

Preparation and Characterization of Zn²⁺ Doped Nano SiC Coating

Liu Lu*, Zhiling Zhao, Xie Ying, Hongyan Tian, Shitao Song

College of Chemical Engineering, Hebei Normal University of Science and Technology, Hebei, China
13633336800@163.com

Gasification of glycerol for hydrogen production in supercritical water was studied in a fluidisation bed system with the presence of Na₂CO₃ and ZnCl₂. The experiment results show that temperature is the key factor and pressure has a minor effect on glycerol gasification. Higher temperature and pressure are in favor of glycerol gasification. Gasification performance of glycerol decreases with the increasing concentration, and 35wt. % glycerol was gamified stably during long time operations. Gasification efficiency increases and molar fraction of CO decreases with Na₂CO₃ addition. ZnCl₂ addition has no significant effect on the gasification efficiency, but it improves the selectivity of hydrogen in gas product. It is implied that the supercritical water fluidisation bed system is effective for hydrogen production by biomass gasification.

1. Introduction

Silicon carbide (SiC) is a new high-performance non-oxide ceramic material. Due to the advantages of low density, high hardness, wear resistance, high modulus of elasticity, thermal conductivity, thermal shock resistance and chemical stability, SiC is an ideal material under high-temperature, strong erosion conditions. The applicability of SiC is expanded by nanotechnology, especially for the preparation of nano-SiC composite coating. We used electro-brush plating procedure to prepare Zn-doped nano-SiC composite coating on the surface of component. This technique can produce uniform, dense and well-bonded deposited layer on the surface of component using simple equipment at low cost and short cycle. The coating prepared can help prolong the service life and erosion resistance of the component.

2. Experimental

2.1 Principle

A certain amount of insoluble nano-SiC particles are added into the plating solution and uniformly dispersed using a stirrer. The nano-SiC particles can adsorb the cations, or Zn ions, in the plating solution. During cathodic reaction, the nano-SiC particles are deposited on the surface of the particles together with the Zn ions, thus forming the composite coating. The nano-SiC particles not adsorbing the cations are also transported to the surface of the component. Though they are not involved in the cathodic reaction, the particles are embedded into the deposited layer as impurities, achieving the effect of enhancing dispersion.

2.2 Single factor design

The influence factors studied were content of nano SiC, content of zinc chloride (ZnCl₂), and voltage and pH value.

2.3 Electro-brush plating procedure

A composite layer was deposited on the surface of aluminium alloy using electro-brush plating from the mixed solution of ZnCl₂, SiC, polyvinylbutyral (PVB) and sodium dodecyl sulfate (K1₂).

2.3.1 Configuration plating solution

Wetting nano SiC, nano SiC is slowly added into the vortex of 20 ZnCl₂ ml solutions, stirring 10 min, forming a first solution, 0.75 PVB g as a binder and 0.025 K1₂ g as a dispersant to form a solution of 30 ZnCl₂ ml solution; the first solution and the second solution mixed with electric mixer, stirring 1.5 H.

2.3.2 Pre-treatment of Electro-brush plating

- (1) The first large cut copper brass sheet cut into standard size with scissors (1 cm * 5 cm).
- (2) First with 400 sandpaper polished brass surface 20 min, with 800 mesh sandpaper brass surface 15 min, finally with 2000 mesh sandpaper brass surface 10 min, burnish finished with lens paper wrapped spare.
- (3) Ethanol wipe: surface polished brass with cotton dipped in ethanol, remove the dust on the surface of oil.
- (4) The electric net oil removal: the negative electrode plate, the positive electrode is connected with the pen, the use of 12 V voltage, brush plating 3~5 times, with distilled water washing.
- (5) Activation process: the negative electrode, the positive electrode is connected to the substrate, 12 V voltage, brush plating until the surface is dark red, as soon as possible with distilled water to maintain the surface of the parts to prevent dry spots, re oxidation.

3. Result and discussion

3.1 XRD

3.1.1 Effect of temperature on the composite coating

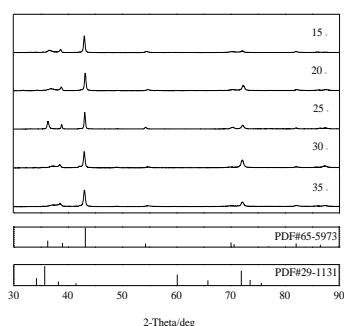


Figure 1: X-ray diffraction spectrum of nano zinc-doped silicon carbide composite coating of different temperatures

In Figure 2, the XRD spectra of zinc doped nano SiC composite coatings were expressed at different temperatures. The peak intensity of X- ray diffraction spectra increased with the increase of brush plating solution temperature, which may be due to the increase of temperature, the conductivity of the coating, and the efficiency of the brush plating. When the temperature rises to 25, the diffraction peak intensity of the zinc doped nano SiC composite coating is the strongest, and the diffraction peak of SiC is obvious. Then, as the temperature continues to rise, the peak intensity of X- ray diffraction pattern is decreased, and the SiC diffraction peaks cannot be found in the composite coating. Because the electric field strength decreases with the increase of the temperature of the plating bath, the decrease of the SiC particle adsorption capacity, and the increase of the temperature, the increase of the ion thermal motion, decreases the viscosity of the SiC particles. So the best temperature of plating solution is about 25 degrees centigrade.

3.1.2 Effect of pH on the composite coating

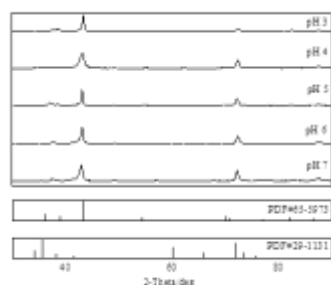


Figure 2: X-ray diffraction spectrum of nano zinc-doped silicon carbide composite coating of different pH values

From Figure 4 it can be seen that with the increase of pH value, the intensity of SiC diffraction peak is gradually increased, but when the pH value is increased to 5, the intensity of SiC diffraction peaks in the coating is decreased. This may be due to the increase of the pH value of the plating solution, the amount of hydrogen will decrease with the concentration of hydrogen ion in the plating solution, and the adsorption capacity of the cathode surface to the SiC particles will be increased, so that the deposition of SiC particles can be improved, and the co deposition of SiC particles is promoted. However, when the pH value rose to 5, the concentration of hydrogen ion in the plating solution is decreased, and the active hydrogen atom on the cathode decreases, so the complex ion is reduced. And the growth rate of nano SiC solid particles cannot catch up with the increase of the deposition of the zinc coating, so the content of SiC particles in the final brush coating decreases with the increase of pH value. So in order to obtain good composite brush plating, plating solution pH value of the best control in 5 is appropriate.

3.1.3 Effect of voltage on the composite coating

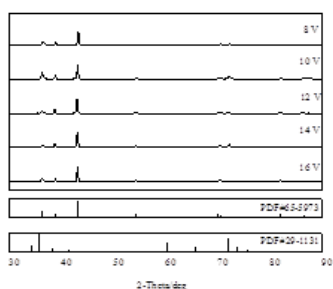


Figure 3: X-ray diffraction spectrum of nano zinc-doped silicon carbide composite coating of different voltages

It can be seen from Fig. 1 that as the voltage increases; the diffraction peak of SiC in the coating is enhanced and becomes the strongest at about 12V. As the voltage further increases, all peaks in X-ray diffraction pattern are weakened. This is because as the voltage increases, the cathode current density increases, and leading to higher overpotential and electric field strength. As a result, the cathode has higher adsorption on SiC particles, which is in favor of the forming of Zn-SiC coating. But as the voltage further increases, too high current density will cause massive hydrogen production and hence the reduction in the adsorption of SiC particles to the cathode. Fewer SiC particles are deposited and there is a decline in the content of SiC particles in the coating. Therefore, the optimal voltage is 12V for depositing the composite layer.

3.1.4 Effect of SiC content on the composite coating

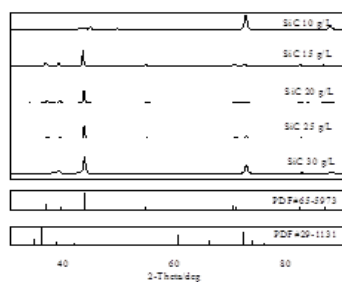


Figure 4: X-ray diffraction spectrum of nano zinc-doped silicon carbide composite coating of different Nano-SiC concentrations

It can be seen from Figure 3 that when the content of nano SiC is 10 g/L, the diffraction peak of SiC is relatively weak. As the content of nano SiC increases, the diffraction peak of SiC is enhanced. But the diffraction peak of SiC is weakened with the increasing content of nano SiC after the content of nano SiC reaches 20 g/L. The reason is that with higher content of nano SiC particles, there will be more SiC particles transported to the cathode in unit time, leading to higher probability of SiC particles being adsorbed and higher probability of SiC particles entering the coating[10]. After the content of SiC particles in the plating solution reaches 20g/L, there will be a balance in the adsorption of SiC particles onto the cathode. As more nano SiC

particles suspend in the plating solution with the increasing content of SiC particles, greater area of the composite coating is occupied by the SiC particles. Consequently, some active sites are covered and lose effect, and the deposition rate of SiC particles decreases. Therefore, the optimal content of nano SiC in the plating solution is about 20g/L.

3.2 SEM

Metal atoms are deposited in a regular pattern in electro-brush plating. They begin to pack together to form a crystal lattice. Fig. 5a shows the SEM image of pure zinc coating deposited from pure ZnCl₂ solution, and Fig. 5b shows the SEM image of composite coating deposited from zinc-doped nano SiC solution.

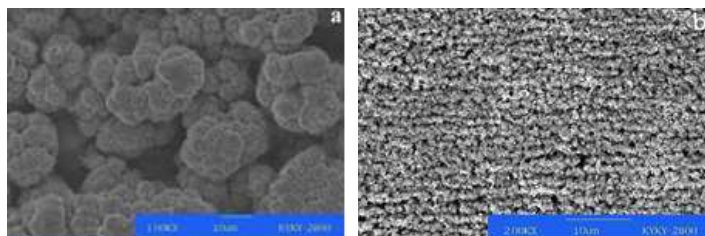


Figure 5: a 25 °C, voltage 12 V from the bath with nothing b 25 °C, voltage 12 V from the bath with nano-SiC

The addition of nano SiC particles makes the composite coating more uniform and denser. As seen from Figure 5b, the coating is denser and has smaller pores and more refined grains [12]. The nano SiC particles not only enhance the polarization of the cathode, but also reduce the over potential of nucleation reaction. This is favourable for the formation of new crystal nuclei and the inhibition of aggregation and growth of the nuclei. As a result, the coated metal substrate is refined with smaller cellular grains. This will effectively reduce the porosity of the coating while increasing the density.

3.2.1 Effect of voltage on composite coating

It is generally believed that the cathode over potential and electric field strength will increase as the voltage and the cathode current density increase. More Zn ions will be adsorbed onto the cathode, and higher cathode current density can increase the deposition rate of metal substrate and decrease the limit time. For this reason, high cathode current density promotes the entry of the Zn ions into the coating.

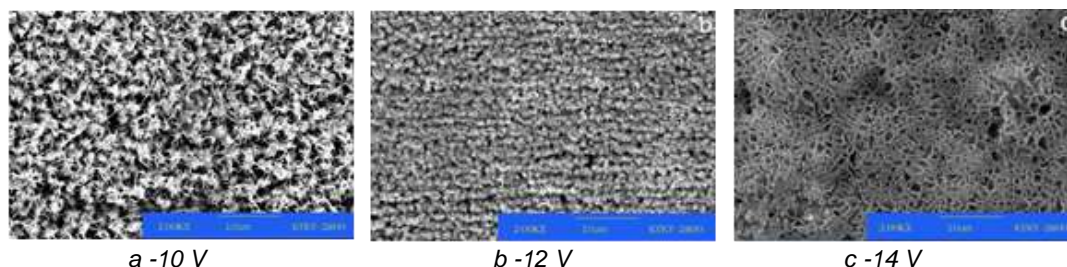


Figure 6: SEM images of the composite coatings obtained under different voltages

Figure 6 shows the morphology of the composite coating obtained under different voltage. It can be seen from Figure 6b that the grains are smaller and more uniform. Figure 6c shows many pores on the surface of coating. As the voltage increases, cathode current density, over potential and electric field strength all increase. Consequently, more SiC particles are adsorbed onto the cathode, which is favourable for the formation of Zn-doped nano-SiC composite coating. As the voltage further increases, hydrogen will be produced massively due to high cathode current density. Fewer SiC particles are adsorbed onto the cathode and the content of SiC particles in the coating decreases. Therefore, the optimal voltage is 12V.

3.2.2 Effect of pH value on the composite coating

As shown in Figure 7a and c, the SiC particles are loosely and unevenly distributed. The grains in Figure 7b are much smaller and refined and evenly distributed. This is probably because the hydrogen ion concentration in the plating solution decreases with hydrogen production and more SiC particles are adsorbed onto the cathode. The code position of SiC particles is enhanced on the surface of the coating. After the pH value increases to 5, the hydrogen ion concentration of the plating solution decreases constantly. The number of

active hydrogen ions on the cathode decreases dramatically, and fewer complex ions are reduced. Thus the optimal pH value is about 5.

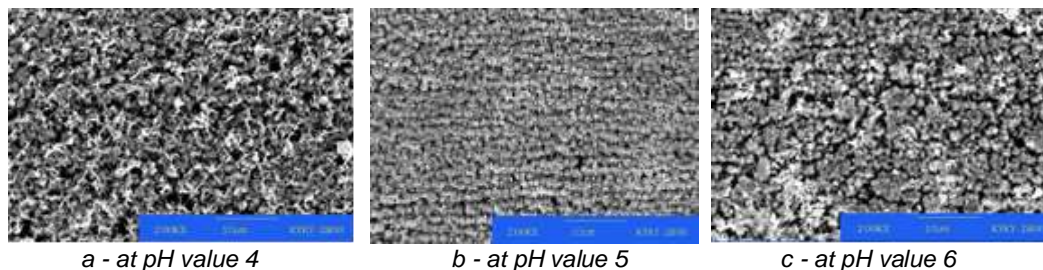


Figure 7: SEM images of the composite coatings obtained under different pH values

3.2.3 Effect of SiC content on the composite coating

Compared with Figure 8a and 8c, the grains in Figure 8b are smaller and more uniform with smaller pores and smoother surface. The SiC particles are loosely and unevenly distributed in Figure 8a. The nano particles in Figure 8c are poorly dispersed and some particles aggregate. The reason is that as the SiC content increases, some nano SiC particles settle to the bottom of the flask and excess SiC particles collide with each other and aggregate. The nano SiC particles not adsorbed onto the cathode and not embedded into the coating will also shed off by colliding with other particles. This explains the reduction in deposition of the composite coating and the phenomenon of particle aggregation [15]. Therefore, in electro-brush plating, the SiC content should be neither too high nor too low, and 20 g/L is considered the optimal.

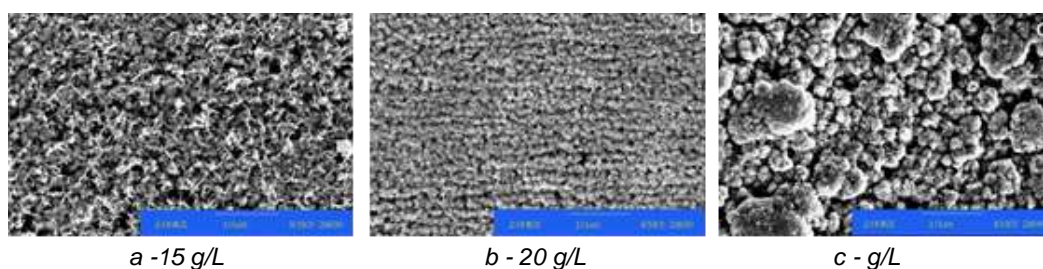


Figure 8: SEM images of the composite coatings obtained under different levels of nano-SiC

3.2.4 Effect of ZnCl₂ content on the composite coating

Figure 9 shows the surface morphology of Zn-doped nano-SiC composite coating under different ZnCl₂ content. In Figure 9a, the SiC particles are loosely and unevenly distributed. The coating surface is smoother in Figure 9b with denser and more evenly distributed grains and smaller pores. The nano SiC particles are poorly dispersed in Figure 9c and some aggregate together.

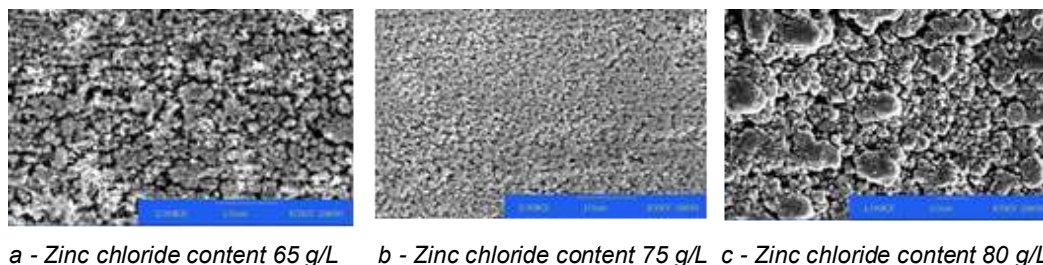


Figure 9: SEM images of the composite coatings obtained under different levels of zinc chloride

4. Conclusions

We prepared the Zn-doped nano-SiC composite coating by electro-brush plating with high hardness, wear resistance and erosion resistance. The optimal conditions were voltage 12V, pH value 5, nano-SiC content 20

g/L and ZnCl₂ content 75g/L. The composite coating obtained under the optimal conditions had much better performance compared with pure Zn coating. The presence of nano-SiC particles made the coating denser and the grains smaller and more uniformly distributed.

Acknowledgments

We acknowledge instrumental analysis center of Hebei Normal University of Science and Technology.

References

- Behrens B., Muller M., 2004, Technologies for thermal protection systems applied on re-usable launcher, *Acta Astronautica* 55: 529-536, DOI: 10.1016/j.actaastro.2004.05.034.
- Bell A.T., 2003, The Impact of Nanoscience on Heterogeneous Catalysis, *Science* 299: 1688-1691 DOI: 10.1126/science.1083671.
- Faraji S., Fara A.H., Noori S.R., 2014, An investigation on electroless Cu–P composite coatings with micro and nano-SiC particles, *Materials and Design*, 54: 570-575, DOI: 10.1016/j.matdes.2013.08.092.
- Jaramillo T.F., et al., 2007, Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nano-catalysts, *Science* 317: 100-102, DOI: 10.1126/science.1141483.
- Kumar R., Kumar A., Kaur M., et al., 2009, Influence of coal tar pitch coating on the properties of micro and nano SiC incorporated carbon-ceramic composites, *Mater Sci*, 44: 4633-4638, DOI: 10.1007/s10853-009-3707-1.
- Lee C.G., Li Q.Y., Kalb W., et al., 2010, Frictional Characteristics of Atomically Thin Sheets, *Science*, 328, 75-79, DOI: 10.1126/science.1184167.
- Leon O.A., Staia M.H., Hintermann H.E., 2003, High temperature wear of an electroless Ni-P-BN Composite Coating, *Surface and Coating Technology*, 162(2): 578-584, DOI: 10.1016/S0257-8972(02)00663-1.
- Li Z.M., Zhou W.C., Su X.L., et al., 2008, Preparation and Characterization of Aluminum-Doped Silicon Carbide by Combustion Synthesis, *American Ceramic Society*. 8: 2607-2610.
- Ma G.Z., Xu B.S., Wang H.D., et al., 2013, Research on the microstructure and space tribology properties of electric-brush plated Ni/MoS₂-C composite coating, *Surface & Coatings Technology*, 221: 142–149, DOI: 10.1016/j.surfcoat.2013.01.039.
- Rajasekaran N., Mohan S., 2009, Structure, microstructure and corrosion properties of brush-plated Cu-Ni alloy, *Appl Electrochem*, 39(10): 1911-1916, DOI: 10.1007/s10800-009-9899-x.
- Roventi G., Bellezze T., Fratesi R., 2013, Electro-deposition of Zn-SiC nanocomposite coatings, *Journal of Applied Electro-chemistry*, 43(8): 839-846. DOI: 10.1007/s10800-013-0571-0.
- Stoyanov P., Strauss H.W., Chromik R.R., 2012, Scaling effects between micro- and macro-tribology for a Ti–MoS₂ coating, *Wear*, 274(275) :149-161, DIO: 10.1016/j.wear.2011.08.021
- Tang J.L., Han Z.Z., Zuo Y., et al., 2011, A corrosion resistant cerium oxide based coating on aluminum alloy 2024 prepared by brush plating, *Applied Surface Science*. 257: 2806-2812, DOI: 10.1016/j.apsusc.2010.10.065.
- Thakur S.K., Kwee G.T., Gupta M., 2007, Development and characterization of magnesium composites containing nano-sized silicon carbide and carbon nanotubes as hybrid reinforcements, *Mater Sci*, 42: 10040-10046.
- Utkin A.V., Matvienko A.A., Titov A.T., et al., 2011, Preparation and Characterization of Multilayered ZrO₂ Coatings on Silicon Carbide Fibers for SiC/SiC Composites, *Inorganic Materials*, 47(10): 1066-1071, DOI: 10.1134/S0020168511090238.