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Photocatalytic Properties of TiO_2 Coatings Prepared by Cold Spray Process

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1.Introduction

The cold spray process was first developed in the mid-1980s at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Science in Novesibirsk[1].TiO_2coating has been widely used because it shows photocatalytic capable effect of purifying pollution such as in air and water. Several coating techniques such as sol-gel, sputtering and, electroplating have been developed to improve the efficiency of the TiO_2 coating. Cold spray technique is studied as an alternative process rather than conventional thermal Spray process (plasma and/or arc). The objective of this study is to evaluate and characterize the cold sprayed TiO_2 coating layers with agglomerated powders, which will be prepared by two different powder processing: spray dry method and evaporated powder method. The effect of different powder agglomeration on the photocatalytic reactivity was investigated.

2.Experimental Procedures

Powder composition of TiO_2 particles with the addition of nano ZnO particles is listed in Table 1. TiO_2 (P-25 Degussa, Korea) and ZnO (Z80204-02 Nanotek, Japan) nanopowders were used. The powder preparation methods used were "spray dry" (spray dry machine: SD-1000 EYELA, Japan) and "evaporated powder" (evaporator machine: R-114 BUCHI, Swiss). The powders were prepared by ball milling technique using pure water for the "spray dry" and ethyl alcohol (Duksan Co., Korea) for the "evaporated powder" method for 24 hours spinning with alumina balls. Cold spray process was used to make coatings on an aluminum substrate. A schematic representation of the cold spray process is shown in Fig. 1.

Table 1. Experiment configuration

Sample	Powder Composition (wt %)	Powder prepared Method
a	100%-TiO_2	Spray dry
b	100%-TiO_2	Evaporated powder
c	90%-TiO_2/10%-ZnO	Spray dry
d	90%-TiO_2/10%-ZnO	Evaporated powder

The characterization of the coatings was performed using SEM (JSM-6700F JEOL, Japan), XRD (X-ray diffractometer D/max2200, Rigaku, Japan), and roughness test (Form Talysurf Plus, Taylor-Hobson, U.K.). Evaluation of the photocatalytic reactivity of the coatings was performed in a device developed in our laboratory; schematic diagram of this device is shown in Fig. 2. The evaluation was made by the detection of benzene in air. Benzene (100ppm concentration) was injected in a lm^3 reactor. After 30minute blank tests were performed (up to 5 hours) to monitor the benzene concentration. By retrieving small portions using a gas chromatography (HP-6890) equipped with a flame ionization detector and a capillary column(HP-5). A discharge photoelectrocatalytic system was an aluminum plate introduced into the reactor. The cold sprayed coatings of TiO_2 on aluminum plate were used. Photoelectrocatalytic degradation of benzene in air was carried out at

room temperature. During the experiment, gas sample were taken out in 30 minute intervals for gas chromatographic analysis to monitor variation in the concentration of the benzene.

3.Results and Discussion

Figures 3 and 4 shows the SEM micrographs and XRD spectra of the cold sprayed coating layers, respectively. As shown inFig. 3, it can be observed that the surfaces of all cold sprayed coating layers are similar, the particle sizes are also similar and the uniformity can be observed. The XRD data (Fig. 4) also shows similar peaks in all samples, therefore, the addition of 10wt% ZnO into TiO_2 does not appear to promote any phase changes. Also the variation of powder prepared method does not show the variation of the surfaces and the Anatase phase transformation. However, the surface roughness (Fig. 5) did show some variation. When the ZnO is added to the TiO_2 powder only a very slight decrease of surface roughness was observed, but the powder prepared method does have a great difference in the surface roughness of the coatings. For the spray dried coatings (samples a and c) the surface roughness is higher than that of the cold sprayed coatings performed by evaporated powder technique (samples b and d). The comparison of the photocatalytic reactivity with various samples is shown in Fig. 6. Inspecting the early stages (first hour) of the coating action to remove benzene from air. It shows that the fastest purifying coatings are those of samples a and c, which are the ones performed by spray drying powder technique, disregarding the type of powder used. However, for the case of the coatings performed using evaporated powder(samples b and d) it is observed that the addition of 10% of ZnO is a promoter of photocatalytic effect. This is also corroborated for the coatings made by spray dry but after long action time. Particularly, Fig. 6 shows that the sample coated by spray dried nano-powder with the addition of 10wt% ZnO achieved perfect purification of the air environment desintegrating all the contaminant agent (benzene) after 600 minutes. All the coatings tended to stabilization in photocatalytic action after 30 minutes (spray dry, samples a and c) and 60 minutes (evaporated powder, samples b and d). After those periods of time the four coatings performed their purification objective at similar rate, only the spray dried coating thatcontained ZnO achieved complete removal of benzene (after 600 minutes), the rest of the coatings yielded a similar value of 3 ppm of benzene approximately.

4.Summary

Four different coatings deposited using cold spray process were studied with two different powder agglomerating techniques (spray dry and evaporated powder) and using TiO_2 nano-sized powders with and without a 10wt% addition of ZnO. Characterization was performed by SEM, XRD and roughness test. Also the photocatalytic effect of the coatings was evaluated. Although the change of powder preparation techniques and the addition of ZnO into TiO_2 did not show appreciable variations in the surface morphology and Anatase phase transformation, it did show influence on the surface roughness of the coatings, the highest roughness being found in the coatings made by spray powder prepared method. Regarding the photocatalytic effect it was observed that the using of spray dry coating and the addition of ZnO are promoters of purification at higher rates.

References

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