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Dispersion and Stabilization of Aqueous TiC Suspension

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Abstract: The dependence of development and characteristics of TiC aqueous suspension on the pH values and/or Darvan C addition has been investigated. Zeta potential studies show that the isoelectric point of TiC particulates is at pH 2. Addition of Darvan C increases the zeta potential in magnitude and modifies the surface to more negative charge in the pH range from 1·8 to 11. Using electro-stabilization as the dispersing mechanism, it was found that the suspensions formed at conditions pH 6·97 with 2 wt% Darvan C addition; pH 9·3 with 0·5 wt% Darvan C addition; or pH 10·1 without Darvan C and are all in well dispersion, as determined by correlation of zeta potential and settling tests.

1 INTRODUCTION

The titanium carbide with high modulus, hardness and electro-conductivity has been widely used as a particulate-reinforcement second phase in ceramic composite for metal-cutting tools and wear-resistance applications. The quality of a ceramic composite is controlled by the state of dispersion of reinforcements in ceramic matrix. Inhomogeneous dispersion of particulate-reinforcements, such as flocculation or agglomeration, is harmful to the sintering of composite materials and always introduces processing flaws.

The dispersion of colloidal particles in an aqueous media by electro-static repulsion and/or steric hindrance has been extensively discussed in the literature.[1–5] The former mechanism is managed by both attractive and repulsive forces between those particles. The net effect of these forces determines the state of dispersion of particulate suspensions. The repulsive forces between particles dominating over the attractive forces result in well dispersions. In general, an electro-static stabilization of suspension can be achieved by manipulating electrostatic charges on the particle surface with controlling pH[6,7] and/or adding a polyelectrolyte surfactant[8–11] into suspension, which absorbs on the surface of particles and increases the repulsive force.

Darvan C, an ammonium salt of polymeric carboxylic acid, has been chosen to disperse TiC because it is widely used as a dispersant in aqueous solution for ceramic materials.[9] In this study adjustment of both pH and Darvan C addition were conducted to disperse TiC particulates in aqueous solution.

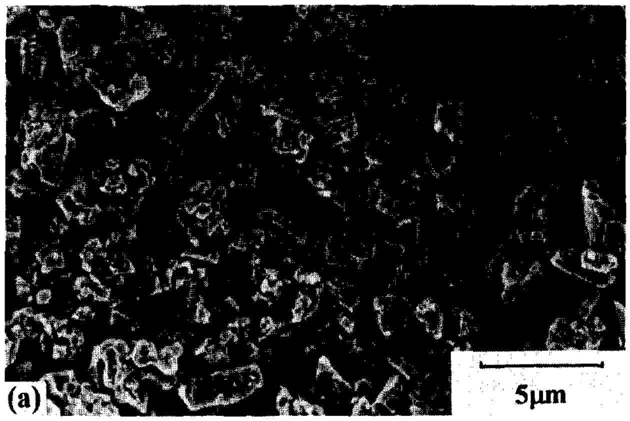
2 EXPERIMENTAL PROCEDURE

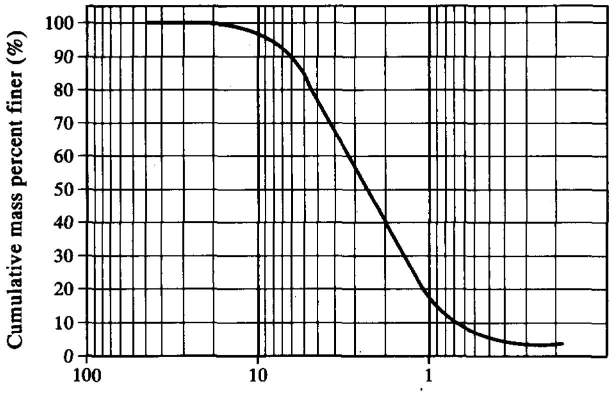
2.1 *Materials*

Commercially available TiC particulate (T-1227, CERAC, cutting tool grade, typical purity 99·5%) and Darvan C (R. T. Vanderbuilt Co., Norwalk, CT, molecular weight 10000~16000, formula

$$-(CH_2-\underset{\displaystyle COONH_4}{\underset{|}{CH}})_n-$$

were used in this investigation. The particle size distribution of TiC using Darvan C as dispersant determined by X-ray sedimentation technology (Micromeritics sedigraph 5100, USA) and its SEM (JSM-5200, JEOL, Tokyo, Japan) micrograph are shown in Fig. 1. The powder consists of angular





(b)

Fig. 1. (a) SEM micrograph of TiC particulate, (b) cumulative mass percent finer vs particle diameters of TiC particulates by X-ray sedimentation measurements.

particles with a distribution of 0·2–40 μm, where d_{90} = 7 μm, d_{50} = 2·5 μm, d_{10} = 0·75 μm.

2.2 Zeta potential measurement

Zeta potential (Zeta III, Zeta-Meter, USA) was measured using 200 ppm concentration dispersions in 10^{-3} M KCl solution. To determine the zeta potential as a function of pH, the 10^{-2} N HCl and 10^{-2} N KOH solutions were used to adjust pH to the desired values. To determine zeta potential versus Darvan C concentration, 10^{-2}–10% of TiC powder was added to the suspensions for examination.

2.3 Sedimentation measurement

Setting experiments were conducted using 2 vol% TiC suspension with various amounts of Darvan C and NH_4OH as a dispersant, which was then ultrasonicated and stirred for at least 1 h. Twenty five millilitres of each resultant suspension was poured into a graduated and sealed test tube to determine the variation of dispersion height versus setting time at various intervals. In this study, the dispersion height is defined as the distance between the dispersion/supernatant interface and the bottom of the tube, including the height of any sediment. Thus, a larger dispersion height indicates better dispersions.

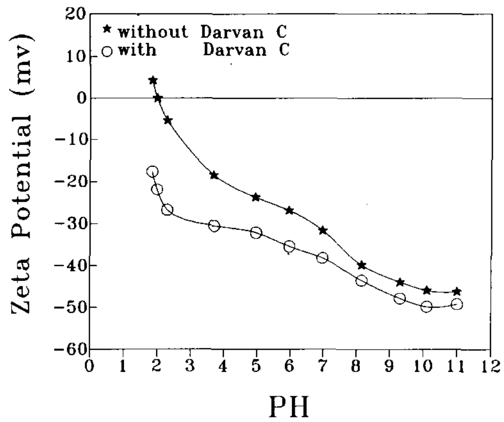


Fig. 2. Effect of pH on the zeta potential of 200 ppm TiC suspension with and without 0·2 wt% Darvan C addition.

3 RESULTS AND DISCUSSIONS

3.1 Zeta potential

Figure 2 shows the results of TiC suspension zeta potential versus pH values with and without Darvan C addition. In the case of TiC suspension without Darvan C addition, the zeta potential changes from -45 mV at pH 11 to +5 mV at pH 1·8, with an isoelectric point (IEP) at pH 2. Above pH 2, it exhibits a negative zeta potential that gradually increases in magnitude with pH value. At pH over 10, the zeta potential approaches a maximum value of -45 mV. In the case of 0·2 wt% Darvan C addition, the zeta potential changes from -50 mV at pH 11 to -17 mV at pH 1.8. Apparently, there is no IEP to be observed in the pH ranges. Besides, for the pH range used, Darvan C addition results in a more negative zeta potential than the one without Darvan C addition. It could be contributed to by the dissociation of Darvan C in the solution producing COO^- groups[10–11] absorbed on the TiC particles which could increase the negative net charge of powder surface, then increase repulsive forces. Similarly, for pH above 10 it also exhibits a maximum zeta potential (~ -50 mV). Based on Fig. 2 it is expected that the TiC particulate should be well dispersed, as the pH is above 10 despite of the Darvan C addition, due to the large zeta potential.

The zeta potential of TiC suspensions as a function of Darvan C concentration at pH 6·97 and pH 9·3 is shown in Fig. 3. The relationship between zeta potential and Darvan C shows concave behavior for both pH values. Increasing Darvan C

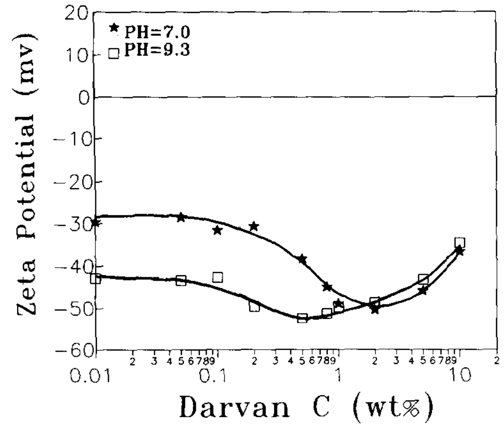


Fig. 3. Effect of Darvan C concentration on the zeta potential; 200 ppm TiC suspension at pH 6·97 and 9·3, respectively.

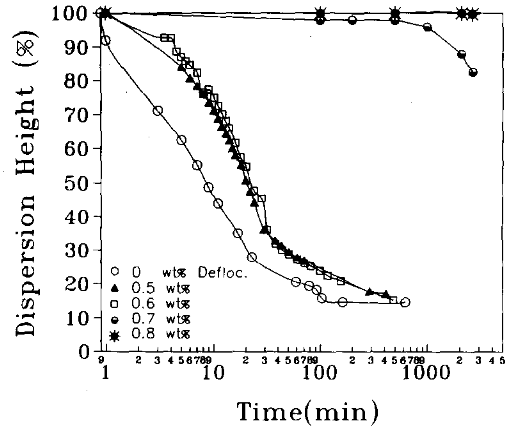


Fig. 5. Dispersion of 2 vol% TiC suspension with various Darvan C addition at pH 6·97.

concentration does not result in the increase of zeta potential. The maximum zeta potential of TiC suspension appears at Darvan C addition of 0·8–2% and 0·2–1% for suspensions at pH 6·97 and pH 9·3, respectively.

3.2 Sedimentation

Figure 4 shows the dispersion quality of TiC suspension in double deionized water at pH ranging from 5·96 to 10·1 by NH_4OH titration. The results show that suspension at high pH generates good dispersions which could be due to the high zeta potential for suspension in a basic environment. The suspension at pH 10·1 decreased only 1% in height after 17 h. On the contrary, pH 5·96, as well as pH 6·97, settle very rapidly and decrease 50% in height after 10 min.

Figure 5 shows the effect of Darvan C concentration on the dispersion of TiC suspensions at pH 6·97. Suspension with 0·8 wt% Darvan C addition demonstrates a better dispersion, without any decrease in height after 17 h. The TiC suspension results above correlate well with the relative zeta potential. As zeta potential is increased, the larger dispersion height was observed, indicating a well dispersion result, while the low zeta potential leads to a lower dispersion height due to floc formation.

The dependence of the cooperation of Darvan C addition and pH adjustment on the dispersion of TiC suspension is shown in Fig. 6. Suspension at pH 9·3 with 0·5 wt% Darvan C addition exhibited a good dispersion with a similar result of those suspensions with individual pH-adjustment (pH 10·1) or 0·8 wt% Darvan C addition, respectively.

Figure 7 shows the dispersion properties of TiC suspensions after the settling of 25 ml in a test tube for two months. The height of the full suspension, consisting of supernatant and sediment, was partitioned into 25 absolute units for convenience. Supernatant turbidity was rated on three scales: 1 = clear, 2 = slightly cloudy, 3 = cloudy. The ratings are clearly subjective. For a long settling time, a poor dispersion is indicated by clear supernatant and high sediment, since flocs have formed and settled, without mutual repulsion existing to keep particles suspended. Suspensions at pH 6·97 with 2 wt% Darvan C addition, at pH 9·3 with 0·5 wt% Darvan C addition, and pH 10·1

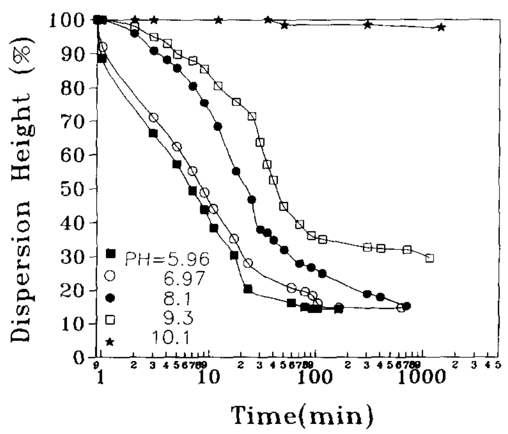


Fig. 4. Dispersion of 2 vol% TiC suspension in pH range from 5·96 to 10·1 by NH_4OH titration.

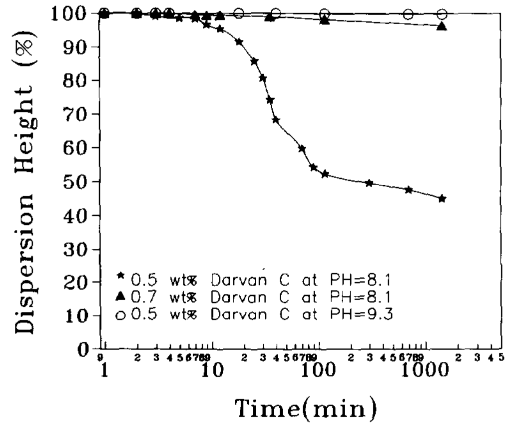


Fig. 6. Dispersion of 2 vol% TiC suspension at pH 8·1 with 0·5 wt% or 0·7 wt% Darvan C addition and pH 9·3 with 0·5 wt% Darvan C addition.

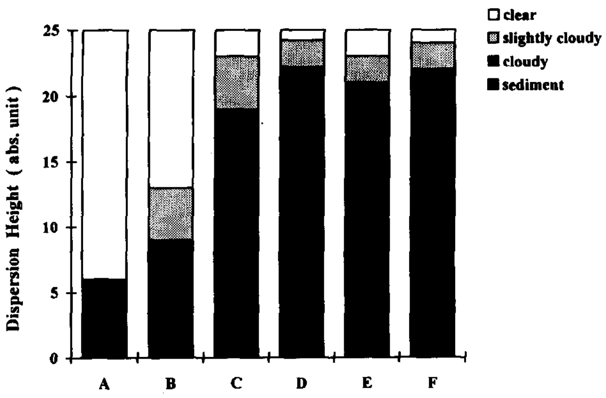


Fig. 7. Dispersion of 2 vol% TiC suspension after settling for 2 months (A: 0·7 wt% Darvan C addition & pH 6·97; B: 0·8 wt% Darvan C addition & pH 6·97; C: 1·0 wt% Darvan C addition & pH 6·97; D: 2·0 wt% Darvan C addition & pH 6·97; E: pH 10·1 & Darvan C free; F: 0·5 wt% Darvan C addition & pH 9·3).

(Darvan C free) display a good dispersion by the observation of cloudy supernatant, as well as a lower sediment height.

4 CONCLUSIONS

The zeta potential, as well as sedimentation, of aqueous TiC suspension has been investigated. It is shown that the zeta potential gradually increases in magnitude with increasing pH, with an IEP at pH 2 for suspension without Darvan C addition. Adding 0·2 wt% Darvan C increases the zeta potential and modifies the surface to a more negative charge in the pH range from 1·8 to 11. At pH above 10, the zeta potential achieves a maximum value of +50 mV. The increase of zeta potential does not increase with the amount of Darvan C addition, but depends on pH values. Aqueous TiC suspension at conditions of pH 6·97 with 2 wt% Darvan C addition, pH 9·3 with 0·5 wt% Darvan C addition and pH 10·1 without Darvan C results in a well dispersion, as determined by correlation of zeta potential and settling tests.

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