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Synthesis of silica coated zinc powder by sol-gel processes

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Silica-coated zinc powders from the ultra fine zinc powder were manufactured by a sol-gel method. The reaction was carried out by controlling various process parameters such as the amount of NH₃ and NaCl, the reaction time and the number of coating process. The silica- coated zinc powders were identified by a variety of characterization techniques such as SEM-EDX, TEM, PSA and ELS analysis.

It was found that the thickness of silica coating layer and particle size could be controlled by the reaction time and the number of coating process. The particle size decreases with the decrement of molar ratio of NH_3 and the increment of concentration. The dispersability of silica-coated zinc powders have improved nearly four times than that of raw zinc powders and their resistance to acid also improved. The silica-coated zinc powder would be used as a pigment for anti-corrosive coatings with high durability.

Key words: Anit-corrosion, Paint, Zinc powder, Silica coating, Sol-gel process.

Introduction

Microsized metallic powders have extended their applications in various fields based on their peculiar properties and functions [1-3]. In particular, zinc powders are very important in anti-corrosion paint industry for use in protecting the surfaces of ships, automobiles, and steel structures such as bridges from corrosion. It is coated with a binder on the iron surface to play a role of sacrificial anode by being oxidized ahead of iron and hindering further corrosion on the iron substrate.

Zinc powders with average particle size of less than $10 \ \mu\text{m}$ are widely used in pigments for anti-corrosion paints at present. However, their high specific gravity of 7.14 has caused problems in operability and storage because rather heavy zinc powder is not well dispersed in binder and solidified after being easily precipitated. And, severe coating conditions often met in highly-developed industries have also made zinc micro powders susceptible to the contact with various corrosion factors and easily oxidized without surface treatments. Thus, various approaches to improve the surface characteristics and solve the aforementioned problems of powder materials have been made as by introducing surface treatments that prevent interparticular coagulation and oxidation.

The powders with surface treatments generally exhibit better transparency, thermal stability, dispersion, fluidity, compatibility with a binder, long-term stability. Surface treatments include a coating, capsulation, precipitation, topo-chemical and mechano-chemical reactions, etc.

This works aims to coat silica on the surface of zinc powder using a sol-gel method with TEOS (tetra ethyl ortho silicate) [4-7]. The effect of reaction parameters such as salt concentration, pH, and mixing time was investigated in relation to the dispersion of silica-coated zinc powders with average particle size of submicron to 3 μ m. The physical properties of silica-coated zinc powders were measured by a particle size analyzer, image analyzer, and scanning electron microscope (SEM, S-2700 Hitachi, Japan). In addition, zeta potential was measured to identify the colloidal property by an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics).

Experimental

Coating

Fig. 1 shows the sol-gel reaction procedure for the preparation of silica-coated zinc powder using a precursor of TEOS. As a starting material, zinc powders with average particle size of 1 to 3 μ m were deposited in TEOS. After being filtered, the starting material was dispersed into a solution of water and



Fig. 1. Silica-coated zinc powder preparation process by a sol-gel reaction.

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Parameters	Values	Reagents
NaCl(aq.)conc. [wt%]	1 6 12	- Raw zinc powder (Average particle size of 1 to 3/m, Taewon Non-ferrous Co.,Ltd.)
	18	
NH ₃ (aq.)conc. [mol]	0.125	 Ethyl alcohol (95%) NaCl (99%, Samchun Chemicals) NH₄OH (28.0~30.0%, Junsei Chemical Co.)
	0.25	
	0.5	
	1	
	2	



Fig. 2. Average particle size of silica-coated zinc powders with the variation of NaCl(aq) concentration at the agitation speed of 50 rpm.

ammonia in ethanol, and then the sol reaction between water and TEOS on the surface of zinc powder progressed under agitation. The pH was controlled in the stable range of 7 to 10.5 by adjusting ammonia concentration. After a certain period of sol reaction to grow silica on zinc powder, the salt was added for the gelation. The final silica-coated zinc powders were obtained by subsequent filtering and drying process. The reaction temperature and agitation speed were set to room temperature and 50 rpm, respectively.

The experimental conditions to find out the effect of salt concentration and pH on the properties of silica-coated zinc powder are summarized in Table 1.

Dispersion

The true density of silica-coated zinc powder was measured by the standard method (KS L 3114:2010). The zeta-potential of powder surface was measured to assess the effect of the electro-chemical property of silica-coated zinc powders on dispersion. The dispersion property was also examined by color analysis on the 10 mL solution sampled from the top side of the solution in which the silica-coated zinc powder of 1.5 g was dispersed in 50 mL distilled water and maintained for 15 min.



Fig. 3. Average particle size of silica-coated zinc powders with the variation of pH and NH_3 (aq.) concentration at the agitation speed of 50 rpm and the NaCl (aq.) concentration of 12 wt%.



Fig. 4. Particle growth with mixing time at 12 wt% NaCl (aq.) and 2.0 mol NH₃.

Results and Discussion

To investigate the effect of salt concentration on the average particle size of silica-coated zinc powders, the NaCl (aq.) concentration was changed to 1, 6, 12, and 18 wt% at the NH₃ concentration of 0.5 mol and 2.0 mol with other parameters set as shown in Table 1. Fig. 2 shows that the average particle size of silica-coated zinc powder decreases as the NaCl concentration increases. With high NaCl (aq.) concentration, the gelation time of silica sol is reduced to complete the chain coating without each silica particle largely grown. On the contrary, the gelation was slow with low NaCl (aq.) concentration so that each silica particle is sufficiently grown.

Fig. 3 shows the average particle size of silica-coated zinc powders with the variation of pH and NH_3 concentration (0.125, 0.25, 0.5, 1.0 and 2.0 mol.). The pH was measured in each time using a pH meter (pH-270L, Istek).

It is seen that the pH is proportional to the NH_3 concentration in the range of pH 7 to 10, known as a range where silica particles are stabilized. The average particle size of silica-coated zinc powders increases



Fig. 5. Particle size distribution of silica-coated zinc powders with the variation of NH_3 (aq.) concentration at the agitation speed of 50 rpm and the NaCl (aq.) concentration of 12 wt%.



Fig. 6. SEM micrographs of (a) raw zinc powders (b) silica-coated zinc powders at the agitation speed of 50 rpm, 2.0 mol NH_3 and 12 wt% NaCl (aq.).

proportionally with the NH_3 concentration. With low NH_3 concentration, the growth of silica is kinetically restricted because NH_3 plays a role of initiator and catalyst for the growth. High NH_3 concentration accelerates the growth in the other way.

In order to find out an operating parameter controlling the particle size of silica-coated zinc powders conveniently, an additional experiment was employed with the change of mixing time (15, 30, 45, and 60 minutes) following the addition of NaCl. Each silica particle is grown homogeneously by sol reaction before the salt is added, and the gelation starts with the addition of salt, where silica particles form chain connection between them. Thus, the extent of gelation is one of the primary factors to determine the thickness of silica coating. Fig. 4 shows that the average particle size of silica-coated zinc powder increases linearly with the mixing time, indicating that the target coating thickness or powder size is attained by controlling the mixing time.

The particle size distribution (PSD) of silica-coated zinc powders is shown in Fig. 5 with the variation of the NH_3 concentration. A narrower PSD is obtained for zinc dust as a reference. When NH_3 is added, the PSD becomes broadened and more as the NH_3 concentration increases. At 2 mol of NH_3 , the particles with larger than 20 μ m are detected probably due to the coagulation between silica-coated zinc particles.



Fig. 7. True density of the silica-coated zinc powders with the increase of NH_3 concentration at the agitation speed of 50 rpm and NaCl (aq.) concentration of 12 wt%.



Fig. 8. Zeta potential of (a) raw zinc powders and (b) silica-coated zinc powders.

SEM observation was employed in order to investigate the morphology of coated silica on zinc powders. Fig. 6(a) and 6(b) show the surface features of the raw zinc powders and the silica-coated zinc powders prepared at 12 wt% NaCl (aq.) and 2.0 mol NH₃, respectively.

It is seen that silica were coated uniformly on the surface of zinc powder and there is no structural deformation on the base spherical zinc powders. In addition, no coagulation is seen despite some individually grown small silica particles.

The true density of silica-coated zinc powders was measured by the following formular and the result is plotted in Fig. 7.

$$D_{t} = \frac{P_{1} - P}{(P_{1} - P) - (P_{3} - P_{2})}$$
(1)

P: the weight of bottle (g)



Fig. 9. Color of the solution with silica-coated zinc powders dispersed with the variation of (a) NaCl (aq.) and NH_3 concentration.

- P_1 : [the weight of bottle + the weight of sample] (g)
- P₂: [the weight of bottle + the weight of distilled water at a certain meniscus] (g)
- P₃: [the weight of bottle + the weight of sample + the weight of distilled water at the same meniscus] (g)

The true density of raw zinc powder and silicacoated zinc powder was 6.598 g/cm³ and 3.5~5 g/cm³, respectively. Approximately 20% decrease in the true density of powder indicates that the porosity increases as the zinc powder size increases with the silica coating.

Fig. 8 shows that the zeta potentials of raw zinc powder and the silica-coated zinc powders prepared at 12 wt% NaCl (aq.) and 2.0 mol NH₃ are + 7.83 mV and -34.30 mV, respectively. These results demonstrate that the dispersion stability of zinc powder is improved by the surface treatment of silica coating. The color analysis is also supplemented to confirm the dispersion stability. The color was gray when zinc powder was dispersed in distilled water and the transparency of the solution was recovered due to the precipitation of zinc powders as the time passed. Thus, the dispersion stability is simply assessed by the color of the top side of colloidal solution. As a result, the color was less than 2,000 CPU for raw zinc powders and it significantly increased to more than



Fig. 10. EDS elemental analysis of (a) raw zinc powders and (b) silica-coated zinc powders at 2 mol NH_3 and 12 wt% NaCl (aq.).

8,000 CPU for silica-coated zinc powders, which represents the dispersion stability is improved about four times. In addition, the dispersion stability was proportional to the NaCl (aq.) concentration and inversely to the NH_3 concentration, as shown in Fig. 9.

For a qualitative confirmation of silica coating on zinc powder, energy dispersive spectroscopy (EDS) was performed as shown in Fig. 10. The silicon peak is clearly detected for silica-coated zinc powders without any contaminant salt component (Na or Cl peak). The remaining salt on the surface of powder has an adverse effect to create an inherent corrosion condition. In this work, the solvent was evaporated at lower than 80 and removed by several cleaning steps, therefore there is no salt peak in EDS spectrum.

Conclusions

The silica-coated zinc powders were prepared via sol-gel method using TEOS precursor and the effects of several reaction parameters on the properties of resulting powders were investigated. The increase of particle size due to the coagulation was found at the NaCl (aq.) concentration of less than 12 wt%. The particle size decreased with incleasing NaCl (aq.) concentration. At the NH₃ concentration of greater than 2 mol, the coagulation started to occur. The lower NH₃ concentration led to the decrease of the particle size of silica-coated powders and narrower PSD. The concentration of NH₃, which plays a role of catalyst for silica growth, was related to pH. The

coagulation occurred at pH > 10, and nano-size silica particles were individually grown and dispersed in colloidal state at pH < 7.

In general, silica coating on zinc powders reduced the true density and improved the dispersion stability. Without any structural deformation of raw zinc powder, the dispersion stability improved four times for silica-coated zinc powders. Finally, it is demonstrated that uniform silica coating was successfully obtained only via sol-gel reaction without additional thermal treatments.

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