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Ultrasonic dispersion of nano TiC powders aided by Tween 80 addition

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Abstract

Nano TiC powders were dispersed in aqueous media. Effects of ultrasonic treatment and Tween 80 addition on dispersion of TiC powders were investigated. The results showed that ultrasonic treatment had a large effect on the dispersion of nano TiC powders, and 30 min of ultrasonic treatment was necessary for fine dispersion from TEM images and particle size measurement. Tween 80 was selected as the dispersant. Sedimentation test indicated that 0.5 vol.% was the optimum addition level of Tween 80 in TiC suspension. FTIR spectrum proved the adsorption of Tween 80 on the surface of nano TiC powders. XPS analysis revealed the existence of TiO_2 on the TiC powder surface, which led to a hydroxylated surface during dispersion. In the presence of Tween 80 in the solution, zeta potential values became more negative. Both electrostatic stabilization and steric stabilization were deduced to be the main mechanisms for well dispersion of the nano TiC powders in aqueous media.

Keywords: Nano particulates and powders; Dispersion; X-ray analysis

1. Introduction

At the present, nano TiC or TiN powders are usually added into Ti(C,N)-based cermets to improve the toughness of cermets [1–3]. However, due to the high surface energy, nano particles tend to agglomerate during the synthesis and post-synthesis processes. The powder agglomerations are harmful to the properties of cermets due to the microstructure heterogeneity [4]. Ball milling in liquid media is a conventional method to break the agglomerations, but it becomes less effective for nano powders than micro-sized powders [5]. Therefore, how to achieve a good dispersion of nano powders into the matrix remains a big challenge during the preparation of nano Ti(C,N)-based cermets with high performance.

Currently, colloidal processing has been successfully applied in the field of structural ceramics [6,7]. Many literatures were focused on the colloidal dispersion of TiC powders. Wang [8] did research on dispersion of TiC powder with a size distribution of 0.1–100 μm. The research showed that TiC powders were well dispersed in the suspension with a proper dispersant addition level, which resulted in the transition of Zeta potential to more negative and larger value. The isoelectric point of TiC was at pH 2. Yeh [9] studied the dispersion and stabilization of TiC in aqueous suspension, which has a size distribution of 0.2–40 μm. The results showed that fine dispersion of aqueous TiC suspension could be achieved at pH 6.97 with 2 wt.% Darvan C(ammonium polymethacrylic acid) addition, pH 9.3 with 0.5 wt.% Darvan C addition and pH 10.1 without Darvan C. It could be concluded that the dispersant addition level and pH values of the suspension were important to the dispersion of TiC powders.

Current researches are mainly focused on the dispersion of micro-scaled TiC powders, but there are few reports on the colloidal dispersion of nano TiC powders. Therefore, in this study, nano TiC powders with an average particle size of 40 nm were ultrasonically treated in aqueous media and Tween 80 was added as a dispersant. The main purpose was to characterize the effect of ultrasonic treatment time, Tween 80 addition level, and pH values on the dispersion of nano TiC powders.

2. Experimental details

2.1. Ultrasonic treatment of TiC suspension

Commercial available nano TiC powders (Hefei Kaier Nanotechnology Development Co., Ltd., China) made by a gas phase reaction method were used in this study, which had a BET

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specific surface area of 75 m^2/g and an average particle size of 40 nm. JEM-100CX Transmission Electron Microscope (TEM, JEOL, Japan) was used to observe the microstructure of the nano powders. Philips X'Pert Pro X-ray diffraction instrument (XRD, Holland) was used for phase analysis with Cu K_α radiation.

0.1 vol.% nano TiC powder was added into de-ionized water during the preparation of the colloid suspensions. Then the suspensions were ultrasonically treated for 10 min, 20 min, 30 min and 60 min, respectively. The ultrasonic treatment was conducted using a KQ3200 DB ultrasonic horn (Kunming ultrasonic machine company, China). The frequency and power of the ultrasound were constant at 40 kHz and 100 W, respectively. The nano TiC powders ultrasonic treated for different time were observed by TEM and zetaplus analyzer to characterize the dispersion degree.

2.2. The addition of Tween 80 in TiC suspension

Tween 80 (polyoxyethylene 80 sorbitan monooleate, Xingang Chemical of China) was used as the dispersant, and its chemical structure is shown in Fig. 1. Suspensions were prepared with different Tween 80 addition in de-ionized water. In order to break agglomerates, all the samples were ultrasonically treated for 30 min. The nominal composition of the suspensions in this study was given in Table 1. The optimum Tween 80 addition level for the well dispersion of TiC suspension was determined by sedimentation test. For this purpose, suspensions was stirred thoroughly for 10 min in beakers and then transferred to the measuring cylinders respectively where they were allowed to stand undisturbed for 12 h in order to observe the sedimentation volume of TiC powders.

Nicolet 6700 FTIR spectrometer (FTIR, Thermo Fisher Scientific, USA) was used for analysis of the functional groups absorbed on the surface of nano-TiC powder. Suspensions were mixed with KBr and compressed to a disk. Infrared transmission spectrum was recorded at room temperature in the range from 400 cm^{-1} to 4000 cm^{-1}.

The surface layer composition of the as-received TiC powders was determined by X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos Ltd., UK) using Mg K_α (1253.6 eV) radiation. Survey spectra were collected in the energy range of 0–1000 eV by a high-resolution scan at 0.1 eV/step. The deconvolution of the high-resolution spectra was performed with the Gaussian function. The binding energies obtained in the XPS analysis were standardized using C_{1s} at 284.8 eV. Atomic sensitivity factors were 1.20 for Ti_{2p} and 0.66 for O_{1s} in this paper.

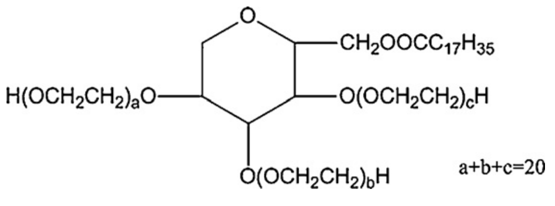

Fig. 1. Chemical structure of Tween 80.

Table 1
The nominal composition of the suspensions.

Suspension	A	B	C	D
TiC (vol.%)	0.1	0.1	0.1	0.1
Tween 80 (vol.%)	0	0.5	1	2

Zeta potential analyzer (Malvern Nano ZS90, UK) was used to measure the zeta potential and particle size of the suspensions. To determine the zeta potential as a function of pH, the standardized analytical-grade HCl and NaOH solutions (0.1–1.0 mol/dm^3) were used to achieve the desired pH values. HCl and NaOH (Shanghai Chemical Reagent Corporation, China) were analytical purity, and they were used without further purification. The dispersion degree of TiC suspensions was evaluated in terms of effective particle diameter as revealed by dynamic light scattering technique using the zeta potential analyzer.

3. Results and discussion

3.1. Effect of ultrasonic time

Fig. 2 shows the TEM micrograph of as-received nano TiC powders. There are many powder clusters and the diameters of these agglomerates are estimated to be several hundreds of nanometers. Powders with the size below 1 μm usually aggregate spontaneously to form clusters. Fig. 3 shows the TEM images of nano TiC powders ultrasonically treated for different time. Fig. 3(a) is the image of TiC powder suspension that ultrasonic treated for 10 min. The agglomeration level decreases and some single particles can be seen. When high-intensity ultrasonic waves are launched into the liquid–powders mixture, energy is transferred into the fluid in the form of pressure waves. Then the induced transient cavitations are subsequently forced to collapse, and release intense pressure waves into the surrounding fluid. Particles adjacent to the cavity are subjected to the normal and shear forces which cause the breakage of the particles [10,11]. With the increase of ultrasonic time to 20 min, more agglomerates disappear from Fig. 3(b). When the ultrasonic time reaches 30 min, ultrasonic

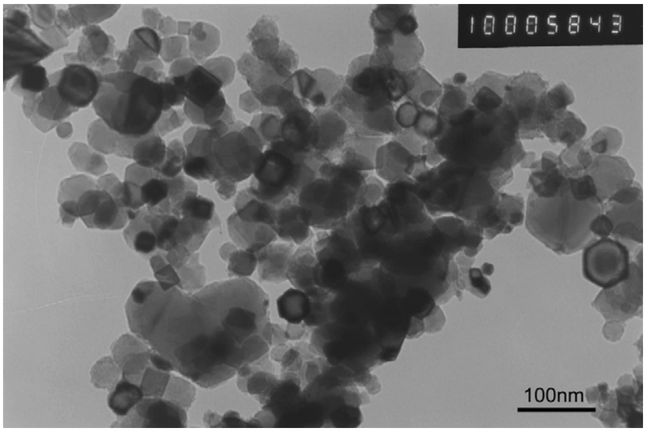

Fig. 2. TEM image of the as-received nano TiC powders.

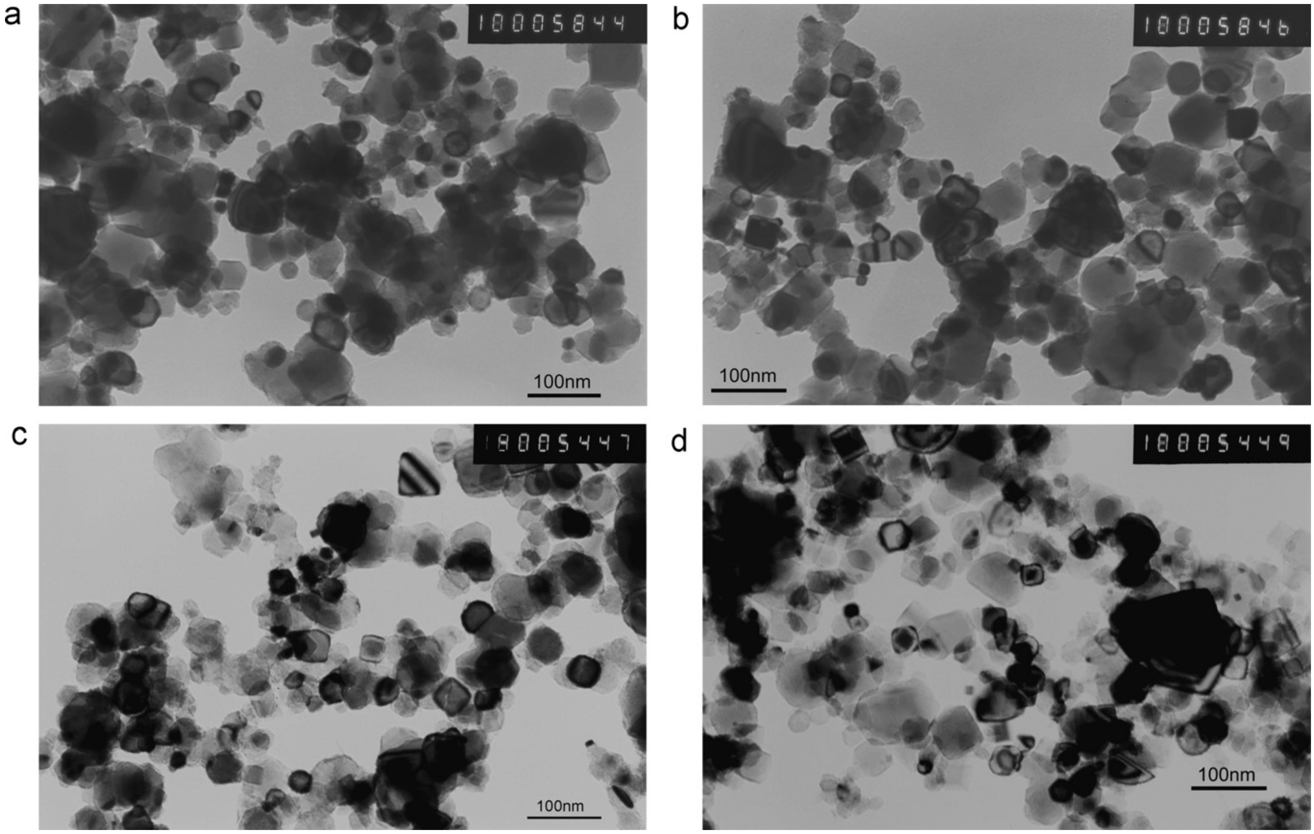

Fig. 3. TEM images of nano TiC suspension ultrasonic treated for different time. (a) 10 min, (b) 20 min, (c) 30 min and (d) 60 min.

agitation reduces the mean size appreciably, and hundreds of single particles about 40 nm can be seen from Fig. 3(c), and well dispersion of nano TiC powders in aqueous solution is achieved. However, the increase of ultrasonic time to 1 h do not result in a more homogeneous dispersion of the nano powders compared to 30 min (see Fig. 3(d)). It seems that ultrasonication cannot break the particle clusters further after the solution have been ultrasonically treated for 30 min, and the Bernoulli force caused by the transient cavitations may result in the reassemble of nano powders.

Fig. 4 shows average particle size versus the ultrasonic treatment time of TiC powder suspension. It can be seen that the average particle size decreases a lot for the first 30 min, it changes from 955 nm at 10 min to 342 nm at 30 min. However, the average particle size does not change obviously after the 30 min, it just fluctuates slightly at about 340 nm. The size measurement result is in accordance with TEM images in Fig. 3. It can be concluded that the ultrasonic treatment can decrease the particle size effectively, and 30 min of ultrasonic treatment is necessary to complete a well dispersion. The optimum ultrasonic time of TiC is similar as that of TiN [12].

3.2. Effect of Tween 80 dispersant addition

In order to obtain well-dispersed and stabilized suspension, Tween 80 was used as a dispersant. Fig. 5 shows the sedimentation volume of TiC suspensions with different amount of Tween 80. When nano TiC powders are well dispersed, the suspension is stable and nano-TiC powder is less likely to subside. As shown in Fig. 5, with the addition of Tween 80, the dispersion volume of TiC suspension decreases and the dispersion behavior become better. The sedimentation volume is the least with the addition of 0.5 vol.% Tween 80. The reason will be discussed in the following part of the paper. However, overfull addition of Tween 80 results in the reagglomeration of the particles due to the winding of the molecular chains [13]. Therefore, the sedimentation volume of TiC suspension

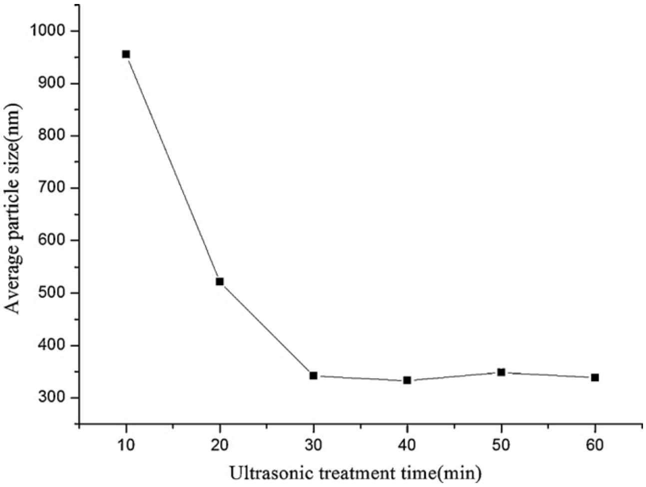

Fig. 4. The average particle size of TiC powders versus ultrasonic treatment time.

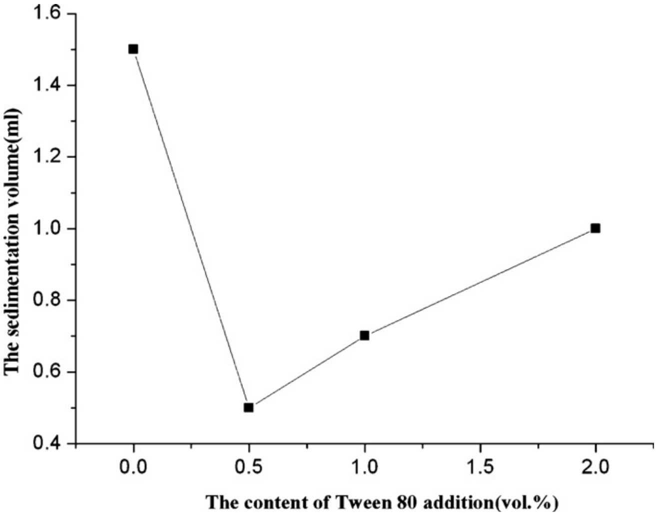

Fig. 5. The sedimentation volume of TiC suspensions with different amount of Tween 80.

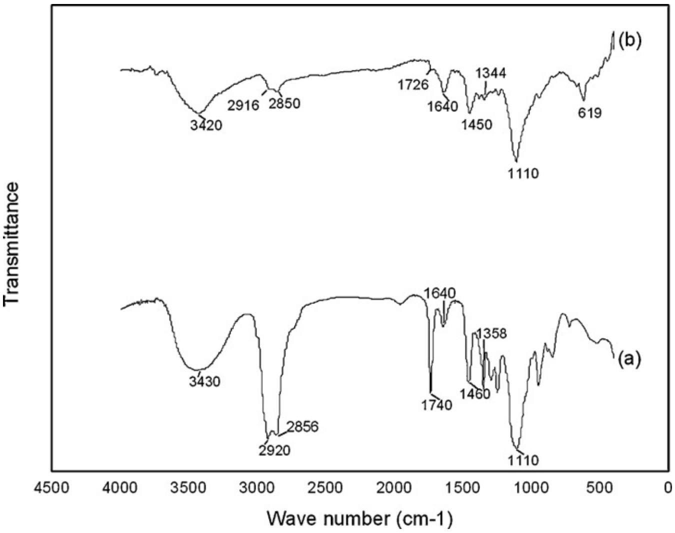

Fig. 6. FTIR spectra of nano TiC powders with Tween 80 addition (curve a) and pure Tween 80 (curve b).

increases with the addition of Tween 80 from 1.0 vol.% to 2.0 vol.%.

Curve (a) in Fig. 6 shows the FTIR spectrum of suspension with 0.5 vol.% Tween 80. The spectrum shows a broad peaks at the wavelength region of 3420 cm^{-1}, corresponding to OH stretching. The peaks at 1110 cm^{-1} and 1644 cm^{-1} are assigned to the stretching of the C–O and C=C bonds, respectively. The peaks at 1726 cm^{-1} is due to the stretching of C=O bonds [14]. Therefore, the existence of C=C, C=O, C–O bonds and OH stretching indicate the adsorption of Tween 80 on the surface of nano TiC powders. Curve (b) in Fig. 6 is the FTIR spectrum of pure Tween 80. Because of the symmetrical and asymmetrical bending vibrations of $–CH_3$, there are peaks in curve (b) at 1358 $cm^{-1}$and 1460 cm^{-1}. The strong bands at 2920 cm^{-1} and 2856 cm^{-1} of curve (a) are due to the asymmetrical and symmetrical stretching of $–CH_2–$, respectively [12]. However, it can be obviously observed that the relative intensity of the peaks assigned to $–CH_2–$, $–CH_3$ and C=O, decreases significantly in curve (a). Compared with the spectrum obtained from the Tween 80-adsorbed nano-TiN [12], the relative intensity of the peaks assigned to $–CH_2–$, $–CH_3$ decreases slightly.

The XRD pattern of the nano TiC is shown in Fig. 7, in which only TiC phase can be seen without other impurities such as TiO_2 and TiO. For further investigation of the dispersion of nano TiC powders, XPS was used to analyze the surface composition of the nano TiC powders. XPS is very sensitive to the chemical composition and environment of the elements with an effective analysis depth of about 10 nm [15]. The XPS spectra of nano TiC particles are shown in Fig. 8. The Ti_{2p} core level spectrum is shown in Fig. 8(a), the observed binding energy value for $Ti_{2p2/3}$ (458.7 eV) and $Ti_{2p1/2}$ (464.4 eV) agrees with the reported data for amorphous TiO_2 ($Ti_{2p2/3}$(458 eV) and $Ti_{2p1/2}$ (464 eV),[16]), $Ti_{2p2/3}$ (455.2 eV) and $Ti_{2p1/2}$ (461.1 eV) agrees with the reported data for TiC ($Ti_{2p2/3}$ (454.9 eV) and $Ti_{2p1/2}$ (460.6 eV), [17]). The O_{1s} core level

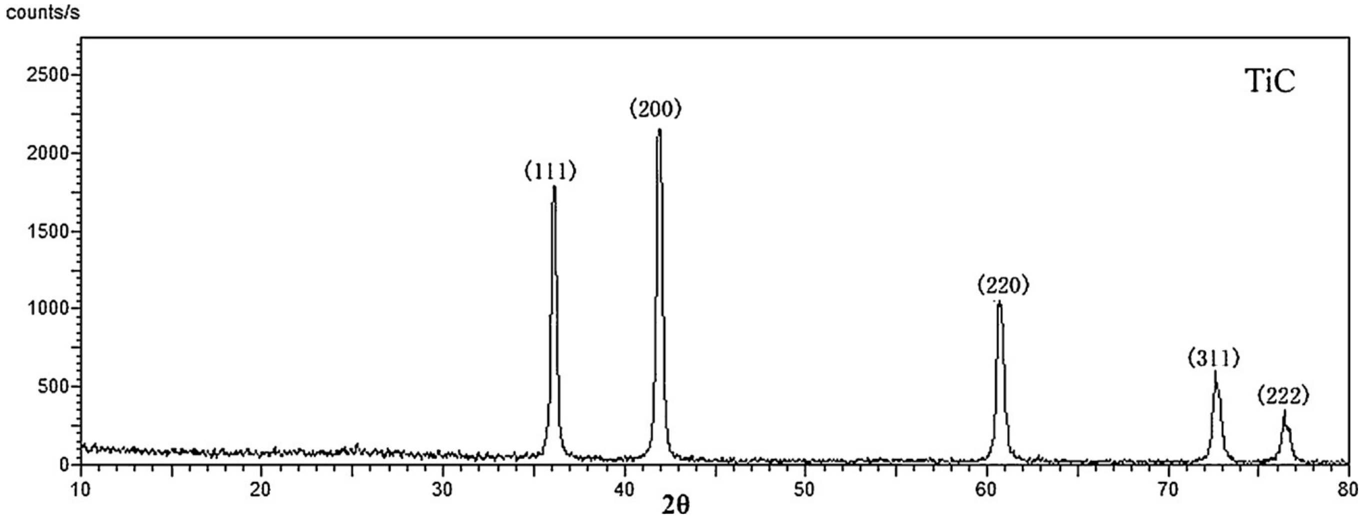

Fig. 7. XRD pattern of the as-received nano TiC powders.

spectrum is shown in Fig. 8(b). There are two peaks in the spectrum, the main peak is at 530.32 eV and one shake-up line is at 532.11 eV, the main peak located at about 530.32 eV could be assigned to titanium dioxide [18]. Fig. 8(c) is the C_{1s} spectrum, the peak located at about 281.73 eV could be attributed to titanium carbide. It can be concluded that there existed TiO_2 and TiC compositions on the surface of the as-received TiC nano powders. TiO_2 on the surface of nano TiC powder can coordinate with H_2O molecules. Therefore, the dissociative chemisorption of H_2O molecules lead to a hydroxylated surface (≡Ti–OH). The adsorption of H^+ and OH^- by the surface of TiC powder can be expressed as follows [19]:

$$\equiv Ti{-}OH + H^+ \leftrightarrow \equiv Ti{-}OH_2{}^+ \quad (a)$$

$$\equiv Ti{-}OH + OH^- \leftrightarrow \equiv Ti{-}O^- + H_2O \quad (b)$$

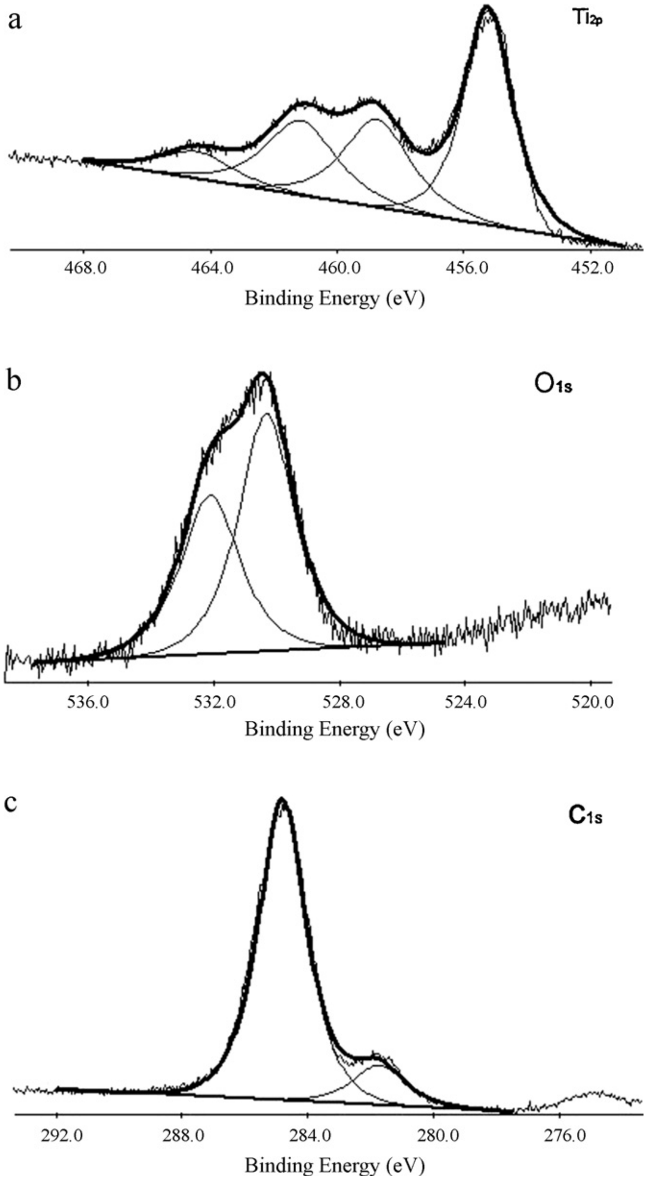

Fig. 8. XPS peaks of nano TiC powders. (a) Ti_{2p}, (b) O_{1s} and (c) C_{1s}.

It can be concluded that the nano TiC powders are charged particles. According to the above discussions, it can deduce that the charged characteristics and dispersion behaviors of nano TiC and TiN powder are similar [12].

Fig. 9 shows the zeta potential value of TiC suspension without and with 0.5 vol.% Tween 80 addition as a function of pH value. In the aqueous suspension, the charged particles develop an extend layer of oppositely charged ions, i.e. so called electrical double layer. High surface charge density generates a stronger repulsive double-layer force to prevent reagglomeration to achieve fine dispersion [20,21]. Curve (a) of Fig. 9 shows that zeta potential changes of TiC suspension without Tween 80 addition change from −26 mv at pH 11 to +7.3 mv at pH 3, with an isoelectric point (pH_{IEP}) at about pH 3.9 and a maximum value of −28.5 mv at pH 9. At the isoelectric point (pH_{IEP}), the number of positive charge sites produced by TiC powder adsorbed H^+ ions is equal to the negative charge sites of adsorption of OH^- ions. Therefore, the net charge equals zero, and the particle in the suspension can be easily agglomerated and flocculated. Curve (b) shows that the zeta potential of TiC suspension with 0.5 vol.% Tween 80 addition changes from −32 mv at pH 11 to +4.37 mv at pH 3, with an isoelectric point (pH_{IEP}) at about pH 3.5. Zeta potential measurements show that the Tween 80 addition resulted in a more negative zeta potential and the shift of pH_{IEP} to a more acidic point than that without Tween 80 addition. The maximum zeta potential is −34.1 mv, in contrast to −28.5 mv for the TiC suspension without Tween 80 addition. It could be attributed to the adsorption of Tween 80 on the surface of TiC powders. Tween 80 has a good wettability with TiC owing to the polarity of nano powders and a thin film of the organic dispersant was formed due to the hydrogen bond. Therefore, on one hand, steric stabilization take place when Tween 80 was adsorbed on the surface of TiC particles thus introducing physical barriers between the particles [22]. On the other hand, since the high zeta potential value was obtained, the

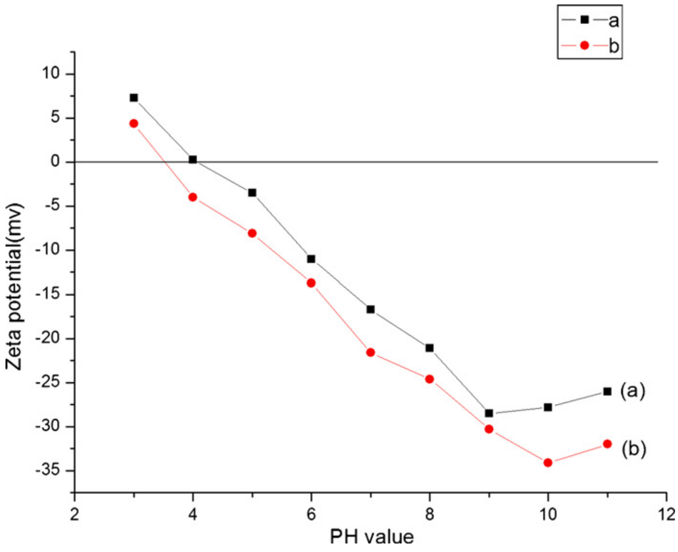

Fig. 9. Zeta potential of TiC suspension in absence (curve a) and presence (curve b) of Tween 80 addition as a function of pH value.

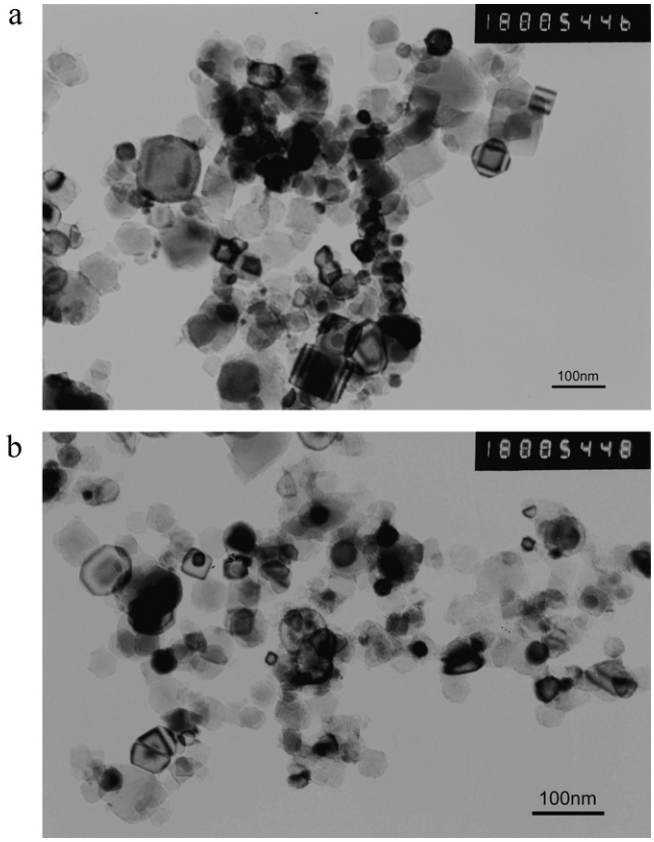

Fig. 10. TEM images of nano TiC powder samples with the largest zeta potential corresponding to Fig. 9. (a) Corresponding to the point pH 9 of Fig. 7 without Tween 80 addition. (b) Corresponding to the point pH 10 of Fig. 7 with Tween 80 addition.

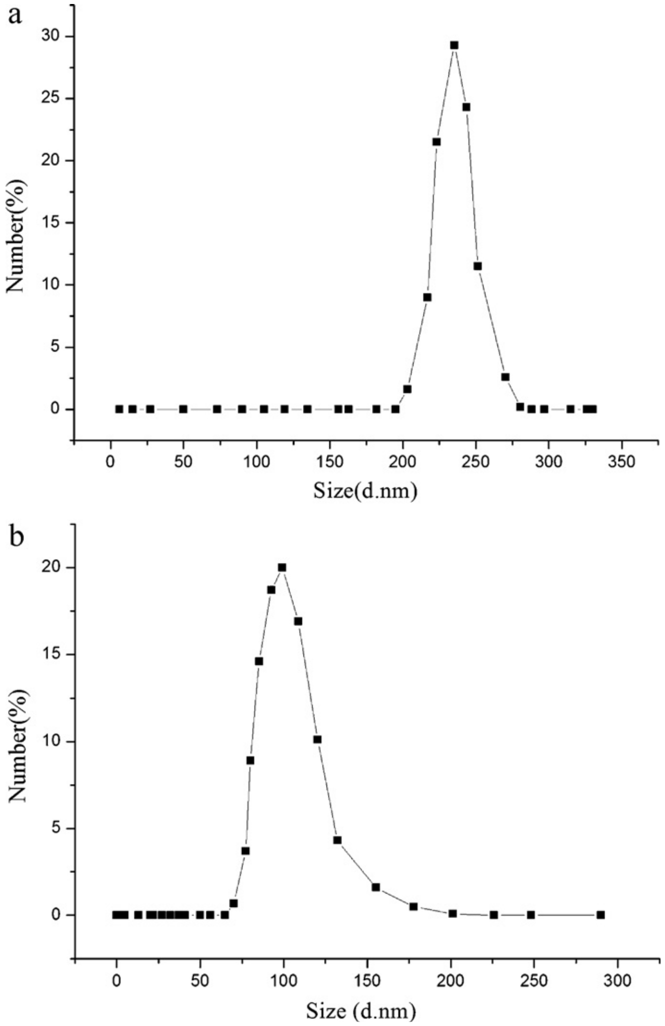

Fig. 11. The size distribution of the nano TiC powder samples at the largest zeta potential value without and with Tween 80 addition. (a) The size distribution of sample at the largest zeta potential without Tween 80 addition. (b) The size distribution of sample at the largest zeta potential with Tween 80 addition.

high surface charge density of powders can generate strongly electric double-layer repulsive force to prevent reagglomeration through electrostatic mechanism. Then the dispersion of nano TiC suspension was improved. In addition, the zeta potential decreases under strong basic conditions. Since more NaOH is needed to adjust the pH values, the increased ionic strength in the suspension compresses the thickness of double electric layer and the zeta potential decreases [23].

The nano TiC powder samples with the largest zeta potential point were picked from both suspensions with and without Tween 80 addition. The TEM images of both samples are shown in Fig. 10. It indicates that better dispersion suspension is achieved after the addition of Tween 80. Fig. 11 shows the size distribution of the nano TiC powder samples corresponding to Fig. 10. Fig. 11(a) is the size distribution of sample at the largest zeta potential without Tween 80 addition. The particle size is around 230 nm, and the decrease of particle size compared to the as-ultrasonic treated TiC is mainly attributed to the improvement of zeta potential value. Fig. 11(b) shows the size distribution of sample at the largest zeta potential with 0.5 vol.% Tween 80 addition. The main particle size is decreased by the addition of Tween 80. It can be seen that the average particle size is about 100 nm with no obvious agglomeration, and nano TiC powders have a narrow size distribution. Therefore, the nano TiC powders are well dispersed with pH value adjustment and Tween 80 addition.

4. Conclusions

In this paper, the dispersion of nano TiC powder was studied. Ultrasonic treatment is an effective way to break nano TiC agglomerates in the aqueous media. After ultrasonic treated for 30 min, the mean particle size was significantly decreased, and hundreds of single particles about 40 nm could be seen. However, longer ultrasonic time became less effective for more homogeneous dispersion.

In order to achieve better dispersion, non-ionic polymer Tween 80 was added as a dispersant. Sedimentation test indicated that 0.5 vol.% was the optimum addition level of Tween 80 in nano TiC suspension. FTIR spectrum proved the interfacial interaction of Tween 80 with the nano TiC powder. XPS analysis revealed the existence of TiO_2 on the surface of TiC, which led to a hydroxylated surface of the nano TiC powder. Zeta potential of TiC suspension was tested as a function of pH value in absence and presence of 0.5 vol.% Tween 80 addition to evaluate the stability of colloidal dispersions. The results showed that the zeta potential was influenced by the pH value through electrostatic stabilization mechanism, and a more negative zeta potential was obtained by the addition of Tween 80. The adsorption of Tween 80 on the surface of TiC particles and the high negative values of zeta potential are beneficial to produce electro-steric stabilization, which prevent nano particles from reagglomeration and form stable suspensions. In conclusion, fine dispersion of nano TiC powders can be achieved by ultrasonic treatment aided by Tween 80 addition. According to the above discussions, it can be deduced that the dispersion behaviors of nano TiC and TiN powder showed many similarities. This study is a good preparation for our following research on nano Ti(C,N)-based cermets.

Acknowledgements

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