

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels



Contents available at: www.informaticsjournals.com/index.php/jmmf

Studies on the Nano TiO2 Photocatalyst Performance Based on The SiC Foam Ceramics

Yan Yan^{1,2}, Liyan Zhang^{1,2*}, Kuankuan Jia^{1,2}, Buqi Shang^{1,2}, Yongjiang Ge^{1,2} and Bo Zhao^{1,2}

¹*Hebei Key Laboratory of Data Science and Applications, North China University of Science and Technology, Tangshan 063000, China; yanjxky@126.com* ²*Engineering Computing and Simulation Innovation Laboratory, North China University of Science and Technology, Tangshan 063000, China*

Abstract

Nano TiO2 photocatalyst is a kind of polymorphism catalyst, it have small particles that make it difficult to disperse, difficult to recovered, and has the little measure contact area. However the SiC foam ceramics material with highly porous, low alloyed steal bulk density and three-dimensional model, coalescence pore structure. To prevent the application of photocatalyst happen, this article aim at studies on the preparation and properties of nano TiO2 photocatalyst based on the SiC foam ceramics, which in order to offer help to the widespread application of photocatalyst. The study results confirms that the optimum dip times is 4 times when load the coating on the surface of SiC foam ceramic with soaking technology; Stereoscopic photograph show that the modified nano TiO2 photocatalyst white coating on the surface of SiC foam ceramic is uniform; EDS analytic result show that the main elements of the modified nano TiO2 photocatalyst white coating on the surface of SiC foam ceramic compose of Ti, O, Al ,Si; The photocatalytic efficiency of A,Si-Codoped TiO2 coating is better than nano TiO2 powders.

Keywords: AZ91 Magnesium, Corrosion Behaviour, Magnesium Matrix Composite, SiC Particles, α Phase and β Phase

1. Introduction

The foam ceramics developed after porous ceramics and honeycomb ceramics have excellent characteristics such as high porosity, low alloyed steal bulk density, specially 3-dimensional network skeleton and coalescence pore structure. The sintering products with foam and ceramic is similar. According to different purposes, silicate mineral, Alumina, SiC and its composites can be used as foam matrix material (Qing-zhu, 2002). SiC foam cetamic has been widely used in molten metal filtration because of its high temperature intension, resistance to heat shocks, softening temperature, low thermal expansion coefficient and thermal conductivity (Alvin, 1991).

Photocatalyst is the most important part of photocatalytic process. At present ,the catalysts for photocatalytic degradation of organic pollutants at the environment are mostly N-type semiconductors. This semiconductor can simply convert organic matter into carbon dioxide and water through light and oxidants: ZnO and TiO2 are common N type semiconductor catalysts (Fujishima, 2000). Nano TiO2 is a kind of polymorphism

*Author for correspondence

compound, transformation of TiO2 photocatalysts pure low temperature, the reaction in the high temperature environment will seriously reduce the photocatalytic activity. In addition, it is difficult to disperse, difficult to recovered, and has the little measure contact area.

Therefore, many scholars have studied how to improve the photocatalytic properties of TiO2 nanoparticles. In order to solve the existing problems of photocatalysis. Chen, et al.(2001) prepared TiO2/SiO2/y-Fe2O3 nano catalyst with magnetic separation ability, which is based on y-Fe2O3 as core, TiO2 as shell, and SiO2 as shielding agent between core-shell. The degradation of fuel under UV and visible light shows that its photocatalytic activity is lower than that of P-25, but it has high stability in cyclic photocatalysis experiments (Chen et al., 2001). Chung, et al. (2004) were prepared by sputtering at high temperature with nickel ferrite as the core and TiO2-SiO2 as the shell. The experimental results show that the photocatalytic activity of the sample is improved, and the photocatalyst is washable and easy to separate (Chung, et al., 2004). The nano TiO2 is loaded on the carrier surface is an important means to solve the photocatalyst loss and difficult separation, the load current is often used in photocatalytic nano TiO2 and nano TiO2 uniform and continuous film formed in the matrix is smooth or in the form of particles distribution in the two kinds of methods of surface of the matrix, the former can improve its photochemical properties, the latter has large specific area and good adsorption performance. Ding, et al. (2000) by chemical vapor deposition TiO2 thin films were prepared on silica gel, the results show that the nano particles can be uniformly distributed on the surface of silica, and has better stability of (Ding et al., 2000). Anpo, et al. (1992) composite photocatalysts were prepared using porous carrier made of heat-resistant glass as Peng Portland, methane and methanol in photocatalysis the reaction of carbon dioxide and water generated by the experiment showed that the photocatalytic activity of (Anpo et al., 1992). Ochuma, et al. (2007) three to two aluminum oxide ceramic foam as photocatalyst carrier nano TiO2 load, The results show that the catalyst has high photocatalytic activity of (Ochuma et al., 2007).

SiC foam ceramics with high temperature resistance, corrosion resistance and other physical properties, so that it became the preferred material for the immobilization of TiO2 photocatalyst. The metal nonmetal Codoped TiO2 photocatalyst by the preparation method of a coating layer is fixed on the surface made of SiC foam ceramic, interconnected the three-dimensional network structure characteristics in order to improve the application of SiC foam ceramic unique nano TiO2 photocatalyst surface area, to enhance the photocatalytic efficiency.

2. Experimentation

2.1 Experimental Reagents and Instruments

Reagent:

CP: tetrabutyl titanate (C16H36O4Ti)

AR: absolute ethyl alcohol (C2H5OH, glacial acetic acid (Hac), hydrogen nitrate (HNO3, tetraethoxysilane (Si(OC2H5)4, aluminium nitrate (Al(NO3)3·9H2O, acetone (C2H6O, acetone and polyethylene glycol (PEH-2000).

Instrument:

Electronic balance (BS223S),Vacuum drying box (DZF-6060), Ultrasonic cleaning instrument (KQ-700DV), Muffle furnace (KSF1600), beaker, cylinder, mortar, dropper, etc.

The surface structure of SiC foam ceramic supported surface was characterized by Stemi2000-C stereo microscope, and the elemental composition and distribution of modified TiO2 coating were measured by PV9900 energy spectrometer (EDS).

2.2 Preparation Method

The preparation process of SiC foam ceramic is shown in Figure 1. The pretreatment of SiC foam ceramic is the cleaning of SiC foam ceramic carrier, and its cleanliness determines the bonding effect between nano TiO2 coating and SiC substrate. The operation procedure is as follows:

Wash with water containing detergent. Clean it with deionized water for 5 minutes.

Placed in acetone solution, ultrasonic treatment for 5 minutes, then placed in deionized water, ultrasonic treatment for 5 minutes.

Place in the vacuum drying box at least for drying.

The process of Al-Si Codoped TiO2 nanopowders is shown in Figure 2.

Solution A: in a certain water bath temperature in three flasks, four butyl titanate is dripped into the ethanol solution, uniform stirring for 30 minutes after adding a certain amount of chelating agent and acetic acid, and then stirred for 30 minutes or so to get solution A. B: after adjustment by nitric acid ethanol solution with a certain pH value is the solution B. mixed solution is A, mixed B two solution.

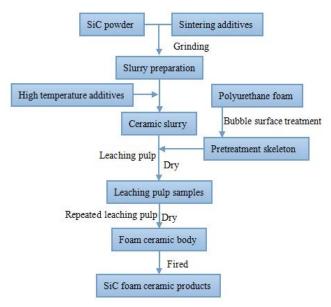


Figure 1. Preparation process flow chart of SiC foam ceramic.

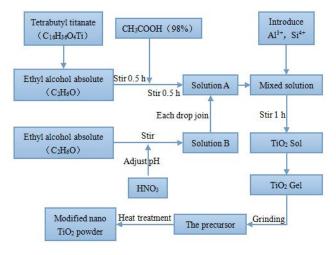


Figure 2. Process flow diagram of Al-Si codoped TiO2 nano powder.

Preparation of slurry: Al-Si Codoped TiO2 nanoparticles modified with PEG-2000 in accordance with the ratio of 4:1 mixture and grinding evenly, adding distilled water to make a certain concentration of slurry.

SiC foam ceramics will be pretreated by dipping process, 100OC dip each time after the completion of the drying process in a dry box for 15 minutes, then remove the dip of treatment time, after heat treatment several times of leaching 1000OC samples in the muffle furnace in plasma processing, the final load uniform Al-Si on the surface of SiC foam ceramics Codoped TiO2 photocatalyst coating layer.

The load samples are numbered according to the molar ratio of the doped 3 valent aluminum ion and the 4 valence silicon ion, as shown in Table 1.

Number		Si4+ : Ti4+	Al3+: Ti4+	
Т	T-C	0:1	0:1	
TS10	TS10-C	1:10	0:1	
TA10	TA10-C	0:1	1:10	
TS10A5	TS10A5-C	1:10	1:20	
TS10A10	TS10A10-C	1:10	1:10	
TS10A15	TS10A15-C	1:10	3:20	

Table 1. Number of nano TiO2 powders and loadingsamples with different doping ratio

2.3 The Content and Purpose of The Study

- The use of SiC as a carrier of ceramic foam, coated by dipping technology of surface doped nano photocatalyst, finally prepared modified nano TiO2 nano SiC ceramic foam surface load coating, and to study the related conditions in the process of preparation.
- 2) Microstructure analysis of TiO2 nano coating modified by SiC foam ceramic surface loading was carried out.
- 3) The photocatalytic efficiency of modified TiO2 coating modified by surface loading of unsupported TiO2 powder and SiC foam ceramic was compared, and the reasons for the performance of modified TiO2 photocatalyst were analyzed according to the surface loading of SiC foam ceramic.

3. Experimental Results Analysis

3.1 Dipping Process on the Quality of Coating

In the process of preparation of TiO2 sol coating dipping system, coating quality has a great relationship with the number of dipping, usually a dipping process is difficult to smooth, smooth sol coating, as shown in Figure 3 using stereomicroscope obtained after three times, four times and five times of extraction the morphology of SiC foam ceramic reinforced surface after the completion of the pulp.



Figure 3. Surface morphology of SiC foam ceramic bars with different dip times.

In the immersion for 3 times, in figure for dipping 4 times, 5 times the number of the dip, SiC foam ceramic reinforced superscript as indicated in the morphology, the three dip after the completion of the thickness of the coating surface of SiC ceramic foam has increased, but there are some areas without reinforcement is completely covered, four dip after the completion of SiC foam ceramics reinforced to form white TiO2 photocatalyst coated layer, prove this coating has been completed, and the 5 dip coating slurry is formed after the completion of the thick.

Therefore, unnecessary dipping times may cause the coating layer and the substrate adhesion is reduced, or even fall off in the sintering process, but not conducive to the photocatalytic effect. In addition, the film thick film will affect the lifetime of photocatalyst, if the film is too thin, will lead to the space charge layer is too thin, increasing the resistance of thin film, thus affecting the photocatalytic process of the separation of electron hole pairs [9]. if too thick, it will make the sol coating is too dense, so as to reduce the surface area, the photocatalytic efficiency decreased by dipping for 4 times is appropriate.

As shown in Figure 4, a sample of SiC foam ceramic samples that have not been coated and treated by 4 dip treatment and sintered by 1000OC.

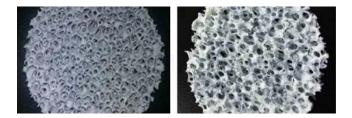


Figure 4. Pictures of SiC foam ceramic before and after load treatment.

In Figure 4 the processing load, the load after treatment. The left shows: not loaded nano TiO2 coating sample is gray brown with three-dimensional space

structure is interconnected, load matrix well. The figure shows: after dipping and sintering process of SiC ceramic foam loaded sample surface is white proof, Codoped nano TiO2 coating layer of uniform load on the surface of SiC ceramic foam.

Therefore, dipping process can be very good to avoid blockage, the sintered samples retained the 3D mesh structure of SiC foam ceramic unique, is conducive to the improvement of nano TiO2 powder specific surface area, promote the photocatalytic reaction.

3.2 Element Analysis of Coating

EDS analysis of the 1 points shown in Figure 4, and the results of the EDS analysis are shown in Figure 5

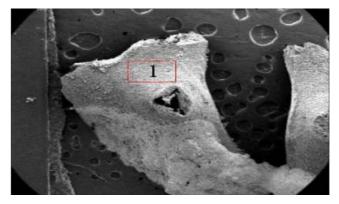


Figure 4. Al-Si codoped modified TiO2 coating on the surface of SiC foam ceramic.

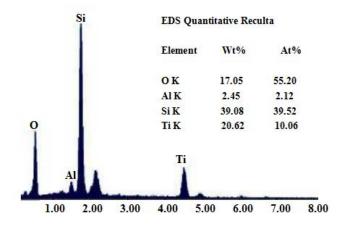


Figure 5. The results of the EDS analysis.

As can be seen from Figure 5, the coating on the surface of SiC foam ceramic is mainly composed of four elements, Ti, O, Al and Si, which proves the formation of Al-Si Codoped TiO2 coating on the surface of SiC foam ceramic

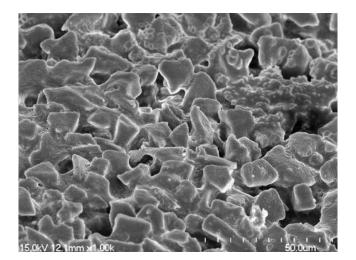


Figure 6. Surface microstructure of SiC foam ceramic sintered sample.

Such as SiC foam ceramic surface is shown in Figure 6 of the SEM photos, it can be seen from the figure, after SiC foam ceramic particles sintering are closely connected and formed a uniform structure and connected with each other, the kaolin slurry composition, bentonite, alumina, talc and other additives is mainly composed of Al2O3, SiO2, MgO, etc. the composition of the oxide, these oxides in the sintering process solution to form liquid phase during the cooling process, the final formation of glass phase. The glass phase is melt forming ceramic body in a part of the material under high temperature, the atomic or molecular separation during cooling was frozen into amorphous solid glass phase deposit [10]. In between the particles, plays a role in the adhesive, a closer connection between particles, so as to promote improved densities of body, increase the compressive strength at room temperature.

3.3 Effect of Loading Structure on Photocatalytic Properties of TiO2

In order to analyze the influence of Al-Si Codoped TiO2 photocatalyst, crystal transition temperature of T, TS10, TA10, TS10A5, TS10A15 six groups of modified nano TiO2 powder respectively in 1000OC, 1100OC, analysis of thermal insulation heat treatment 2 hours after 1200OC XRD, the XRD map as shown in Figure 7.

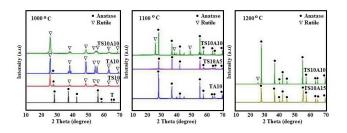


Figure 7. XRD spectra of heat treatment at different temperatures.

After 1000OC heat treatment, T samples in 27.31O, 38.08O, 43.68O, has obvious diffraction peak at 56.11O, the TiO2 angle and the Jin Hongshi type standard card (PDF21-1276) corresponding to that of TiO2 nano powder under this temperature after heat treatment has been completely transformed into Jin Hongshi, and after Al or Si single doping treatment the sample most maintained anatase phase and double doped TS10A10 samples with no change of crystal doped with Al or Si, that can play a certain heat and increase of nano TiO2 powder The stability effect of Al-Si co doping can play a synergistic effect of CO doping effect is better than single doping. After 1100OC heat treatment, most of the doped samples have been transformed into rutile phase transition, while TS0A10 is only partially occurred. After 1200OC heat treatment, TS10A10 samples still have anatase phase.XRD diffraction pattern the results show that the peak in different doping levels, TS10A10 is the best doping proportion.

	1					
Number	1000OC		1100OC		1200OC	
	A101	R110	A101	R110	A101	R110
Т	/	R	/	R	/	R
TS10	21%	79%	/	R	/	R
TA10	4%	96%	/	R	/	R
TS10A5	88%	12%	/	R	/	R
TS10A10	A	/	34%	66%	3%	97%
TS10A15	73%	27%	/	R	/	R

 Table 2. The content of anatase and rutile in samples of different temperature treatments

In order to have a comparative study on the effect of load structure on the photocatalytic performance of TiO2, in the same condition and modification of TiO2 nano powder under six load samples on the photocatalytic degradation of methylene blue test results of photocatalytic degradation of the A-Si and TiO2 Codoped nano powder catalytic results were compared the fitting the comparison results are shown in Figure 8.

We can see from Figure 8, the load samples all increased the efficiency of photocatalytic degradation of corresponding sample loading, the completion time of the photocatalytic degradation of T-C was significantly shorter than samples of light degradation time of T samples was shortened by 10 minutes, TS10A10-C samples than in TS10A10 samples was shortened by 5 minutes, although TS10-C samples and TS10-c samples but close to light degradation the reflection rate is faster.

Therefore, SiC foam ceramic carrier special interconnected three-dimensional structure for photocatalytic provides a huge surface area, improve the photocatalyst with methylene blue contact area, which increases the reaction rate between the two, which is made of coated nano TiO2 samples modified layer load than TiO2 powder without load in photocatalysis performance has improved.

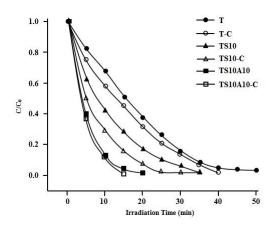


Figure 8. Comparison of photocatalytic efficiency between sample and powder.

4. Conclusions

The Al-Si Codoped nano TiO2 photocatalyst prepared by coating the load, the best dipping times is four, stereo microscope and EDS element analysis proved by dip process to form a uniform white modified nano TiO2 coating layer on the surface of SiC ceramic foam.

The photocatalytic degradation of methylene blue test proved the surface of SiC ceramic foam supported Al-Si Codoped nano TiO2 coating layer on the photocatalytic efficiency is superior to the same temperature, nano TiO2 powder as photocatalyst quality. This is due to the load of SiC matrix unique interconnected three-dimensional pore structure improves the photocatalytic reaction of the contact surface area. To promote the photocatalytic reaction.

5. Acknowledgement

This work was supported by the National Natural Science Foundation of China (no. 51674121), by the National Natural Science Foundation of Hebei Province (no. E2017209178), Science and technology project of Hebei province (no. 15214104D), the National Natural Science Foundation of Hebei Education Department (no. QN2016088).

6. References

- 1. Qing-zhu, W, *et al.* (2002). Foam ceramics and its application. *Journal of Ceramics*, *36*(2), 12–14.
- 2. Alvin, M.A., *et al.* (1991). Assessment of porous ceramic materials for hot gas filtration applications, *The Bulletin of the American Ceramic Society*, 70(9), 1941–1948.
- Fujishima, A., *et al.* (2000). TiO2 photocatalysts and diamond electrodes, *Electrochimica Acta*, 99(45), 4683–4690. https://doi.org/10.1016/S0013-4686(00)00620-4
- Chen, F., *et al.* (2001). Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation, *Chemosphere*, 44(21), 1159–1168. https://doi.org/10.1016/S0045-6535(00)00277-0
- Chung, Y.S., et al. (2004). Magnetically separable titaniacoated nickel ferrite photocatalyst, *Materials Chemistry* and Physical, 86(15), 375–381. https://doi.org/10.1016/j. matchemphys.2004.03.027
- Ding, Z., *et al.* Novel silica gel supported TiO2 Photacatalyst synthesized by CVD method. *Langmuir*. 37(16), 6216– 6222. https://doi.org/10.1021/la000119l
- Anpo, M., *et al.* (1992). Photocatalytic reduction of CO₂ on anchored titanium oxide catalysts, *Journal* of *Molecular Catalysis*, 74(4), 207–212. https://doi. org/10.1016/0304-5102(92)80238-C
- Ochuma, I.J., *et al.* (2007). Three-phase photocatalysis using suspended titania and titania supported on a reticulated foam monolith for water purification. *Catalysis Today.* 128(12), 100–107. https://doi.org/10.1016/j.cattod.2007.05.015
- 9. Song-dong, Y, *et al.* (2003). Fe3+/TiO2 Porous nanometer thin film preparation and photocatalytic activity research. *Science and Photochemical Senses.* 21(5), 426–431.
- Padtude, P.N. (1994). In situ-toughened silicon carbide, Journal of the American Ceramic Society, 77(15), 519–523. https://doi.org/10.1111/j.1151-2916.1994.tb07024.x