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Fabrication and characterization of hybrid micro/nano-structured hydrophilic titania coatings deposited by suspension flame spraying

Jianhui Yuan, Qing Zhan, Qiang Lei, Siyue Ding, Hua Li*

Division of Surface Engineering, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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A B S T R A C T

Nanostructured titania coatings have been a research focus for many years owing to their excellent photocatalytic activity. The major persistent challenge yet is development of competitive deposition techniques for fabricating the nanostructured coatings. Here we report a novel deposition approach by flame spraying the mixtures of nano titania-contained suspension and micron-sized titania powders feedstock. Promising hybrid micro/nano-structured TiO_2 coatings comprising micron-sized splats (50–80 μm) and nano particles (10–40 nm) were successfully produced. Anatase-rutile ratio and proportion of the nanostructures in the coatings can be tailored in a wide range depending on the concentration of nano TiO_2 particles (10–30 nm in size) in the starting suspension. Up to 30 wt.% of anatase in the coatings was achieved. The hybrid micro-/nano-structured TiO_2 coatings exhibit super-hydrophilic performances (~0° contact angle). Effect of the suspension concentration (concentration of the nano titania particles in the suspension) on the microstructure and mechanical properties of the coatings was also investigated. Compared to the coating deposited using the suspension alone, the hybrid micro/nano-structured TiO_2 coatings exhibited markedly enhanced adhesive strength (by up to 1.8 times) and microhardness (by 9 times). The behavior between the TiO_2 particles with micro- and nano-sizes was also elucidated.

1. Introduction

Titanium dioxide (titania, TiO_2) has been extensively studied because of its chemical stability, low cost and non-toxic characteristics. Owing to its excellent photocatalytic performances, nanostructured TiO_2 attracted intensive research attentions [1,2]. In practice, TiO_2 can be used as powder or coating that is deposited on various substrates by numerous techniques. However, the separation of powder (from liquid state used in water treatment) during recycling processes is very tricky, due mainly to the formation of aggregates. On the other hand, the aforementioned difficulties can be avoided by taking advantages of thin films and coatings and the applications of TiO_2 can also be expanded by employing various materials as substrates [3]. Nanostructured TiO_2 thin films or coatings have been fabricated by various techniques such as sol–gel [4–8], chemical vapor deposition (CVD) [9], physical vapor deposition (PVD) [10] and plasma spraying [11]. Sol–gel method is a complex process and constrained to flat substrates [12], since it involves heat-treatment after dip-coating. CVD or PVD approach is capable of fabricating pure TiO_2 films. However, the cost pertaining to the film deposition is a big concern and the vacuum apparatus limits the sizes of the substrates. Thermal spraying process is one of the potential candidates that offer fast forming rate, a wide selection of materials and easy operation [13]. Because of its poor flowability, nano-sized powder cannot be directly applied for the thermal spraying process. Alternatively the starting nano-sized powder is usually agglomerated using spray drying [14,15]. However, during conventional thermal spray process, the sprayed powders experience high temperatures, triggering significant grain growth with the initial nanostructure being retained only in limited unmelted fraction of the particles [16]. The emerging technology of suspension thermal spraying seems to be a promising candidate for fabricating nanostructured coatings [17]. The suspension thermal spraying method for the deposition of ceramic coatings offers several advantages over the conventional plasma spray techniques, such as circumvention of the powder-feedstock preparation step, better control over the chemistry of the deposit and deposition of nanostructured coatings [18]. Toma [19], Jaworski [20] and Li [21] et al. have successfully made nanostructured TiO_2 coatings using liquid feedstock. However, it was realized that adhesion of the TiO_2 coatings was a major challenge. To solve this problem, incorporation of micron-sized TiO_2 powder in suspension thermal spraying process might be useful. In this research, hybrid micro/nano-structured TiO_2 coatings were deposited by flame spraying the mixtures of suspensions and powders feedstock. The

* Corresponding author. Tel.: +86 574 86686224, fax: +86 574 86685159.
E-mail address: lihua@nimte.ac.cn (H. Li).

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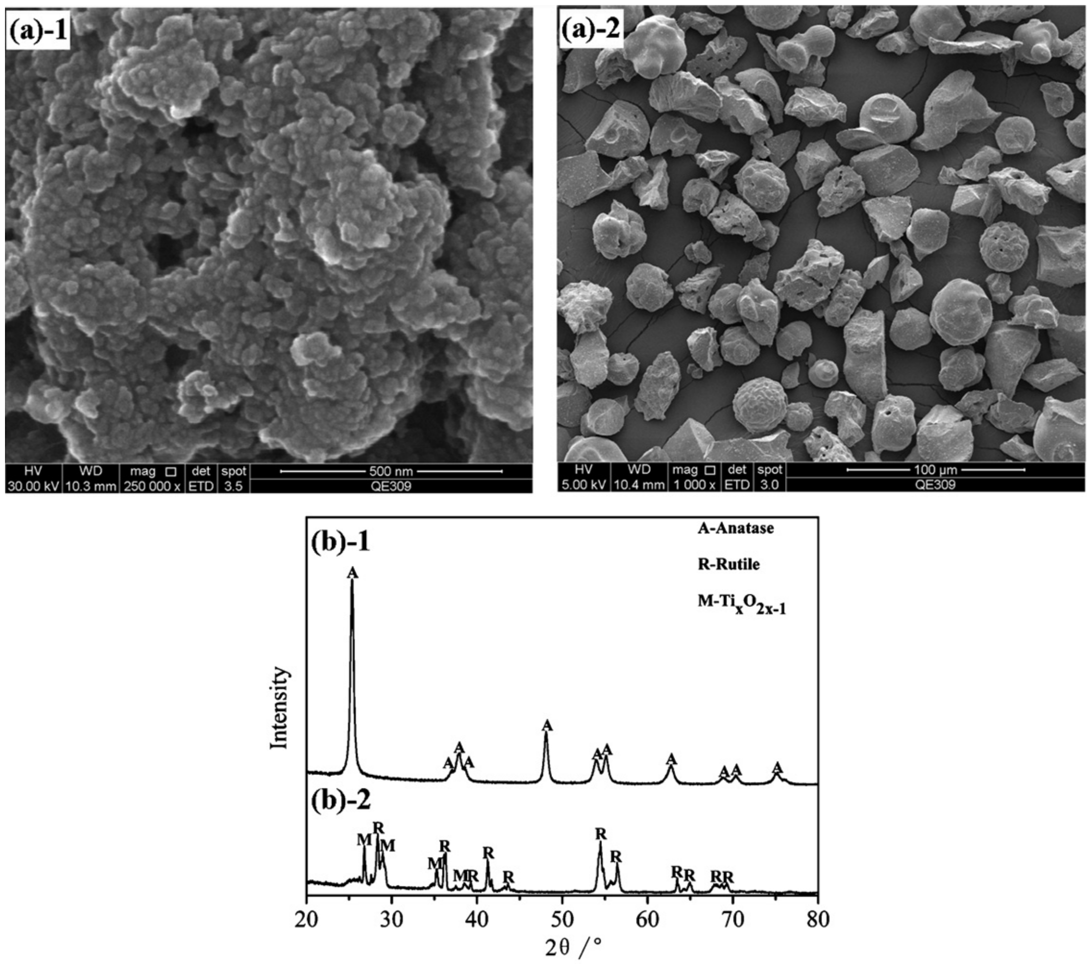

Fig. 1. Topographical SEM morphology (a) and XRD spectra (b) of the starting nanosized (−1) and micron-sized (−2) TiO_2 powders.

microstructure and mechanical properties of the coatings were analyzed.

2. Materials and experimental setup

For nano TiO_2 suspension preparation, anatase TiO_2 nano powders (Aladdin Chemistry Co. Ltd.) with particle size range of 10–30 nm were added to the solvent (mixture of distilled water and ethanol with the ratio of 1:1). The suspensions with TiO_2 particle concentration of 1 wt.%, 4 wt.% and 7 wt.% were investigated. During the coating deposition, the suspension was delivered into atomizer and injected into flame. The injector was 15 mm away from the flame torch. Compressed air of 0.4 MPa was used as the atomizing gas. Micron-sized commercial TiO_2 powders (−45+15 μm, Sun-spraying Science and Technology Co. Ltd.) were used as the powders feedstock. The topographical SEM morphology and XRD patterns of the initial TiO_2 powders are shown in Fig. 1. The micron-sized powders are composed of both rutile phase and Ti_xO_{2x-1} ($5 < x < 9$) Magneli phases [3].

Stainless steel plates (10 mm × 20 mm × 1 mm in dimension) were used as the substrates. The FS-4 flame torch (Wuhan Research Institute of Materials Protection) was employed for the coating deposition on the grit blasted substrates. The spray parameters are listed in Table 1. For the coating deposition, the micron-sized powders and nano-titania contained suspension were fed into the flame separately. There is an outlet bore at the center of the torch, from which the powders feedstock is fed in. And at the same time, the suspensions feedstock is injected into the flame by using the atomizer. In this study, four different types of TiO_2 coating samples were investigated. They are: coating A – made from sole 7 wt.% suspension; coating R1A – made from mixture of 1 wt.% suspension and powders feedstock; coating R4A–made from mixture of 4 wt.% suspension and powders feedstock; and coating R7A – made from mixture of 7 wt.% suspension and powders feedstock. For comparison purpose, the coating made from pure micron-sized titania powders was also deposited and characterized.

Chemical composition of the powders and coatings was determined by X-ray diffraction (Bruker AXS, German) using Cu Kα radiation operated at 40 kV and 40 mA. The scan rate was 0.02°/s with the 2θ ranging from 20° to 80°. Morphology of the powders, splats and the coatings was characterized using field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, Netherlands) equipped with a detector of secondary electrons and an energy dispersive spectrometer (EDS). Hydrophobicity/hydrophilicity of the

Table 1
Flame spray parameters.

Parameter	Value
C_2H_2 pressure	0.1 MPa
C_2H_2 flow	1.5 Nm^3/h
O_2 pressure	0.5 MPa
O_2 flow	3 Nm^3/h
Atomization gas (air) pressure	0.4 MPa
Suspension flow rate	25 ml/min
Powder feed rate	50 g/min
Spray distance	150 mm

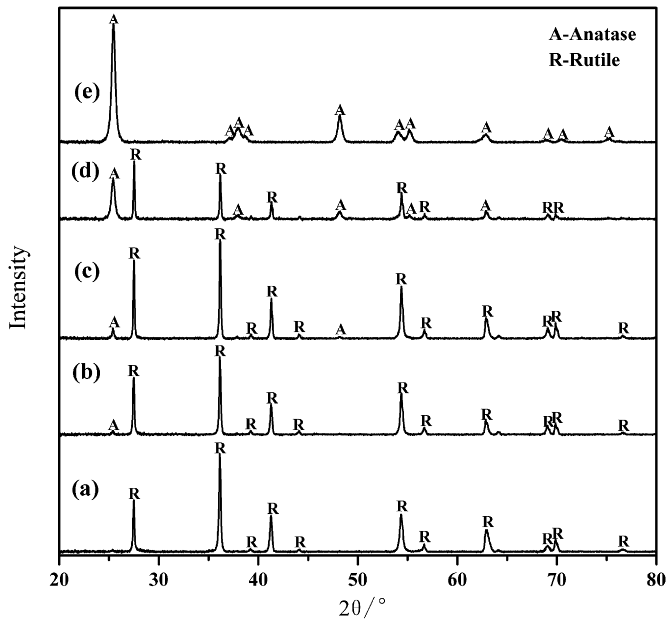

Fig. 2. XRD spectra of the TiO_2 coatings deposited using (a) micron-sized powders feedstock, (b) mixture of 1 wt.% suspensions and powders feedstock (coating R1A), (c) mixture of 4 wt.% suspensions and powders feedstock (coating R4A), (d) mixture of 7 wt.% suspensions and powders feedstock (coating R7A), and (e) sole 7 wt.% suspension (coating A).

coatings was evaluated by measuring the contact angle of deionized distilled water droplet spread on their surfaces using a contact angle measurement instrument (Dataphysics OCA20, Germany). Vickers microhardness measurements (Instron Tukon 2100B Hardness tester) were conducted on polished cross-sections of the coatings under a load of 25 g for 10 s. An average microhardness was calculated from 5 indents per specimen. The adhesion of the coatings was evaluated by scratch test with an Automatic Scratch Tester (WS-2006, Kaihua Science and Technology Co. Ltd., China) equipped with a diamond indenter having a tip radius of 0.2 mm. The scratches were linear with progressively increasing load. The test was carried out using an initial load of 0.05 N and a final load of 60 N. The increase rate of the load was 12 N/min and the loading speed of the indenter was 1 mm/min. Scratch length of 5 mm was employed. The acoustic and friction signals were used for the estimation of the critical load, Lc.

3. Results and discussion

Fig. 2 shows the XRD spectra of the TiO_2 coatings. The coating deposited using the suspension only (coating A) contains anatase with no other phases being detected. It is clear that anatase structure in the starting nano particles (Fig. 1) was completely retained after the suspension flame spraying (Fig. 2e). Whilst the Magneli phases in the starting micron-sized titania powders transformed to rutile (Fig. 2a). The coatings deposited using the mixtures of the suspension and powders feedstock comprise both anatase and rutile (Fig. 2b–d). It has been found that fully melted particles contain rutile phase, whereas anatase structure is mostly present in partially/non-melted particles [22]. In this study, microstructure characterization of individual splats indicates a complete melting state of the micron-sized titania powders (data not shown). It is therefore believed that the anatase and rutile detected in the coatings are attributed to the suspensions and the powders feedstock respectively. Quantitative evaluation of the phases was also determined by using intensity of the XRD peak, [1 0 1] peak for anatase and [1 1 0] peak for rutile [23]. Results showed significant increase of anatase content in the coatings (4 wt.% vs. 30 wt.%) as the concentration of the nano TiO_2 particles in the suspension was increased from 1 wt.% to 7 wt.%.

During the suspension thermal spraying, injection of the suspension into flame results in consumption of part of the energy to disintegrate the primary drops and form smaller liquid droplets and to evaporate the solvent of the droplets [24]. Heat transfer from the flame to the solid particles is limited because part of the energy is used to evaporate the liquid from the droplets. The slight heating effect exerted on the titania nano particles leads to minor changes in their nano feature and effectively retained anatase structure. It has been well acknowledged that anatase is presumably preferred in most applications of the coatings such as photocatalytic application. The flame spraying of mixture of nano titania suspension and micron-sized titania powders might be an effective approach for depositing nanostructured titania coating with adjustable anatase content.

Microstructural characterization of the coatings showed granular structural feature for the coating made from the suspension alone (Fig. 3a). Apart from the presence of the nano titania particles (~15 nm), porous structure with particles of 0.5–2 μm in diameter are also observed in the coating. It obviously indicates agglomeration of the nano titania particles during the spraying. The coatings deposited using the mixture of the suspensions and the powders feedstock show typical bimodal structure (Fig. 3b–d). The splats resulted from the micron-sized particles act as the matrix that entraps the nano titania particles. The proportion of the micron-sized structure increases with the decrease of concentration of nano titania in the suspension. For the coatings made from less nano-titania-contained suspension (coatings R1A and R4A), the nano-sized titania particles are located on the pits or at the interfaces between the splats (Fig. 3b and c). More obvious anchoring phenomenon is seen as the content of nano titania particles increased (coating R7A, Fig. 3d). Further microstructure examination showed identical features of the nano titania particles on the surfaces of the coatings A, R1A, and R4A (Fig. 4a). The presence of the nano titania particles of 10–30 nm suggests that the starting nano titania particles retained their sizes after the flame spraying. However, as the concentration of nano titania particles in the suspension increased to 7 wt.%, enlarged particles (20–40 nm) are seen on the coating surface (Fig. 4b for coating R7A), indicating a partially molten state and slight growth by agglomeration of the particles, which is a common phenomenon during coating formation stage [20,25].

For photocatalytic applications of the TiO_2 coatings for decomposing organic compounds, they are essentially required to possess excellent hydrophilic ability so that materials can be absorbed on their surfaces [26,27]. It is noted in this study that the coatings with hybrid micro-/nano-structured coatings exhibit super-hydrophilic performances (Fig. 5b–d). During the contact angle measurement, it was realized that upon contact of the water droplet with the coating surface, the droplet immediately spread out, attaining a contact angle of ~0°. Only the coating made from the least suspension of nano titania showed remarkable hydrophobicity (106.38° of contact angle, coating R1A shown in Fig. 5a). Furthermore, the coating made from the micron-sized titania powders alone exhibits a contact angle of 88.58°. This feature can be well explained by topographical morphology of the coating that presence of micro-sized pores is evident on its surface (data not shown). For coating R1A, its hydrophobic characteristic should be attributed to specially arranged micro-/nano-feature at coating surface, which needs further investigation. Studies have already shown changes between hydrophobicity and hydrophilicity of nanostructured titania coatings by exposure to UV as a result of valence state of Ti and oxidation of positive holes [28]. The present hybrid structured TiO_2 coatings are much promising since they are always hydrophilic

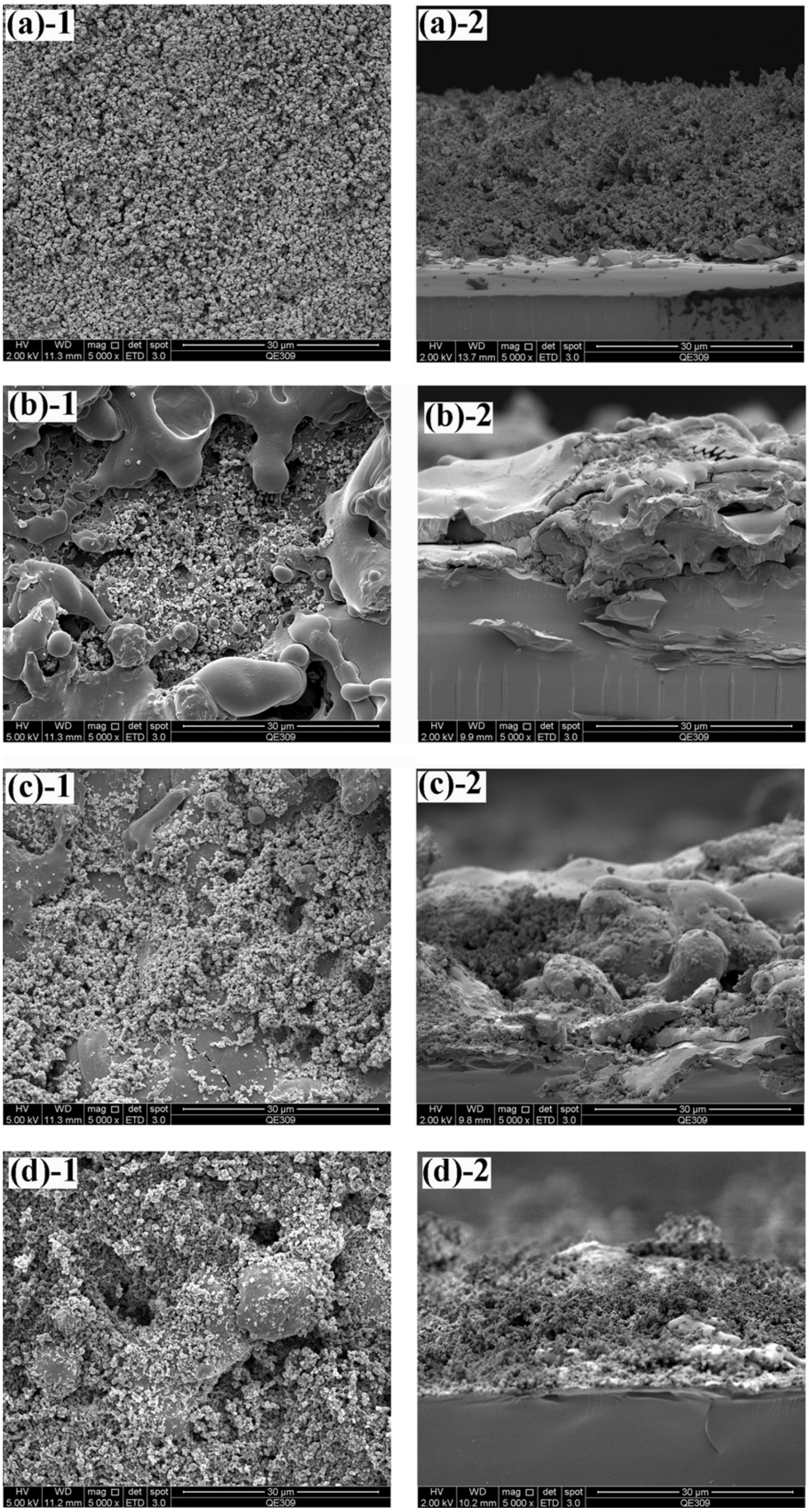

Fig. 3. FESEM characterization of the TiO_2 coatings showing hybrid micro/nano-sized microstructure, the coatings were made using (a) sole 7 wt.% suspension (coating A), (b) mixture of 1 wt.% suspensions and powders feedstock (coating R1A), (c) mixture of 4 wt.% suspensions and powders feedstock (coating R4A), and (d) mixture of 7 wt.% suspensions and powders feedstock (coating R7A), −1: topographical view, −2: cross-sectional view.

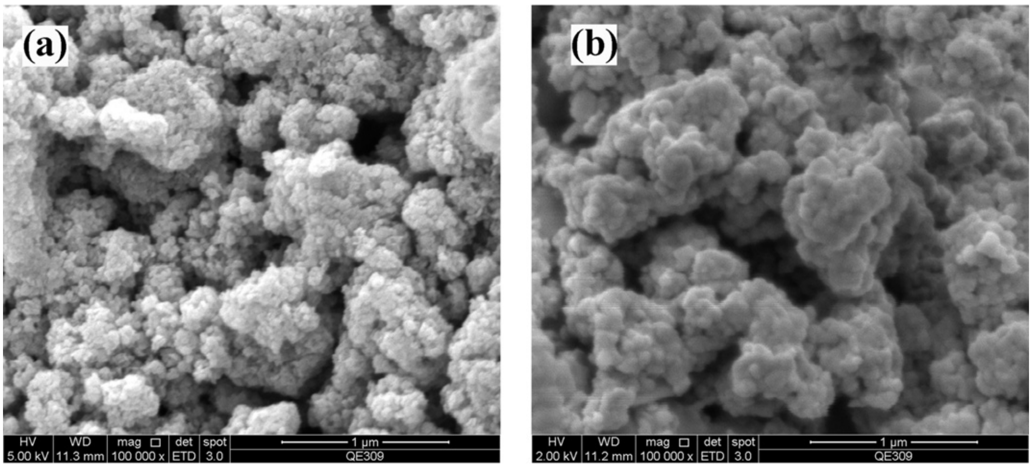

Fig. 4. Topographical view of the hybrid micro/nano-structured titania coatings showing predominant presence of the nano titania particles (10–30 nm) on the surfaces of the coatings A, R1A and R4A (a), and coexistence of the nano titania particles (10–30 nm) with agglomerated particles (0.5–2 μm) on the surface of coating R7A (b).

regardless of UV illumination or not. It has been proven that the intrinsic property of the nanostructures of TiO_2 (high specific surface area and nano-sized pores) gives rise to hydrophilic surfaces [29]. The micron-sized TiO_2 does not possess hydrophilicity. In this study, as the ratio of hydrophilic area (produced by nano TiO_2) to hydrophobic area (resulted from micron-sized TiO_2) is low (coating R1A in this case), the coating exhibits the characteristic of hydrophobicity. Overall hydrophilic feature was achieved as the content of the nanostructures is further increased (coatings R4A and R7A).

For functional purposed applications of the titania coatings, apart from the nanostructures, sufficient mechanical properties are also a big concern. Among those that play the key roles in determining the long-term stability of the functional coatings, microhardness and adhesion between coating and substrate are important variables. The thickness of all the TiO_2 coatings investigated in this study is in the range of 20–40 μm, far from the thickness required by the adhesion testing standard, e.g. ASTM C633. Other approaches are usually utilized for the nanostructured thin coatings [30,31]. The scratch test was employed in this study as the alternative technique for evaluating the adhesion of the coatings. The suspension sprayed TiO_2 coating (coating A in Fig. 6) exhibits the lowest Lc (9.2 N), while the coating deposited using the mixtures with 7 wt.% TiO_2 suspension shows the highest Lc value (25.5 N). All the coatings deposited by flame spraying the mixtures of suspension and powders feedstock (coatings R1A, R4A and R7A) have much higher Lc than that of coating A. The microhardness values of all the TiO_2 coatings deposited by flame spraying the mixtures of suspensions and powders feedstock (coatings R1A, R4A and R7A) are significantly higher than that of the suspension sprayed TiO_2 coating (Fig. 6). Furthermore, the increase of the concentration of nano TiO_2 particles in the suspensions from 1 wt.% to 4 wt.% yields a little decrease in the microhardness (220.8 HV_{25} to 173.1 HV_{25}). However, with further increase of the suspension concentration to 7 wt.%, the microhardness of the coating dramatically increases and reaches the maximum value of 534.1 HV_{25}. The microhardness of the coating deposited using only suspension (coating A) is very low (52.2 HV_{25}). Compared to coating A, coating R7A exhibits an improvement in microhardness by more than 9 times, coatings R1A and R4A show improvement by 3.2 and 2.3 times, respectively. For the coating deposited using the micron-sized titania powders alone, a microhardness vale of 851.8 HV_{25} was obtained. It is noted that the trend of Lc values of the coatings (25.3 N to 17.7 N to 25.5 N) is consistent with the changes in microhardness, suggesting a most likely optimum starting feedstock for successful deposition of the hybrid micro/nano-structured

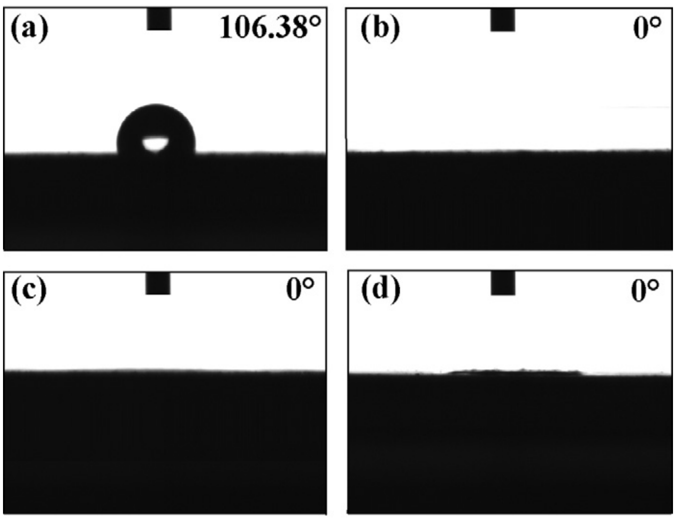

Fig. 5. Hydrophilic/hydrophobic property of the coatings by measuring the contact angle of water droplet spreading on (a) coating R1A, (b) coating R4A, (c) coating R7A and (d) coating A.

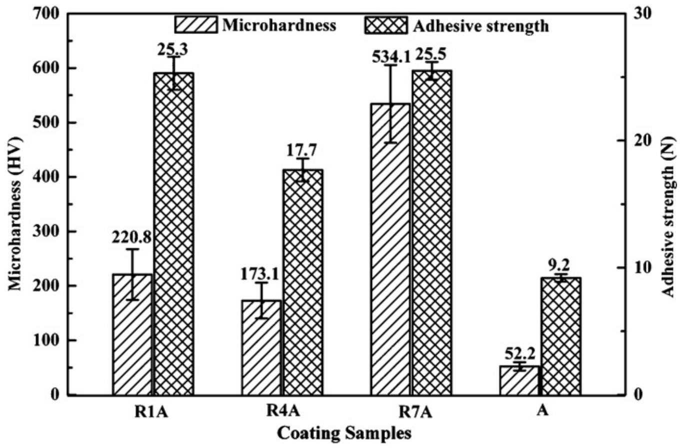

Fig. 6. Vickers hardness and adhesive strength (represented by the Lc) of the hybrid micro/nano-structured titania coatings.

titania coatings. Further investigation on the coating made form pure micron-sized titania powders showed an Lc value of 31.1 N. Taking into account the effect of microstructure on mechanical properties of the coatings, the varied microhardness and adhesion values of the TiO_2 coatings with hybrid micro-/nano-structures are attributed directly to the amount of non-melted particles (nano anatase particles in this case). It is clear that certain amount of micron-sized titania enhanced the microhardness and adhesion of the nano-titania based coatings. In this study, three kinds of promising TiO_2 coatings were fabricated by flame spraying the mixtures of suspension and powders feedstock in the hope of combining the benefits of suspension flame spraying and conventional flame spraying. As both the suspension and the micron-sized powders were ferried into the flame at the same time, the resultant coatings contain unmelted or partially melted TiO_2 nano particles together with the splats formed by the well-melted micron-sized TiO_2 particles. Furthermore, with more solvent being injected into the flame, the flame became colder because of evaporation of water. So when the suspension concentration is low, the TiO_2 nano powders in suspensions kept in un-melted state and were preserved well in the coatings (coatings R1A and R4A). These un-melted TiO_2 nano powders would deteriorate the contact of the well-melted micron-sized TiO_2 particles and hence are detrimental to the adhesion of the overall coatings. Nevertheless, when the suspensions concentration is raised to a certain high level (7 wt.% of nano titania particles in the suspension in this case), the TiO_2 nano powders attained a partially melting state and got anchored in the skeleton lamellar structure formed by the micron-sized TiO_2 powders. The improved microstructure predominantly accounts for the further enhanced mechanical properties of the coatings. The micro/nano-structured titania coatings fabricated in this study meet the essential requirements by their potential environmental purposed applications that demand large surface area and sufficient mechanical properties [32]. Co-existence of rutile and anatase might favor the photocatalytic performances, since according to previous studies [33,34], it is speculated that certain amount of rutile could enhance the photocatalytic activity of anatase-based titania. Further study on photocatalytic properties of the coatings is being conducted. The hybrid micro/nano-structured titania coatings investigated in this study open a window for fabricating the coatings with controllable anatase content and proportion of nanostructures.

4. Conclusion

Super hydrophilic hybrid micro/nano-structured TiO_2 coatings were deposited by flame spraying the mixtures of suspensions and powders feedstock. By using this novel approach, the relative contents of anatase and rutile in the coatings can be tailored by altering the concentration of nano titania particles in the suspension. The crystalline structure and nano feature of the TiO_2 nano particles in the suspension feedstock were retained. The micron-sized particles in the powders feedstock were well-melted and flattened to form a skeleton structure, responsible for remarkably enhanced mechanical properties of the hybrid micro/nano-structured TiO_2 coatings. There is an optimum concentration (∼7 wt.%) at which the nano TiO_2 powders in the suspension are partially melted and anchored in the lamellar structure resulted from the micron-sized TiO_2 powders.

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