Effects of process parameters on morphologies of titanium carbide powder by thermal plasma treatment

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Keywords: porous ceramics, thermal plasma treatment, surface morphology, high sphericity

Abstract

High sphericity titanium carbide (TiC) powders with uniform distribution and favorable dispersity were obtained by thermal plasma treatment. By optimizing the process parameters, the spheroidization rate of TiC powders is almost 100%. During solidification process, a transformation from typical dendrite structure to cellular structure microstructure occurs with the increase of feeding speed. It ascribes to the decrease of heat absorbed from plasma torch, resulting in decreasing constitutional undercooling and improving solidified interface stability. Consequently, it promotes the formation of cellular structure.

Introduction

Porous ceramics with high specific surface area and high volume fraction of porosity, have attractive properties, such as high temperature resistance, high permeability and high adsorption [1, 2]. Therefore, they can be widely applied in industries and engineering fields, including filters, absorbers, catalyst carriers and reactors etc [3–5].

Pore structure is a significant factor to evaluate the quality of porous material, which is highly depended by the powder shape [6]. Spherical powders with uniform particle size and low sintering activity are significant for controlling the pore structure. Compared to irregular powders, spherical particles are beneficial to fabricate the porous skeleton with homogeneous pore distributions. Sun et al [7] reported that porous silica ceramics, with uniform and fully interconnected pores, could be obtained by sintering spherical SiO\textsubscript{2} particles. It indicated that the packed pores were well-reserved and uneven shrinkage was restrained effectively. Particularly, spherical particles allow regular packing, which facilitates the formation of contiguous and interlinked pores [8, 9]. For another, TiC has many excellent properties, such as high melting point, high hardness, high chemical/thermal stabilities, and high wear resistance [1, 2, 10, 11]. Porous TiC ceramics have already been used in some fields, such as ceramic composites [12], water purifying [13]. Besides, TiC powders with high sphericity can be used in the fields of additive manufacturing and thermal spray for their excellent flowability, which also attract great interests. Furthermore, spherical ceramic particles as reinforcements also help to improve the comprehensive properties of metal matrix composites. For example, when the mixture of Ti-TiB\textsubscript{2} composite powders was processed by selective laser melting (SLM) technology, spherical particles exhibited higher relative density, greater compressive strength and compression strain than other shapes [14]. Spherical TiC powders reinforced Ni\textsubscript{3}Al matrix composites were also reported to improve hardness, fracture strength and oxidation resistance of the composites [15]. Accordingly, it is meaningful to find a way for preparing spherical ceramic powders.

The methods can be used to prepare spherical powders including gas atomization (GA) [16–18], plasma rotating electrode process (PREP) [19, 20], and radio frequency plasma spheroidization (RF plasma...
spheroidization [21–23], etc. Indeed, GA is very common for metal spherical powders preparation. However, the GA method powder has inherent weakness of entrapped inert gas, and which may prevent full dense during the powders consolidation process [24]. Additional, the spherical powders fabricated by GA usually accompanied with satellites, which affects the powders flowability. Furthermore, the melting temperature of TiC is so high that GA method is not suitable to prepare it. Chen et al. [25] and Ahsam et al. [26] found that the porosity of the porosity of Ti6Al4V powders fabricated by PREP is lower than that of GA. Thus, PREP is an effective method to fabricate high quality powders with spherical shape. But, the works mechanism of PREP is that with plasma as heat source and powders as consumable electrode, the electric extreme melted into liquid film by plasma, and then formed spherical powders under high speed centrifugal force and surface tension. Based on this, this method is more suitable for Ti-based and Ni-based materials, rather than ceramic materials. Additional, From Entezarian [27] and Chen [25] et al reports, it could be found that typical PREP powders average size is larger than 100μm. Compared to PREP, RF plasma spheroidization could prepare high quality spherical ceramic powders due to its high temperature in plasma torch and rapid cooling speed, besides it is also suitable for the powders with different size distribution.

Therefore, in this paper, we try to prepare TiC powders with high sphericity through RF plasma spheroidization technology, and particularly study the effects of feeding speed on surface morphology in detailed. The formation mechanism of TiC powders with different microstructures is discussed.

Experimental

Commercially available TiC powders with a size distribution 45–105 μm were used as raw materials in this paper. Raw TiC powders were treated by a radio frequency induction plasma spheroidization apparatus (TEKNA Plasma Systems Inc. TekSphero 40 kW Plasma System Model #: SY165). During the processing, raw powders with irregular shape were injected into the plasma arc through the feeding gun under the action of carrier gas, then quickly heated and melted. The molten particles subsequently formed a highly spherical droplet as a function of surface tension, and rapidly solidified under a very high thermal gradient, next spherical TiC powders were obtained. The optimizing process parameters were fixed at: plasma power = 40 kW, center gas flow rate = 20slpm (Ar), sheath gas flow rate = 50slpm (Ar) and 15slpm (H2), carrier gas flow rate = 3slpm (Ar). In order to study the influence of feeding rate on powders morphology, the feeding rate was varied from 10 g min⁻¹ to 25 g min⁻¹.

The morphology of TiC powders was observed by scanning electron microscopy (SEM NOVA NANOSEM 430), the phase composition was tested by x-ray diffraction (XRD) (X’pert pro PANalytical, Netherlands), the particle size distribution of powders were measured using a Bettersize 2000LD laser particle size analyzer. Statistical methods and the following formula [28] were used to calculate the spheroidization rate.

\[
k = \frac{B}{A} \times 100\%
\]

Where, \(k\) is the spheroidization rate, \(A\) is the total number of powders randomly selected from a region in the SEM image, and \(B\) is the total number of spherical particles in the region.

Results and discussion

Figure 1 shows the morphologies of the raw and spherical TiC powders. The raw TiC powders have irregular massive body with sharp edges or corners. After thermal plasma treatment, TiC powders possess a favorable dispersion and high sphericity. Irregular TiC powders passed through the high temperature plasma torch region, and then rapidly melted and finally condensed to spherical shape due to the surface tension.

The particle size distributions of raw and spherical powders are shown in figure 2. According to the previous work [29], the equation (2) can be used to describe the particle size distribution intervals:

\[
\Psi = \frac{(D90 - D10)}{(2*D50)}
\]

Where, \(\Psi\) represents the value of particle size distribution span. Since, \(\Psi_{raw} = 0.72, \Psi_{spherical} = 0.51\), that is, \(\Psi_{raw} > \Psi_{spherical}\). Particles mean size and distribution intervals of plasma treated TiC are smaller than that of raw powders due to the evaporation during melting process.

Figure 3 shows the phase structures of raw and spherical TiC powders. After plasma treatment, no additional phases rather than TiC appears. However, a systematical shift to a lower angle of diffraction peaks can be detected for spherical TiC powders. According to Bragg equation, lattice parameter of spherical TiC is about 0.4349 nm, which is slightly larger than that of raw TiC powders (~0.4328 nm).

\[
\lambda = 2d_{hkl} \sin \theta
\]
Where, $\lambda$ is x-ray wavelength, $\theta$ is diffraction angle, $d_{hkl}$ is interplanar spacing, $a$ is lattice parameter, and $(h, k, l)$ is Miller index.

Ishigaki et al [30, 31] found that the lattice parameter of TiC depended on the ratio of carbon and titanium atoms. After plasma treatment, the oxygen atoms could replace carbon atoms in TiC lattice. As a result, the lattice parameter of TiC slightly decreased. However, this is probably due to carbon atoms or oxygen atoms could remove from their lattice site and form vacancies, which expands the lattice parameter of TiC.
Spheroidization rate is an extremely important index to evaluate the effect of plasma spheroidization. The effect of powder feeding speed on spheroidization rate has been investigated as shown in figure 4. Figures 4(a)–(e) show that TiC powders morphology were magnified at 200 times, and figure 4(f) is the spheroidization rate statistical result of TiC powders at different feeding rate from theses morphology figures. Figure 4 indicate that feeding speed highly affect the efficiency of powder spheroidization. When the feeding speed increases, the spheroidization rate decreases rapidly. In fact, the spheroidization effect of TiC powders is closely related to absorbed energy in plasma torch [28].

The energy absorbed by the powder in the plasma flame region \( W_{in-flight} \) can be obtained from equation [32]:

\[
W_{in-flight} = \rho \cdot A_0 \cdot t_{dwell}
\]

\[
\rho = k \cdot (T_{\text{plasma}} - T_{\text{particle}})
\]

Where \( \rho \) and \( k \) are the heat flux density and heat transfer coefficient respectively; \( A_0 \) is the particle surface area; \( t_{dwell} \) is the dwelling time of the particles in the plasma torch zone; \( T_{\text{plasma}} \) and \( T_{\text{particle}} \) are the temperature of the plasma and the temperature of the particles, respectively.

Therefore, the energy absorbed by the powders in plasma torch zone is primarily dependent on the dwelling time and heat transfer coefficient. In the case where particles size of powder and heat transfer coefficient are constant, the powders feeding speed could determine the dwelling time of powder in the plasma torch zone. Based on above analysis, when the powder feeding speed gradually increases, dwelling time of TiC powders in the plasma torch region would decrease and the energy absorbed by individual particle become lower. Therefore, spheroidization rate decreases with increasing the feeding speed due to insufficient melting of powders.

Figure 5(a) presents the morphologies of spherical particles with the small size flakes deposits on the surface, and its surface contains many bumps and deep trenches. These bumps could be regarded as the outer surface of many small grains, which are produced by relatively rapid cooling [23]. Figures 5(b)–(f) show that the morphologies of TiC powders changes from dendritic to cellular structure with increasing the feeding speed. For binary systems, solute enrichment in the liquid near the solidified interface locally change the equilibrium liquidus temperature and produce an unstable, constitutional undercooling condition, which induce the unstable solidified interface and propagate forward. For these reasons, grains develop into cellular or dendritic structure. After thermal plasma treatment, TiC grain could achieve a large growth rate because of rapid cooling, which is beneficial to produce constitutional undercooling for the formation of cellular/dendritic microstructure. According to the above-mentioned discussions, the heat absorbed by TiC powders would decrease with increasing the feeding speed. Moreover, both the cooling rate and grain growth also decrease. On the other hand, the amount of evaporated particles from molten TiC would also reduce. These evaporated particles, acted as nuclei, could be detrimental to the stability of solidified interface, which leads to increasing the
number of grains and forming dendritic grains. Consequently, as a function of grain growth rate and evaporated particles, it restrains the formation of dendritic structure.

Conclusions

The highly spherical TiC powders with uniform distribution and well dispersity were obtained by thermal plasma treatment. There are no additional phases appear after thermal plasma treatment, and the spheroidization rate is almost 100% by adjusting feeding speed. As the feeding speed increased, the morphologies of TiC powders changed from dendritic to cellular structure due to the slower cooling rate and fewer numbers evaporated particles.

Acknowledgments

This work was supported by Guangdong Provincial Science and Technology Program (Grant No. 2015A050502015), the Guangzhou Municipal Science and Technology Program (No. 201707010056), the Fundamental Research Funds for the Central Universities, Natural Science Foundation of Guangdong Province (No. 2016A030313494, 2018A030313615, 2018A030310406), the Fundamental Research Funds for the Central Universities, the Opening Project of National Engineering Research Center for Powder Metallurgy of Titanium & Rare Metals, Zhongshan Municipal Science and Technology Program (Platform construction and innovation team) (Grant Nos. 2015F1FC00036, 2016F2FC0005, and 2017G1FC0003), Zhongshan Collaborative Innovation Fund (Grant Nos. 2018C1001) and Zhongshan Science and Technology Research Program (2017B1138).

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