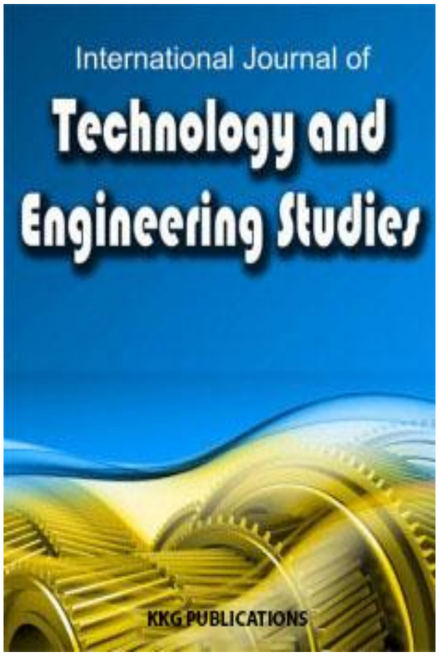

Key Knowledge Generation
Publication details, including instructions for author and
Subscription information:
http://kkgpublications.com/technology/

Plasma Sprayed TiO_2/Na-Titanate Composite Coating for Photocatalytic Degradation of Methylene Blue

SITI MARIAM.M[1], ZUHANA.A.Z[2], A.NIZAM. ABD[3]

[1, 2, 3] SIRIM Berhad, Advanced Materials Research Centre(AMREC), Malaysia.

Published online: 21 Jun 2015

To cite this article: M. Siti Mariam, A. Z. Zuhana, A. Nizam Abd, “Plasma sprayed TiO_2/Na-titanate composite coating for photocatalytic degradation of methylene blue,” *International Journal of Technology and Engineering Studies*, Vol. 1, no. 1, pp. 20-25, 2015.
DOI: ______________________

To link to this article: ______________________

KKG PUBLICATIONS

International Journal of Technology and Engineering Studies

IJTES

Vol. 1, no. 1, pp. 20-25, 2015

PLASMA SPRAYED TIO_2/NA-TITANATE COMPOSITE COATING FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

SITI MARIAM.M[1*], ZUHANA.A.Z[2], A.NIZAM. ABD[3]

[1, 2, 3] SIRIM Berhad , Advanced Materials Research Centre(AMREC), Malaysia

Keywords:

Titanium Oxide
Sodium Titanate
Photocatalytic Activity
Methylene Blue
Plasma Spray

Received: 16 March 2015

Accepted: 13 May 2015

Published:21 June 2015

Abstract. Photocatalytic degradation of methylene blue (MB) in aqueous solution using plasma sprayed TiO_2 coating has to be improved. Hydrothermally prepared Na-titanate which has wire-like structure was spray dried into granules and mixed with nanostructured TiO_2 granules the ratio of 50(TiO_2):50(Na-titanate) wt% to form the composite feedstock powder for plasma spraying. The prepared composite feedstock TiO_2/Na-titanate was deposited on the metal substrate using one of the thermal sprays coating method which is plasma spray. In this coating technique, the feedstock material in the form of powder is injected into the plasma stream where the particles are heated and accelerated at high velocity towards the substrate. The particles are impacted, splatted and rapidly cooled on the substrate and formed the coating. The microstructure of the coatings was observed by field emission scanning electron microscope (FESEM) and it showed that the coating was composed of melted and partially melted particles. The phase composition of the coatings was analysed by X-ray diffraction (XRD) and the result showed the presence of rutile and small amount of anatase phase. The photocatalytic activity of the coatings was determined by measuring the degradation of methylene blue (MB) dye in an aqueous solution under UV-irradiation. The MB degradation of the prepared composite coating was 67.3% after 8h UV-irradiation.

INTRODUCTION

Plasma sprayed TiO_2/Na-titanate composite coating for photocatalytic degradation of methylene blue.

Titanium oxide (TiO_2) has been used as photocatalyst for the degradation of many organic pollutants in water and air. It is a very important photocatalyst material due to its strong oxidizing power, non-toxicity and photostability [1]. TiO_2 photocatalyst can be used in the form of powder or coating. However, the powder form is difficult to be removed completely from the slurry photoreactor and subsequent recycling process also was not easy. Therefore, it has to be immobilized on the support in the form of coating.

Various coating method have been used such as sol-gel process, chemical vapor deposition (CVD), physical vapor deposition (PVD), atomic layer deposition (ALP) and thermal spray [12-16]. Among these coating technologies, thermal spraying process such as plasma spray (PS), high velocity oxy-fuel spraying (HVOF) and suspension plasma spraying (SPS) have been used to obtain TiO_2 coatings for photocatalyst application [2-7]. The advantages of thermal spraying methods are simple operation, fast deposition process, forms thicker and porous coatings, low cost and wide selection of materials. Besides, it can produce large active coatings with excellent mechanical properties [9,10]. Thermal spraying is a process where the feedstock powders are injected into the flame, heated and accelerated at high velocity and impacted on to the substrate. The projected particles were flatten, rapidly cooled and solidified on the substrate which resulted in typically quenched microstructure. The process parameters such as power, plasma gases flowrate, carrier gas flowrate, spraying distance and powder flowrate influenced the coatings characteristics. In this research, plasma spray technique which is one of the thermal spray methods was used to prepare coatings.

Nanostructured TiO_2 coatings have been researched using nanosized TiO_2 powders by plasma spraying [2-10]. Research showed that nanostructured coating has improved mechanical properties over the conventional coatings [9-11]. The nanopowders are reconstituted into sprayable size prior to plasma spraying because the nanopowders cannot be fed directly into plasma stream because of their low mass and poor flowability [2-10]. Therefore the nanopowders are agglomerated by spray drying process [18].

Many research works on plasma spraying anatase phased TiO_2 powders resulted with rutile phase due to instability of mestastable anatase phase and rutile is not a favourable phase for photocatalytic activity [2-7]. Retaining

*Corresponding author: Siti Mariam.M
E-mail: smariamm@sirim.my

high amount of anatase phase using plasma spray coating technique is the main issue for photocatalyst application. Various adjustment such as feedstock powder modification, spraying parameters and suspension spraying have been studied in order to reduce the phase transformation of anatase to rutile during plasma spraying [2-7].

In this work, a composite feedstock was prepared by mixing Na-titanate nanowire powder (spray dried) and TiO_2 nanopowder (spray dried) for plasma spray coating. The reason of using Na-titanate nanowire was because it has high thermal stability compared to TiO_2 nanoparticles [17, 19-20]. It can be produced using facile hydrothermal process by heating TiO_2 nanopowder in alkaline solution [17]. The post-heat treatment on Na-titanate nanowires at about 600°C have transformed it into anatase TiO_2 nanowires and this phase remained stable at 800°C with wire-like structure [17]. The spray dried Na-titanate nanowire powder was utilized to obtain anatase phase in the coatings. The prepared composite feedstock (TiO_2/Na-titanate) was plasma sprayed and the photocatalytic activity of the coating was evaluated.

METHODS

Feedstock Powder

The feedstock powder was prepared by mixing two types of spray dried powder which are Na-titanate nanowires and TiO_2 nanopowders at the ratio of 50:50 weight percent. Both nanosized powders were spray dried separately. The particle size range of the feedstock powders were about 10-30 microns. The morphology of the spray dried feedstock powder of Na-titanate nanowires and TiO_2 nanopowders are shown in Fig.1, respectively.

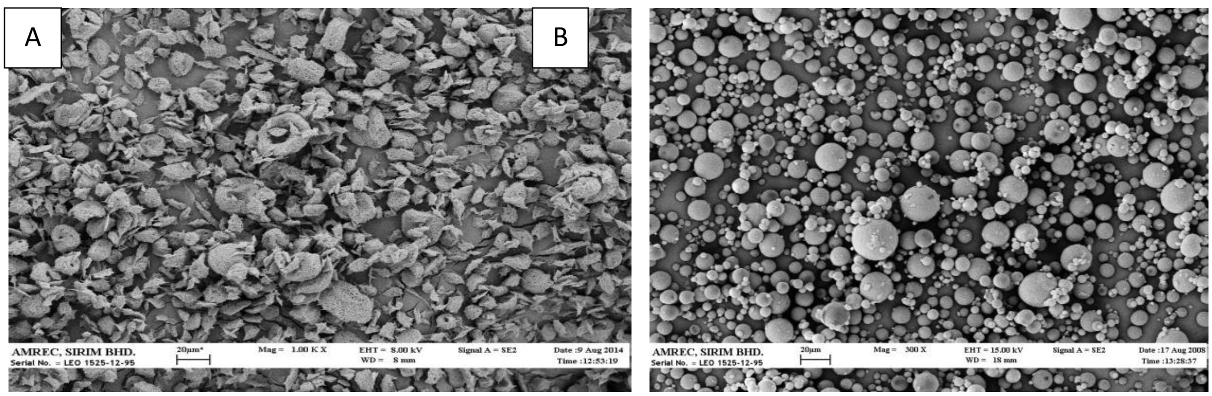

Fig. 1. SEM micrograph of spray dried (A) Na-titanate powder and (B) TiO2 powder

Coating process

The prepared feedstock powders was deposited on to stainless steel substrates (20mm x 5mm) using Praxair plasma spray with SG-100 torch mounted on a five-axis robot. Prior to coating the substrates were sand blasted and ultrasonically cleaned in ethanol and deionized water. The operation parameters used for the coating process is presented in Table 1. The substrates are preheated before coating. TiO_2 coating was also prepared using TiO_2 feedstock for comparison purpose.

TABLE 1
PLASMA SPRAY COATING PARAMETER

Current (A)	Primary gas Argon (lpm)	Secondary gas Helium (lpm)	Spraying distance (mm)	Number of coating cycle
300	72.0	8.7	80	8

Notes. A= Ampere, lpm = liter per minute, mm = milimeter

Coating Characterisation

The produced coatings were characterized for microstructure and phase composition using field emission scanning electron microscope (FE-SEM, LEO-1525) and X-ray diffraction (Bruker D8) with Cu Kα radiation. Raman spectroscopy (Renishaw, laser λ=633nm) was used to determine the phase composition of the coating.

Photocatalytic Evaluation

The photocatalytic experiment of the coatings was carried out by immersing the coated samples in 90ml of 5ppm methylene blue (MB) aqueous solution. The surface areas of the sampels were 6.28cm^2. The immersed samples were left in dark for 24h prior to UV-irradiation.

The samples were irradiated using UV-lamp (λ=365nm, 45W) for 8h at room temperature. The changes of MB concentration at every 2h were determined by measuring the absorbance intensity at maximum absorbance wavelength 665nm by UV-Vis spectrophotometer (Perkin Elmer-Lambda 25).

RESULTS AND DISCUSSION

Microstructure and Phase Composition of the Feedstock and Coatings

Fig. 2 (a & b) shows the XRD spectra of the feedstock powder TiO_2 anatase phase and Na-titanate nanowires which was spray dried prior to deposition. The morphology of both spray dried powders is shown in Fig.1 (A & B). The spray dried TiO_2 powder in Fig.1 (B) showed spherical shape, while the phase composition showed the same anatase phase as the initial nanopowder. The spray dried Na-titanate XRD spectrum showed a low crystalline structure as in Fig.2 (b).

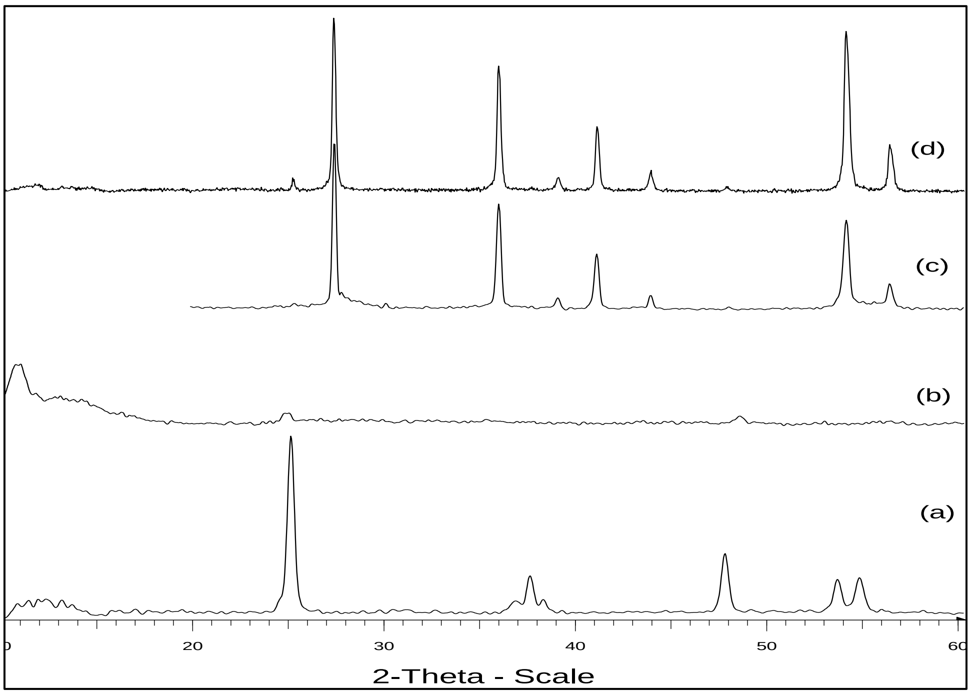

Fig. 2. XRD spectrum of the spray dried feedstock powder (a) TiO2 anatase, (a) Na-titanate nanowires and plasma sprayed (c) TiO2 and (d) TiO2/Na-titanate

Fig. 2 (a) and (b) shows the XRD spectra of the feedstock powder TiO_2 anatase phase and Na-titanate nanowires which were spray dried. The morphology of both spray dried powders is shown in Fig.1 (A) and (B). The spray dried TiO_2 powder in Fig.1 (B) showed spherical shape granules and the XRD pattern shown in Fig.2 (a) belongs to anatase phase same as the initial powder. The spray dried Na-titanate showed a low crystalline structure as in Fig.2 (b). The spray dried powders have advantages such as free-flow characteristic and sprayable micrometer-sized powders that make the powder to flow easily through the powder feeder system [18].

The plasma sprayed TiO_2/Na-titanate composite resulted with mixture of anatase and rutile phase and there was no traces of Na-titanate in the XRD pattern of the coatings as shown in Fig.2 (d). This showed that Na-titanate was recrystallized and decomposed to major phase rutile. The main peak (101) anatase at 2theta ≈25.4° was observed in the XRD result (Fig.2 (d)). This indicates that anatase phase structure could be retained in the prepared TiO_2/Na-titanate composite coatings.

The XRD result of plasma sprayed TiO_2 alone as shown in Fig.2 (c) was compared with plasma sprayed TiO_2/Na-titanate composite. In this TiO_2 coating (Fig.2(c)) the anatase phase from the initial feedstock powder has transformed fully to rutile phase after plasma sprayed.

The surface and cross-section microstructure of the prepared coating was observed under FE-SEM and it showed that the coating was constructed with two kinds of regions which are melted (M) and partially melted (PM) as shown in Fig.3(a & b). The melted region is mainly consisted of rutile phase because it is the stable phase [21]. Only a few partially melted regions were observed on the surface and cross-section of the coatings that could be influenced by the coating condition or the composite powder.

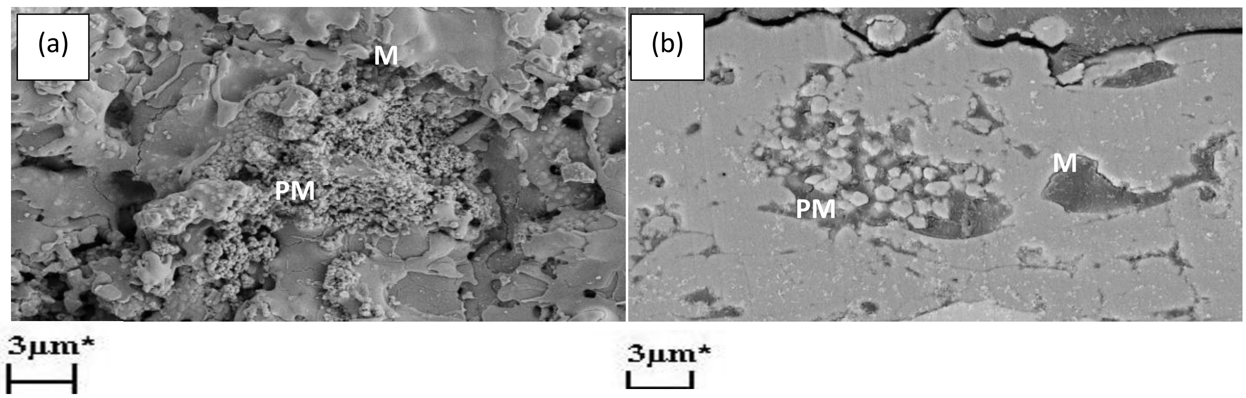

Fig. 3. SEM images of TiO2/Na-titanate composite coating (a) surface (b) cross-section. Notes. Melted area is marked as (M) and partially melted area is marked as (PM).

Besides, the coating contained with some trapped partially melted particles of due to fast deposition and rapid cooling as shown in Fig.3(b) marked with PM. The coating also appeared to be porous as in Fig.3 (a). Some microcracks also observed on the cross-section of the coating. Various factors such as plasma spray condition, particle size of the powders and plasma temperature and gases could influence the coating condition and final phase composition [21]. The small amount of anatase phase as in Fig.2 (d) could be related to these factors.

Fig.4 shows Raman spectra which were collected on the surface of the prepared coating. Three spectrums corresponds to different area of the coated surface, which is spectrum 1, 2 and 3 as shown in the Fig.4. The obtained spectrums were found to fit with anatase and rutile reference spectrum, respectively, as shown in Fig.4 (d). The peaks at band 143.1cm^{-1}appeared in spectrum 2 and 3 matched with TiO_2 anatase and the peaks at band 238.2, 447.9 and 611.9 cm-1 of the three spectrums (1-3) matched with rutile reference spectrum, respectively. The results from Raman analysis have further confirmed the presence of anatase phase in the coatings.

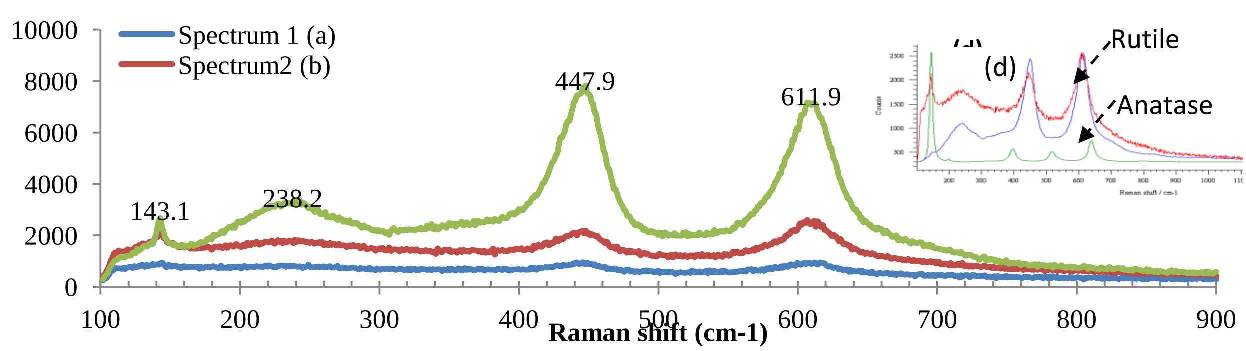

Figure 4. Raman spectra of the TiO2/Na-titanate composite coating, collected at three different area on the surface of the coating marked as (a) spectrum 1,(b) spectrum 2, (c) spectrum 3 and (d) reference spectrum for anatase and rutile peaks.

Photocatalytic Activity of the Coating

The photocatalytic activity was determined by measuring the degradation of MB in aqueous solution. The blank (uncoated) and the coated samples (TiO_2 and TiO_2/Na-titanate composite) were left in contact with MB under UV light irradiation (λ=364nm). The UV-irradiation was conducted for 8h with an interval of every 2h for sampling purpose. The MB absorbance at λ =664nm was obtained from the UV-Vis results for the uncoated and coated samples. Fig.5 showed the degradation of MB using blank sample that showed no significant degradation. The TiO_2 coatings (Fig.5) resulted with poor degradation profile. However, the TiO_2/Na-titanate coating has improved the degradation efficiency of MB. The percentage of MB degraded from initial amount using TiO_2/Na-titanate coating was about 67.8%. The degradation percentage was improved about 36.1% by comparing the degradation obtained using TiO_2 coating (31.7%). This result indicated that the presence of anatase phase in the coating (Fig.2(d)) which is an important phase required for photocatalytic activity has proven its photoactive capability under UV-light irradiation as compared to rutile phase (Fig.2(c)). The use of Na-titanate as composite feedstock for plasma spray has showed its effect on improving the MB degradation efficiency by preserving anatase phase in the coating..

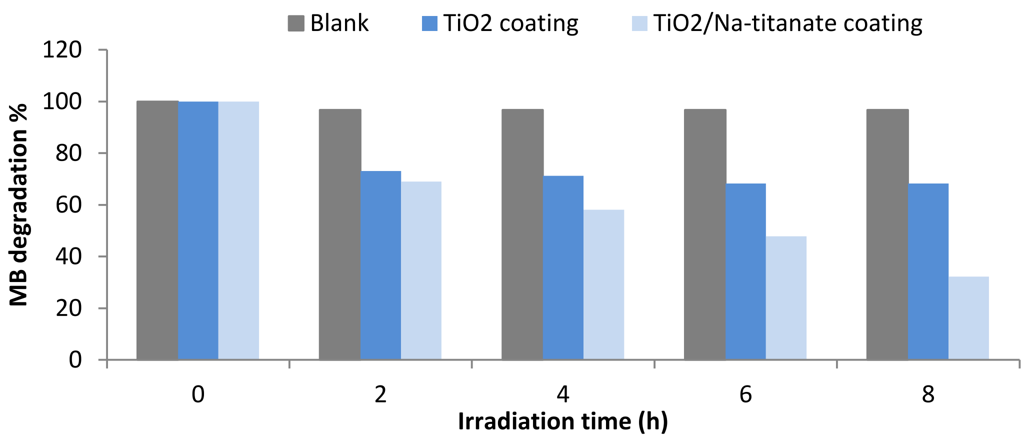

Fig. 5. The photodegradation percentage of MB in aqueous solution with respect to UV irradiation time for blank, TiO2 coating and TiO2/Na-titanate coating, respectively.

CONCLUSION

Plasma sprayed TiO_2/Na-titanate composite was successfully prepared , characterized and evaluated photocatalytic activity using MB aquoes solution as an organic pollutant. The plasma sprayed TiO_2 coating was also discussed in this work for comparison purpose. The XRD results detected the presence of anatase phase in TiO_2/Na-titanate coating and it was not detected in TiO_2 coating. Raman analysis further revealed the presence of anatase in the coating. This explains that the addition of Na-titanate (nanowire) has shown significant improvement in retaining anatase crystalline phase in the coating. The photocatalytic activity of the TiO_2/Na-titanate coating has improved the degradation of MB from 31.7% (TiO_2 coating) to 67.8%, which explained that the anatase phase in the coating with UV-light irradiation influenced the catalytic properties of the TiO_2/Na-titanate coating. Further study has to be carried out by using Na-titanate (100%) as feedstock in future work to clarify its influence.

REFERENCES

[1] J. Yu and H. Yu. C. Bei. M. Zhou and X. Zhao, “Enhanced photocatalytic activity of TiO_2 powder (P25) by hydrothermal,” *Journal of Molecular Catalysis A: Chemical*, Vol. 253, no. 1, pp. 112-118, 2006.

[2] Z. Yi, J. Liu, W. Wei, J. Wang and S. W. Lee, “Photocatalytic performance and microstructure of thermal-sprayed nanostructured TiO_2 coatings,” *Ceramics International*, Vol. 34, no. 2, pp. 351–357, 2008.

[3] E. Bannier, G. Darut, E. Sanchez, A. Denoirjean, M. C. Bordes, M. D. Salvador and E. Rayon, “Microstructure and photocatalytic activity of suspension plasma sprayed TiO_2 coating on steel and glass substrates,” *Surface & Coatings Technology*, Vol. 206, no. 2, pp. 378-386, 2011.

[4] S. Kozerski, F. L. Toma, L. Pawlowski, B. Leupolt, L. Latka and M. L. Berger, “Suspension plasma sprayed TiO2 coatings using different injectors and their photocatalytic properties,” *Surface & Coatings Technology*, Vol. 205, no. 4, pp. 980-986, 2010.

[5] M. Bozorgtabar, M. Rahimipour, M. Salehi and M. Jafarpour, “Structure and photocatalytic activity of TiO_2 coatings deposited by atmospheric plasma spraying,” *Surface & Coatings Technology*, Vol. 205, no. 2(S), pp. 229-S231, 2011.

[6] G. Mauer, A. Guignard and R. Vaßen, “Plasma spraying of efficient photoactive TiO_2 coatings,” *Surface & Coatings Technology*, Vol. 220, pp. 40-43, 2013.

[7] M. C. Bordes, M. Vicent, A. Moreno, R. Moreno, A. Borrell, M. D. Salvador and E. Sánchez, “Microstructure and photocatalytic activity of APS coatings obtained from different TiO_2 nanopowders,” *Surface & Coatings Technology*, Vol. 220, pp. 179-186, 2013.

[8] D. Chen, E. H. Jordan and M. Gell, “Porous TiO_2 coating using the solution precursor plasma spray process,” *Surface & Coatings Technology*, Vol. 202, no. 24, 6113-6119, 2008.

[9] M. Gell, E. H. Jordan, Y. H. Sohn, D. Goberman, L. Shawa and T. D. Xiao, “Development and implementation of plasma sprayed nanostructured ceramic coatings,” *Surface & Coatings Technology*, Vol. 146-147, 48-54, 2001.

[10] A, Ibrahim, R. S. Lima, C. C. Berndt and B. R. Marple, “Fatigue and mechanical properties of nanostructured and conventional titania (TiO_2) thermal spray coatings,” *Surface & Coatings Technology*, Vol. 201, no. 16, pp. 7589-7596, 2007.

[11] S. M. Forghani, M. J. Ghazali, A. Muchtar and A. R. Daud, “Mechanical properties of plasma sprayed nanostructured TiO_2 coatings on mild steel,” *Ceramics International*, Vol. 40, no, pp. 7049-7056, 2014.

[12] C. S. Lee, J. Kim, J. Y. Son, W. Choi and H. Kim, “Photocatalytic functional coatings of TiO_2 thin films on polymer substrate by plasma enhanced atomic layer deposition,” *Applied Catalysis B: Environmental*, Vol. 91, no. 3, pp. 628-633, 2009.

[13] C.Y. Wu, Y. L. Lee, Y. S. Lo, C. J. Lin and C. H. Wu, “Thickness-dependent photocatalytic performance of nanocrystalline TiO_2 thin films prepared by sol–gel spin coating,” *Applied Surface Science*, Vol. 280, pp. 737-744, 2013.

[14] S. R. Patil, B. H. Hameed, A. S. Škapin and U. L. Štangar, Alternate coating and porosity as dependent factors for the photocatalytic activity of sol–gel derived TiO 2 films. *Chemical Engineering Journal*, Vol. 174, no. 1, pp. 190-198, 2011.

[15] H. Lee, S. H. Park, S. J. Kim, B. H. Kim,., H. S. Yoon, J. S. Kim and S. C. Jung, “The effect of combined processes for advanced oxidation of organic dye using CVD TiO_2 film photo-catalysts,” *Progress in Organic Coatings*, Vol. no. 74, pp. 758-763, 2012.

[16] C. C. Chen, W. J. Yang and C. Y. Hsu, “Investigation into the effects of deposition parameters on TiO*2* photocatalyst thin films by rf magnetron sputtering,” *Supperlattices and Microstructure*, Vol. 46, no. 3, pp. 461-468, 2009.

[17] R. Yoshida, Y. Suzuki and S. Yoshikawa, Syntheses of TiO_2(B) nanowires and TiO_2 anatase nanowires by hydrothermal and post-heat treatments. *Journal of Solid State Chemistry*, Vol. 178, no. 7, pp. 2179-2185, 2005.

[18] M. Vicent, E. Sánchez, A. Moreno and R. Moreno, “Preparation of high solids content nano-titania suspensions to obtain spray-dried nanostructured powders for atmospheric plasma spraying,” *Journal of the European Ceramic Society*, Vol 32, no. 1, 185-194, 2012.

[19] S. Pavasupree, Y. Suzuki, S. Yoshikawa and R. Kawahata, “Synthesis of titanate, TiO_2 (B), and anatase TiO_2 nanofibers from natural rutile sand,” *Journal of Solid State Chemistry, Vol. 178*, no. 10, pp. 3110-3116, 2005.

[20] R. A. Zá rate, S. Fuentes, A. L. Cabrera and V. M. Fuenzalida, “Structural characterization of single crystals of sodium titanate nanowires prepared by hydrothermal process,” *Journal of Crystal Growth*, Vol. 310, no. 15, pp. 3630-3637, 2008.

[21] G, Bertrand, N. Berger-Keller, C. Meunier and C. C. Coddet, “Evaluation of metastable phase and microhardness on plasma sprayed titania coatings,” *Surface & Coatings Technology*, Vol. 200, no. 16, pp. 5013-5019, 2006.

— This article does not have any appendix.—