Fabrication of Cold Spray Ti-O Coatings Engineered from Agglomerated Powders

（凝集粉末作製技術によるコールドスプレーTi-O 皮膜の創製）

July, 2016

Doctor of Engineering

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Abstract

Current attention has focused on the preparation of thick ceramic coating using nanostructured materials as feedstock materials using thermal spray process. Cold spray method has appeared as a promising process to form ceramic nanostructured coating without significantly changing the microstructure of the initial feedstock materials whereas many conventional thermal spray processes do due to its low processing temperature. However, deposition of ceramic powders by cold spray is not easy due to brittle characteristics of the material. Moreover, the bonding mechanism on how the ceramic coating was formed on the substrate is still unclear as this method requires plastic deformation of particles upon the impact onto the substrate.

Therefore, in this study, focused have been made on the TiO_2 nanostructured feedstock materials which were synthesized throughout of the study. The properties of the powders also have been altered by several conditions in order to make it suitable for cold spray deposition. The mechanism of coating deposition and properties of the feedstock powders were investigated in this study. The following results which obtained by this study were summarized as below:

1. In this work, the synthesis of agglomerated TiO_2 powders, which are ready to be used as feedstock materials for a cold spray process after synthesis via a simple hydrolysis (TiO_2-H) and hydrothermal (TiO_2-HT) process, is described. The XRD patterns showed that single phase anatase TiO_2 was able to be produced using a low temperature process for the hydrolysis and hydrothermal methods. However, the results showed that TiO_2-H powders have a smaller crystallite size and broader peaks compared with TiO_2-HT powders. SEM and TEM analysis confirmed that the TiO_2-H powders were built up from nano-sized particles, and were further agglomerated into micrometer-size, which is a preferable size for the cold spray process. On the other hand, TiO_2-HT powders showed a formation of agglomerated particles with minimal particle agglomeration which was revealed by the SEM image and the particle size analyzer. A preliminary study on coating

deposition using cold spray showed that TiO_2-H powders can be deposited onto ceramic tile substrate with a ~50μm thickness. Meanwhile for TiO_2-HT powders, only particle embedment can be observed on the surface of the substrate. The results reveal that porosity contained in the agglomerated morphology is important in order to build up the coating by cold spray due to the tendency of the porous structure to break easily upon impact onto the substrate.

2. To further clarify the effect of porosity contain in the powder for the cold spray deposition, effect of low calcination on the as-synthesized TiO_2 by hydrolysis method have been conducted. Then, as-synthesized TiO_2 and calcined TiO_2 powders were studied on coating deposition by cold spray process. The results of this study indicated that a post treatment on TiO_2 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 TiO_2 powders in the agglomerated form were able to be deposited on the substrate and formed a thick coating. A stacking of agglomerated TiO_2 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. The results of this study also reveal that, when the feedstock powders have denser packing of particles and minimum number of porosity in the powder, breaking of particles during the spraying become more difficult. This hard and dense particle made them resistant to fragmentation and adherence on surface of the substrate.

3. Further study have been conducted by addition of ammonium sulfate; $(NH_4)_2SO_4$ during the powder synthesis. Addition of structure-directing agent, $(NH_4)_2SO_4$ promotes the agglomeration to occur with denser closed packing of particle arrangement which reduce the number of existing porosity in the synthesized powder. The addition of $(NH_4)_2SO_4$ addition was found to be very effective to unite the nano-sized particles together to form agglomeration in order to form the tertiary particles. The preliminary study of coating

formation depicted that the powder obtained could be used as the feedstock powder for cold spray process to make coating as it can be deposited onto the ceramic tile substrate. Once again, porosity in the powders was deduced as one of the crucial factors that contribute to better deposition of TiO_2 coating by cold spray process. Plastic deformation also may contribute to the formation of coating due to the used of nanostructured powders which received high local compact pressure during the spraying process.

4. Further studies on the obtained coating have been investigated. The study reveals that the properties of the coating (hardness, roughness and porosity) also depend on the properties of the initial feedstock powders. Moreover, anatase phase was preserved as revealed by the XRD analysis. This finding proves that cold spray process is suitable process to fabricate TiO_2 coating which can prevent phase transformation to occur due to low processing temperature. Details observation on the surface and cross-section of the coatings show that nanostructured particles from the feedstock powders were well-retained in the coating structure.

5. In order to study the individual particle impact morphologies, wipe tests were conducted on aluminum, copper and ceramic tile substrate. From the SEM observation, the results showed that the collided particles were plastically deformed and adhered on the hard ceramic tile substrate during deposition. However, in the case of aluminum and copper substrate, the splat diameters were smaller than the feedstock powder size and both particles and substrates were deformed during the collision. Moreover, many craters were observed on these metal substrates. It was found that the deposition behavior of TiO_2 particle and the crater formation by the cold spray process was affected by the hardness and surface roughness of the substrate materials.

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1 Introduction

1.1 Titanium Dioxide (TiO_2)

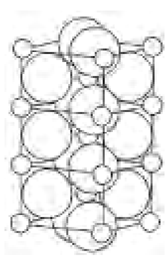
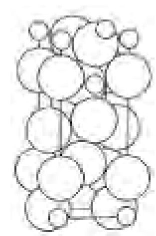
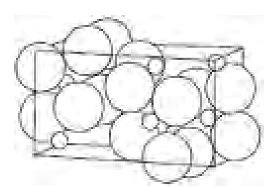
1.1.1 Phase Structure of Titanium Dioxide

There are three types of crystal structures of TiO_2 that exist naturally and mainly sourced from ilmenite ore which are known as rutile, anatase and brookite. All these types are known as TiO_2 which using the same chemical formula, but their crystal structures are different. However, brookite type is less common using in the industry as it can transform into rutile phase at very low temperatures. Meanwhile, rutile is well known as a very stable phase compared to anatase type. The anatase type can convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range 600°- 800 °C. Generally, anatase and brookite are more common phase exists in nanoscale natural and synthetic samples, but conversely rutile is the stable phase at high temperatures [1,2].

1.1.2 Properties of TiO_2

The properties of TiO_2 depend largely on its particle size, crystal structure, morphology and crystallinity [3]. Titanium dioxide (TiO_2) is widely known as a crucial material in photocatalysts, gas sensors, water and air purification, electrochromic devices, solar cells, and many more [4–15]. TiO_2 is well known as a wide gap semiconductor oxide. It works based on the UV light; electron and hole pair is generated by the UV irradiation, inducing chemical reactions at the surface. Hence, the most promising characteristic of TiO_2 lies in its photochemical properties such as high photocatalytic activity. In terms of solubility, TiO_2 is insoluble in dilute alkali, dilute acid. Though, this oxide material is soluble in hot concentrated sulfuric acid, hydrochloric acid, nitric acid. The solubility of titanium dioxide is related to solutes. TiO_2 also has excellent electrical properties as it has high dielectric constant. It can be transformed into rutile when anatase and plate TiO_2 are at high temperatures, so melting and boiling points of the board of rutile and anatase TiO_2 actually does not exist. Only rutile TiO_2 has a melting point and boiling point. TiO_2 has hydroscopicity, but not too strong. The hydrophilic is related to surface area. When the surface area is large, the moisture absorption is high. The moisture absorption of TiO_2 is relevant to the surface treatment and the nature too. Moreover, TiO_2 has a good thermal stability. Table 1 summarizes the characteristics of each types of these TiO_2.

Table 1.1: Properties of TiO_2 based on Crystal Structure

Type of TiO_2 / **Properties**	**Rutile**	**Anatase**	**Brookite**
Crystal system	Tetragonal 	Tetragonal 	Orthorhombic 

No. of unit cell	2 a = 0.459 nm c = 0.296 nm	4 a = 0.379 nm c = 0.951 nm	8 a = 0.917 nm b = 0.546 nm c = 0.514 nm
Density (g/cm^3)	4.13	3.79	3.99
Melting Point (°C)	1840 ± 10	change to rutile	change to rutile
Refractive Index	2.605–2.616, 2.890–2.903	2.561, 2.488	2.583, 2.700
Band gap value (eV)	3.0	3.2	-

1.1.3 Applications of TiO_2 as Photocatalyst

Environmental pollution has drawn attention in the world today due to the need of safe and clean environment. Industrial activities and transportation are some examples that contribute to the unhealthy surroundings especially in the urban areas. Of the technologies recently use to reduce the pollution in our environment are by the applications of photocatalysts. TiO_2 have attracted much attention to be used as photocatalyst materials among the photocatalytically active materials due to its availability, low cost, chemical stability and nontoxic properties [16–22]. TiO_2 is the widely studied photocatalyst for waste water purification owing to its biological and chemical inertness, strong oxidizing power, nontoxicity and long term stability against chemical and photochemical corrosion [23].

The brookite phase has not been used and studied widely as a photocatalyst due to presents of many defects in its crystal structure [24]. Moreover, the brookite structure is more difficult to obtain as compared to anatase and rutile structure [25]. Among these three structures of TiO_2, anatase phase with fine particles are more preferable for high photoactivity with the absence of rutile phase which has lower photoactivity than anatase [2,5,24,26]. There are several studies reported that the properties of the as-synthesized TiO_2 including its polymorphic transformation from anatase to rutile was likely dependent upon on the precursor and the preparation method [1,2].

TiO_2 is an effective photocatalyst for water and air purification, treatment of indoor air and for self-cleaning surfaces. Moreover, it can be used as an antibacterial agent because of its strong oxidation activity and superhydrophilicity [27]. It has been reported that for the photocatalytic applications, TiO_2 can be used in powder form (slurry) or coating deposited by several methods [28,29]. Despite the fact that TiO_2 powders have an outstanding photocatalytic activity compared to the coating due to their higher specific surface area, separation of powder from the liquid state used in water treatments and recycling processes can reduce their effectiveness [30]. Coating of TiO_2 on various materials as substrates can be one of the solution to this problem. Therefore, coating of TiO_2 for photocatalyst applications are the main focused in this study.

1.2 Titanium Dioxide Coatings

1.2.1 Conventional Coating Processes

Moreover, many attempts have been made to prepare TiO_2 coatings, such as chemical vapor deposition, (CVD), pulsed laser deposition, sputtering, electrodeposition, hydrothermal crystallization, chemical spray pyrolysis, sol gel and also thermal spray process. The photocatalytic activity of the coating depends on several factors such as crystal size, surface area, crystal structure and also coating thickness [31]. These factors are largely affected by the preparation methods and deposition conditions. Table 1.2 is a summary of the TiO_2 coating or film deposited on different substrates using different methods for photocatalytic applications. Major drawbacks using these conventional coating techniques are difficulties to deposit thick coating. Moreover, coating techniques such as PVD and CVD requires large and complicated equipment. Therefore, a more simpler and economic coating method such as thermal spray process can be used to prepare thick coating on large surface substrates.

Table 1.2: Summary of surface modification technologies to prepare TiO_2 coatings using conventional method for photocatalyst applications.

Method	Substrate materials	Typical coating thickness	Ref.
CVD	Steel sheet	Less than 5 μm	[32]
Dip coating	Stainless steel mesh	155 nm	[33]

Sol-gel	Soda lime glass or quartz plates	Less than 300 nm	[31]
Magnetron sputtering	Stainless steel mesh	165 nm	[33]
Spray pyrolysis	Stainless steel	Less than 2.5 µm	[34]

1.2.2 Thermal spray process

Nowadays, surface treatments of engineering materials have become significant for serviceable engineering components. Recently, thermal spray processes have been used for industrial surface treatment application due to coating properties such as adhesion strength to substrate, low porosity-oxide content and microstructural characteristics. Thermal spray coatings have become an important part of modern industry, offering customized surface properties for a variety of industrial applications ranging from thermal barrier coatings for high tech turbine blades to erosion resistant coatings for boiler tubes.

Thermal spraying is a coating process where the metallic and non-metallic materials are deposited in a molten or semi-molten condition to form a coating using a thermal source. Metals, alloys, carbides, ceramics, plastic, composites, blended materials and cermets are the most widely used coating materials for this process. The initial coating material for thermal spray process which usually in the form of rods, wires, or powders is heated, generally to a molten state and projected onto a substrate thereby forming a coating.

Usually, the surface of the substrate is degreased, masked, and roughened prior the coating process in order to activate the surface by increasing the free surface energy which will lead to increase of surface area for bonding of the sprayed particles. In principle, any material that can withstand blasting procedures to roughen the surface can be used as thermal spray coating base material. One of inherent advantages of thermal spraying is the process covers diverse range of substrate materials and substrate sizes. Moreover, thermal spray process also having the greatest range of coating materials. Basically, any material that does not decompose to other material once melted when expose to heat generated during the thermal spray process can be used as the coating feedstock material. Thermal spray process also known as a faster rate coating process and it is also possible to do coating on-site work. Furthermore, the coating can be done in a dry process thus less environmental impact.

1.3 Current Studies/ Developments of Thermal Spray Titanium Dioxide Coating

1.3.1 Conventional Thermal Spray Processes

Thermal spraying is an effective and low cost process to prepare thick and large coatings to modify the surface properties of the component. During the conventional thermal spray process, some parts of the feedstock powders will melt to assure coating integrity, i.e., adhesion and cohesion. Therefore, the processing temperature use is usually above the melting temperature of the spray particles. Figure 1.1 shows the simplified principle of conventional thermal spray process using agglomerated ceramics powder from nanostructured materials as spray materials. Since the use of nanostructured materials show superior properties in various applications when compared to their conventional powders, it opens remarkable possibilities to be used as feedstock materials in agglomerated form to prepare coating by thermal spray process. Moreover, when nanostructured materials have been used as spray particles to prepare coating by thermal spray process, the molten particles will act as a binder to the non-molten spray particles during the spraying process [35]. It is important to point out that during the thermal spraying; the molten particles have loss the characteristics or properties of nanostructured materials as it experienced grain growth. This will reduce the performance of the coating as compared to its powder when uses for real application. Therefore, the preservation of the small grain size which originally from the nanostructured powder is very crucial as the TiO_2 photocatalytic reaction depends strongly on its grain size. Photodecomposition of nanostructured TiO_2 coating can be higher than the microstructured coating prepared with similar process and conditions.

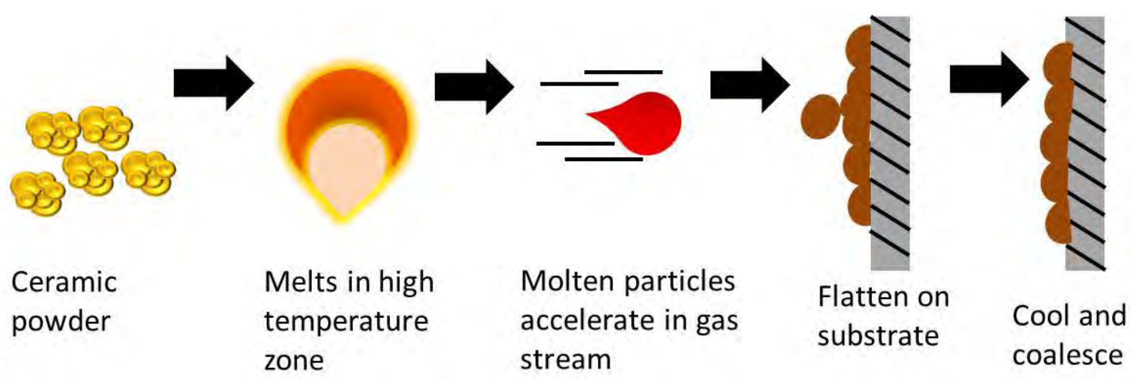


Figure 1.1: Simplified principle of the conventional thermal spray process using ceramic as feedstock materials.

While thermal spraying have significant progress in preparing coating for wide area with more cost effective and minimum operation time, challenges still exist in various aspect especially when it involves ceramic materials such as TiO_2. The drawback of the conventional thermal spray process to prepare TiO_2 coating is the irreversible phase transformation of TiO_2 structure from anatase to a less photocatalytic rutile phase at 500-600°C under normal conditions [36] as shown in Fig. 1.2. Moreover, Table 1.3 shows the summary of some thermal spray methods that have been used to prepare TiO_2 coating. The results show that, it is quite challenging to preserve the anatase phase in the as-prepared coating by conventional thermal spray method.

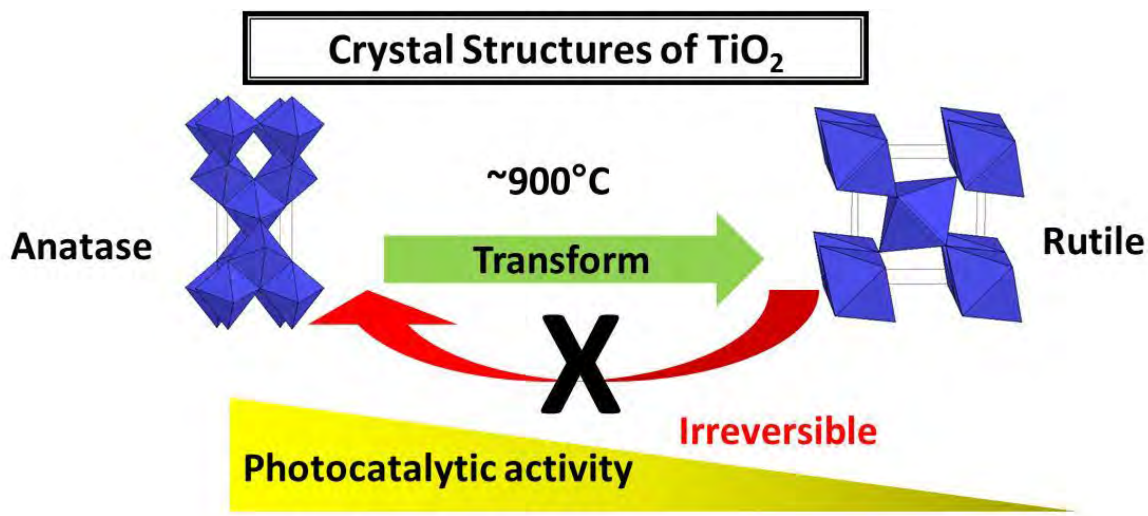


Figure 1.2: Schematic diagram showing the phase transformation of anatase TiO_2 to rutile TiO_2 during the conventional thermal spray process.

Table 1.3: Summary of preparation method to deposit TiO_2 coatings using conventional method for photocatalyst applications.

Spray technique	Size of agglomerated feedstock material	Substrate	Coating thickness	Phase structure in the obtained coating	Reference
Air Plasma Spraying	10 to 50µm (from 7 nm)	Stainless steel	~30 µm	Anatase, rutile & different titanium suboxides	[30]
High Velocity Oxygen Fuel	10 to 50µm (from 7 nm)	Stainless steel	~20 µm	Rutile & anatase	[30]
Suspension Spraying	10 to 50 µm (ranging from 6-12 nm)	Stainless steel	~20 µm	Anatase and small amount of rutile	[37]
Flame Spraying	20-50 µm (from 20 nm)	Stainless steel & Carbon steel	150 µm	Rutile	[38]

Therefore, a proper selection of coating process is crucial due to the goal to obtain coatings with higher photocatalytic activity. Anatase and rutile has differences of photocatalytic properties. Several studies suggested that anatase is more efficient as photocatalyst and this structure can be preserved if only the processing temperature of the thermal spray process is below the transformation temperature of anatase to rutile. Moreover, low processing temperature of thermal spray process also can maintain the initial grain size of the feedstock materials which also has significant effect on the catalytic activity of TiO_2. This might due to the characteristics of smaller crystallites size which can promote the photocatalytic activity of TiO_2. Preservation of the anatase phase after the thermal spray is desirable for photocatalytic applications. Consequently coating process of a high temperature which above the transformation temperature of anatase to rutile phase is one of the major challenges in conventional spray thermal spray.

The results obtained to date, strongly indicated there is necessity for development of thermal spray coating of TiO_2 or any other ceramic materials that can avoid phase transformation to occur during the process. Due to this problem, it encourage new discoveries of new process of thermal spray which utilize kinetic energy instead of thermal energy by increase particle velocity to project the feedstock powders to the substrate. The kinetic energy will transform to thermal energy upon impact on the substrate in order to permit sticking of particles. There are two new technologies of thermal spray methods that utilize low processing temperature during the process and working based on the kinetic energy of the particles for deposition. The processes are cold spray and aerosol deposition method.

1.3.2 Low Temperature Process

Aerosol deposition method (ADM) and cold spray deposition is the low energy consumption processes dissimilar to conventional deposition processes. The aerosol deposition method is a room temperature process which has been used to coat ceramics materials on metal, ceramic and polymer substrates. This process uses an aerosol mixture of nano-sized ceramic particles and a carrier gas which will be accelerated by the carrier gas through a nozzle. For the acceleration of the particles, pressure difference is required. For this reason, the ADM method consists of two vacuum chambers; an aerosol-generation chamber and deposition chamber which were connected by a tube. During the process, the ceramic particles were aerosolized by aerosol-generation chamber which has a carrier gas system and a vibration system to mix the powder with the carrier gas and conveyed to the deposition chamber. The kinetic energy of the particles is used for bonding during the impact [40]. This process is widely used as it can be carried out at low temperature. Therefore, thermal damage of the substrate can be minimized. Despite of these advantages, ADM process requires vacuum condition during the process and the deposited coating only limited to several micrometer of thickness.

Meanwhile, cold spray process is deposition technique to deposit micro-sized particles using a high pressure gas. This process does not require vacuum condition. During the process, the particles are accelerated to supersonic velocities and impact onto a substrate surface without melting before the impact. This technique can produce thicker coating thickness as compared to ADM process. Unfortunately, this process does not permit the direct spraying of nanostructured powder which can cause blockage in the feeding system during the powder supply to the nozzle. However, the use of nano-powders as spray materials for this process can be achieved by modification of the size of feedstock powders by agglomeration of the particles. Moreover, since deformability is important for cold spray coating to build up, this method shows more potential to deposit metal materials rather than ceramic materials. However, ceramic coatings are possible to be deposited by cold spray process. This part will be discussed in details in Chapter 1.4.2. Therefore, in summary, based on the principle of particle collisions by utilizing kinetic energy at a low-process temperature, ADM and cold spray process can be used to fabricate ceramic