image revealed that the obtained TiO2 powders were composed of nanometer primary particles. XPS analyses showed that TiO2 powders without calcination and calcined at different temperatures were formed through the Ti-O bonds. The influences of post treatment at low calcination temperatures of the as-synthesized TiO2 powders were studied on powder deposition. The results of this study indicated that a post treatment on TiO2 powder improved powder deposition on ceramic tile substrate via the cold spray method. The cross-section of the obtained coating which was observed using SEM showed that nanoparticles TiO2 powders in the agglomerated form were able to be deposited on the substrate and formed a thick coating. A stacking of agglomerated TiO2 powders was found on the cross-section observation which is due to the breaking up of ceramic particles which was induced by porosity in the powder and is believed to be responsible for the formation of the coating. [doi:10.2320/matertrans.F-M2016817]

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1. Introduction

Titanium dioxide (TiO2) has been reported to be widely used for photocatalyst to degrade harmful and toxic organic pollutants. This material has been used for a self-cleaning application on the external surfaces of buildings. TiO2 also known as road warrior as to clean the nitrogen oxide (NOx) in the air that was produced by vehicles emissions. Various techniques have been used to fabricate TiO2 coating for photocatalyst applications including chemical vapor deposition (CVD), physical vapor deposition (PVD), dip-coating and sol gel method. However, these methods have some restrictions such as high production cost and complex large-scale equipment. In the case of CVD and PVD, vacuum condition is needed during the fabrication of the coating. Meanwhile for dip-coating technique, the process requires long production time, careful manufacturing process and also high temperatures for post-deposition treatment. Moreover, these techniques are limited to produce thin and small scale coatings.

Cold spraying is an alternative method to fabricate large scale thick TiO2 photocatalyst coating with less time consumption and more cost effective. However, a significant challenge in the conventional thermal spray techniques including atmospheric plasma-spray (APS) process and high-velocity oxy fuel (HVOF) is high processing temperature uses during the process to melt the feedstock powders for coating deposition. The high process temperature may lead to the phase transformation of TiO2 from anatase to rutile and also increase the initial crystallite size of the TiO2 powders. The change in crystal structure and crystallite size is not favorable as it reduces the photocatalytic property of the coatings. A lower temperature process, such as cold spraying, offers a great advantage in the deposition process as this process generally operates below the melting temperature of the feedstock materials. Thus, this technique can prevent phase changes after the coating process.

Cold spraying is a thermal spray process that uses supersonic gas stream to accelerate the feedstock particles below its melting temperature. Therefore, cold spray process is one of the suitable processes to fabricate thick and large scale of anatase TiO2 coating. Generally, in cold spray process, the feedstock materials are usually plastically deformed on the substrate upon impact, forming layer of coating. TiO2 is a ceramic material which has a brittle characteristic, making it difficult to be deposited by this method. However, several studies have been conducted and demonstrated that TiO2 coating can be produced by cold spray method. Anatase TiO2 coating was deposited by cold spraying when the surface of steel substrate was coated with titanium sub-oxide layers. The titanium sub-oxide layer was prepared by APS method provides rough and hard surface on the substrate which ease the adherence of TiO2 powders when impacting onto the substrate due to chemical bonding. A cold-sprayed coating with 150 µm thickness was fabricated using agglomerated TiO2 powders synthesized with addition of ammonium sulfate and hydrothermally treated prior to the coating process. The NH4+ and SO42− ions adsorptions on surface of TiO2 and post hydrothermal treatment have contributed to the formation of an oriented agglomerated structure in a single crystal axis were believed as the factors that lead to the building-up of the coating. Moreover, cold-sprayed TiO2 film about 15 µm with rough and porous structure was also achieved when the ultra-fine TiO2 powders were agglomerated into micrometer sized using polyvinyl alcohol as binder. In that study, the deformation of TiO2 powders was assisted by ductility of the binder during the particles impact under high transient impact pressure.

In this work, a low temperature process method has been utilized to obtain the TiO2 powders used as the feedstock materials for cold spray. The powders were synthesized via a
simple hydrolysis method for photocatalyst application. In order to avoid progressive grain growth and also the existence of internal pores within the particles, study on the effect of low calcination temperatures on the as-synthesized TiO$_2$ powders were also explored in this work. The as-synthesized TiO$_2$ and calcined TiO$_2$ powders were used to study the possibility to produce TiO$_2$ coating by cold spray process.

2. Experimental Procedure

The TiO$_2$ powder synthesized by the hydrolysis method in this work was prepared by simple hydrolysis method. Titanyl sulfate solution was prepared by mixing TiOSO$_4$ with distilled water. The ratio of TiOSO$_4$ with respect to distilled water was 1:9. The white solution was stirred on a hot plate to maintain the temperature of the solution at ~80°C. The precipitate was then oven dried at 120°C for 10 h. The dried powder was crushed to obtain a well-defined TiO$_2$ powder, hereafter referred to as TiO$_2$-0. In order to study the effect of heat treatment at low calcination temperatures on the morphology, crystallinity and powder deposition of the TiO$_2$ coating, as-synthesized powders were calcined at 200°C, 300°C and 400°C for 1 h, hereafter designated as TiO$_2$-2, TiO$_2$-3 and TiO$_2$-4 respectively.

The coatings were deposited on a grit-blasted ceramic tiles substrate (INAX ADM-155M). Prior to spraying, the ceramic tiles were rinsed with acetone. The spray powders were deposited via the cold spray process using CGT KINETIKS 4000 (Cold Gas Technology, Ampfing, Germany) with a custom made suction nozzle. Nitrogen was used as the process gas with an operating temperature of 500°C and at a pressure of 3 MPa. The spray distance and traverse speed of the process was 30 mm and 20 mm/s, respectively.

A Differential Thermal Analyzer (DTA: DTA-50, Shimadzu) was used to investigate the thermal property of the as-synthesized TiO$_2$ with a 10°C/min heating rate. An X-ray Photoelectron Spectroscopy (XPS: Quantera SXM-CI, ULVAC-Phi, Inc.) was used to measure the chemical composition of the TiO$_2$ powders. The X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT 2500 with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å) over the 2$\theta$ range of 20–80°. The crystallite size of each powder was calculated from the (101) plane by the Scherrer equation. The morphology of the resulting powders and the obtained fractured cross sections of the coating samples were examined using a Scanning Electron Microscope (SEM: JSM-6390, JEOL) and a Field Emission Scanning Electron Microscope (FESEM: SU8000, Hitachi). A Transmission Electron Microscope (TEM: JEM-2100F, JEOL) was used to measure the primary particle size of the as-synthesized TiO$_2$.

3. Results and Discussions

Figure 1 shows the DTA curve of the as-synthesized TiO$_2$ powders. The DTA curve of as-synthesized TiO$_2$ powders indicates that a broad endothermic peak exists at ca. 75°C which attributes to desorption of water molecules. The partial presence of water molecules on the surface of the precursor was expected as the reaction was carried out using distilled water as the aqueous media. There is a small endothermic peak maximum at ca. 180°C due to loss of organic residues and chemisorbed water. An exothermic peak observed at 480°C can be attributed to the progressive growth of crystallites size and crystallinity of the TiO$_2$ powders. The exothermic peak with a maximum at ca. 950°C is corresponded to the phase transformations from anatase phase to rutile phase.

The XRD pattern of the as synthesized TiO$_2$ powders at different calcination temperatures is shown in Fig. 2. Identification of the phases in the analyzed powders was achieved by comparing the obtained XRD patterns with PDF Card No. 021-1272. The crystallite size on (101) plane was calculated using the Scherrer equation by using the full width at half maximum (FWHM) data of their XRD patterns, and the results showed that increase of crystallite size occurred as the powders were calcined at 200°C, 300°C and 400°C.
powders were calcined below 500°C, and the XRD patterns responded to Ti shows the binding energy of ~459.5 eV and ~465 eV corresponding to Ti which was used during the XPS analysis. Figure 3(b) shows the carbon peak at ~285 eV originated from the carbon bon were confirmed by XPS measurement as shown in Fig. 3(a). Carbon peak at ~285 eV originated from the carbon tape which was used during the XPS analysis. Figure 3(b) shows the binding energy of ~459.5 eV and ~465 eV corresponded to Ti 2p3/2 and Ti 2p1/2, respectively. These binding energies are a characteristic of Ti in the TiO2 lattice, which is also an indication of increased crystallinity of the TiO2 as revealed in the XRD pattern. Moreover, J. Huang et al. reported that the peak that is located with this particular binding energy could be attributed to adsorbed oxygen which in turn is attributed to lattice distortion and porous structure. Meanwhile, N. T. Salim et al. and A. Di Paola et al. reported that this peak might also correspond to the sulfate (SO42-) bonding.

The XPS analysis also revealed the presence of sulfur ion on the surface of TiO2 powders as illustrated in Fig. 3(d). This result indicates that the presence of SO42- ions reduced as the calcination temperature increased to 400°C. The SO42- ions, which originated from the precursor, were also reported after annealing at 600°C. Sathyamoorthy et al. reported that the sulfate ions detached from the surface of anatase TiO2 particles only when the powder was calcined at 650°C. The removal of the sulfate ions was via the liberation of highly acidic sulfur trioxide fumes. Since our objective is to maintain a small crystallite size at the primary level and to avoid the formation of internal pores in nanoparticles, calcination at a lower temperature of 650°C was conducted. Moreover, N. T. Salim et al. showed that powder that was annealed at 600°C showed a growth in primary particle size from 3 nm to 25 nm. Also, the thickness of the coating that has been fabricated using annealed TiO2 powder modified by adding ammonium sulfate during the synthesis was only about 75 µm.

The particle morphologies of TiO2 powders after synthesis and calcination at 200°C, 300°C and 400°C were observed by SEM at low and high magnification, as shown in Fig. 4 and Fig. 5 respectively. No obvious changes were observed in terms of the size of the agglomerated particles even though the powders were calcined up to 400°C. However, the calcination Table 1 Calculated crystallite size using the Scherrer equation of TiO2 powders calcined at different temperatures.

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Phase</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>Anatase</td>
<td>11.09</td>
</tr>
<tr>
<td>200</td>
<td>Anatase</td>
<td>18.76</td>
</tr>
<tr>
<td>300</td>
<td>Anatase</td>
<td>19.33</td>
</tr>
<tr>
<td>400</td>
<td>Anatase</td>
<td>21.96</td>
</tr>
</tbody>
</table>

Fig. 3 The XPS spectra of (a) wide scan spectra of TiO2 powders that calcined at different temperatures and narrow scan spectra of TiO2 powders that calcined at different temperatures corresponds to (b) Ti 2p, (c) O 1s, and (d) S 2p.

Figure 3(c) shows the O 1s spectra of as-synthesized TiO2 and calcined TiO2 at different temperatures. The binding energy at 530.9 eV is due to the characteristic of the Ti-O bond. The peak located at ~532 eV corresponded to the OH groups. This peak appeared in all samples. However, by increasing the calcination temperature, the peak decreased. The results show that the calcined TiO2 powders contain less hydroxyl groups due to the removal of water during heat treatment which is also an indication of increased crystallinity of the TiO2 as revealed in the XRD pattern. Moreover, J. Huang et al. reported that this peak might also correspond to the sulfate (SO42-) bonding.
tion of powders improved the densification of particles by reducing the number of pores which can be seen in Fig. 5. TEM image (Fig. 6) depicts that the as-synthesized and calcined TiO$_2$ powders were composed of nanoparticles which were highly agglomerated. A slight increase in the size of the primary particles was observed with TEM when the TiO$_2$ powders were calcined at $200^\circ$C to $400^\circ$C which attributed to crystal growth. Previous studies by other researchers also revealed a slight growth of anatase nanocrystallites at low calcination temperatures, such as below $400^\circ$C\textsuperscript{15,16,19,24). S. Baskardjieva et al.\textsuperscript{24} reported that slow growth of the anatase nanocrystallites occurred due to the transformation of leftover amorphous parts, together with the growth of existing anatase nanocrystallites during the heat treatment.

Coating deposition in this study shows that heat treatment of as-synthesized powder at low temperature not only improved the crystallinity of the as-synthesized TiO$_2$ slightly which is preferable for photocatalytic activity but also increased the deposition of powder on the ceramic tiles substrate. After cold spraying, the average thicknesses of the TiO$_2$-0, TiO$_2$-2 and TiO$_2$-3 powders were 50 µm, 130 µm and 120 µm, respectively (Fig. 7).

The formation of coating can be explained by the tamping effect\textsuperscript{25) during the collision between the feedstock powders and the substrate. When a high kinetic energy was supplied during the process via application of pressure and temperature, the particles collide on the substrate. The powders fragmented and formed a coating due to the stacking of the powders during impact. The TiO$_2$ coating was produced from a recombination of broken crystallite links during the cold spray process, which was initiated by the porous structure of the agglomerated powders. During the process, the loosely agglomerated powders with nano-scale primary particles fractured, leaving an unstable surface with a dangling bond structure\textsuperscript{26). To reobtain a stable surface, the fractured parti-
cles recombined and formed a surface with improved stability. These were achieved by the adhesion of fractured particles with the substrate upon collision, and also with the previously-deposited TiO₂ coating layer.

It is therefore important to note that development of coating using only TiO₂ powders calcined at 400°C was unsuccessful. From the XRD, SEM and TEM results, no significant results found which contributes to the progressive improvement on the crystallinity and densification of the particles when the powders were calcined from 200°C to 400°C. However, it is likely that crystalline bridges became stronger between the primary particles when the calcination temperature was increased up to 400°C. This can be seen by decrease in average size of the pores which play an important role in the particle-particle attraction of the primary particles of TiO₂ powders as shown by SEM image in Fig. 5. This might occur due to the higher degree of crystallinity and also the formation of strong/hard agglomerated particles by a densification of particles during the heat treatment at higher calcination temperature. These hard agglomerated particles, which have less porosity, were difficult to fracture upon impact during the deposition as the particles were strongly bonded together. These strong bonds, which are formed by the crystalline bridges between the particles, made them resistant to fragmentation and adherence on surface of the substrate. This result also shows that a further increase of post heat treatment temperature on as-synthesized TiO₂ powders; at 400°C and above lead to difficulties in building up the coating during collision, and this finding is in good agreement with previous study reported by Salim et al.12).

It seems that porosity in the ceramic powder has an important role for powder deposition. Conversely, the result of this study shows that the as-synthesized TiO₂ powders which contain more porosity and less crystallinity as comparable to the calcined TiO₂ powders at 200°C and 300°C produced a thinner coating thickness. There are considerable reasons for the as-synthesized TiO₂ powders results in poor deposition using cold spray. Higher magnification image of SEM in Fig. 5 shows that as-synthesized TiO₂ powders were composed of highly porous structure which indicates that the primary particles were loosely bound together by weak attraction force. The SEM image shows that the primary particles were not already in contact with each other as bigger pores were observed. The as-synthesized TiO₂ powders which have the lowest density due to higher amount of porosity and poor crystallinity experienced heavy breakage when exposed to harsh condition during the cold spray process. The tertiary particles tend to fracture into very small particles due to the weak attraction force that hold the primary particles together. Thick coating was difficult to achieve due to low impact energy of smaller particles onto the substrate during the collision. Moreover, higher porosity that was contained in the upcoming particles of as-synthesized TiO₂ led to poor inter-particle contact upon the collisions; producing only thin coating.

The SEM image analysis of TiO₂-3 confirmed that the TiO₂ powder was not melted during the impact (Fig. 8). However, the image has revealed that the collided particles were fragmented as the dimensions of the individual particles on the coating were smaller than the feedstock materials. The figure also shows that the coating had some porosity. This might be due to the porosity which originally existed in the agglomerated particles. This was expected, as the feedstock powder was in an agglomerated form and plastically deformed in CS. During the impact of agglomerated TiO₂, high kinetic energy from the CS process initiated the breaking up of agglomerated TiO₂. Having nanoparticles in ceramic materials make it possible for the feedstock powders to experience dislocation which relates to plastic deformation due to the high kinetic energy and pressure applied during the cold spray process.

4. Conclusion

In this study, TiO₂ powders have been successfully synthesized by a simple hydrolysis method without the addition of binder and/or inorganic salt. The method that has been employed successfully produced agglomerated anatase TiO₂ powders which were able to be used directly as feedstock powder for cold spray process. However, only as-synthesized TiO₂ and TiO₂ powders, that calcined at 200°C and 300°C showed the successful deposition of TiO₂ coating on the ceramic tile substrate by the cold spray method. The calcined TiO₂ powders indicated a better crystallinity and thicker coating compared to the as-synthesized powder. A higher calcination temperature of 400°C not only promotes grain growth and the crystallite size of the as-synthesized TiO₂ powders, but also reduces the porosity present in the agglomerated powder by densification of the particles. The presence of a certain amount of porosity in the ceramic feedstock powder is crucial in order to build up the coating during deposition.

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