Powder Technology 274 (2015) 393–401

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Fabrication of titanium carbide nano-powders by a very high speed planetary ball milling with a help of process control agents

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ARTICLE INFO

Article history:
Received 28 July 2014
Received in revised form 13 October 2014
Accepted 20 January 2015
Available online 26 January 2015

Keywords:
Titanium carbide
Very high speed planetary ball milling
Particle refinement
Process control agent
Particle size characterization

ABSTRACT

Nano-sized TiC ceramic powders were fabricated by very high speed planetary ball milling, especially using coarse (micron-sized) starting powders with the help of process control agents, and their refinement behavior was investigated as a function of the milling time and ball size. Fine and uniform TiC nano-particles were achieved through a short-time mechanical milling for 60 min, in which small-sized milling balls were fairly advantageous to homogeneous particle refinement by inducing low-energy, but high-frequency collisions. Moreover, a liquid-type process control agent such as toluene played a crucial role in refining the TiC nano-particles, owing to its superior capability for heat dissipation during the milling process. Under the estimated optimal milling conditions, it is notable that the particle size of the TiC powders was effectively reduced well below 50 nm, which was reliably characterized by direct transmission electron microscopy along with a complementary acoustic particle size analysis.

1. Introduction

Titanium carbide (TiC) particulates have been demonstrated as an excellent ceramic reinforcement for various metallic materials such as Al, Cu, and Fe-based alloys, owing to their high melting point, high hardness, low friction coefficient, and good corrosion resistance [1–3]. In particular, nano-sized TiC particles are considered as a promising microstructural modifier and mechanical strengthener for particle-dispersed composite alloys, since the fine TiC dispersoids in the metallic matrix improve the overall properties of the materials without an adverse effect on the ductility or toughness [4,5].

To obtain the desirable properties of the particle-dispersed alloys, the nano-sized TiC particles should be distributed homogeneously in the metallic matrix, where the beneficial effect of the particle dispersion becomes more significant with a decrease in the particle size [6]. Conventionally, there is a particle size limitation of available TiC nano-powders with a minimum value of 100 nm, and even industrially-usable powders show a large inhomogeneity in the size distribution in spite of their quite high cost [7,8]. This shortcoming has restricted the application field of the TiC nano-powders for producing particle-dispersed composite alloys.

Among the various physical and chemical methods, a mechanical ball-mill technique is recognized as a simple and cost-effective method to produce fine and homogeneous powders [9,10]. By employing this technique, however, most attempts have been conducted to fabricate metal-matrix composite powders incorporating finely-dispersing ceramic particles [11–13], and little information has been reported on the fragmentation of pure or unmixed ceramic powders alone. Moreover, the conventional ball-mill process used in these studies presented relatively low impact energy owing to its low milling speed, thereby causing a long processing time of over several tens of hours, as well as an insufficient refinement of the ceramic particles [14,15]. Owing to this deficiency, the initial raw powders were usually prepared from very costly nano-sized ceramic powders and coarse powders with micron-sizes were not applicable to this low-energy process.

In this respect, very high speed planetary ball milling, which was recently developed with our own design [16,17], would be potentially more advantageous to fabricate fine ceramic particles from initially coarse powders. The relevant studies showed that the metal-matrix composite powders with a homogeneous dispersion of nano-sized ceramic particles were reliably synthesized in a very short time (less than 1 h) using just the coarse starting powders with particle sizes of several tens of micrometers [18,19]. This process is thus expected to be certainly capable of refining the cheaper coarse ceramic powders down to a nanometer level using short-time milling, if the process conditions are optimized for pure ceramic powders. Along with high milling energy, a small addition of the process control agents (PCAs) such as

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http://dx.doi.org/10.1016/j.powtec.2015.01.047
0032-5910/

stearic acid, toluene, ethanol, and acetyl-acetone can offer supplementary assistance in refining the ceramic powders during the milling process. Although the experimental results, up to now, have been focused mostly on the refinement of metal-based powders [20–23], it is also supposed that the PCAs play an appropriate role in the mechanical milling of pure ceramic powders, in such ways not only to decrease the cold welding and agglomeration among the particles by preventing sticking, but also to improve the pulverization by minimizing a rapid temperature rise.

In the present study, very high speed planetary ball milling was employed to fabricate fine TiC nano-powders by pulverizing the initially coarse ones (size: ~10 μm) with a help of the PCA addition. The very high speed ball milling behavior was first investigated for the pure TiC powders, and the proper milling conditions were determined in view of the milling time and ball size. Thereafter, two types of PCAs, i.e., stearic acid and toluene, were introduced to the milling process and their effect on the particle refinement was comprehensively examined.

2. Experimental procedure

2.1. Very high speed planetary ball milling

The starting material used was TiC powders (99.5% purity) with an average particle size of 10 μm. The TiC particles exhibited an irregular shape and faceted surface morphology, as presented in Fig. 1. The raw TiC powders were ball-milled as functions of milling time and ball size using a planetary ball mill machine specially designed to carry out the mechanical milling at a very high disk rotation speed of up to 850 rpm [18]. The steel balls (AISI 52100) with diameters of 10, 8, 5, and 3 mm were employed and the ball-to-powder weight ratio was kept at 40:1. The milling time varied from 3 to 120 min. Prior to milling, the hardened steel jar (SKD-11) was sealed in a glove box filled with high purity argon (99.999% purity). For some milling experiments, a small amount of PCA was introduced into the jar together with the TiC powders and the steel balls. Two kinds of PCAs, i.e., solid stearic acid ($CH_3(CH_2)_{16}COOH$) and liquid toluene ($C_6H_5CH_3$), were used. Table 1 summarizes the details of the very high speed planetary ball milling process. For a comparative purpose, the TiC powders were also mechanically-milled using a conventional planetary ball mill machine (Fritsch Pulverissette 7) at a disk rotation speed of 550 rpm [17]. The volume of the jar was 100 cm^3 and the ball weight was reduced to about 133 g. Other milling conditions were similar to those for the very high speed planetary ball milling.

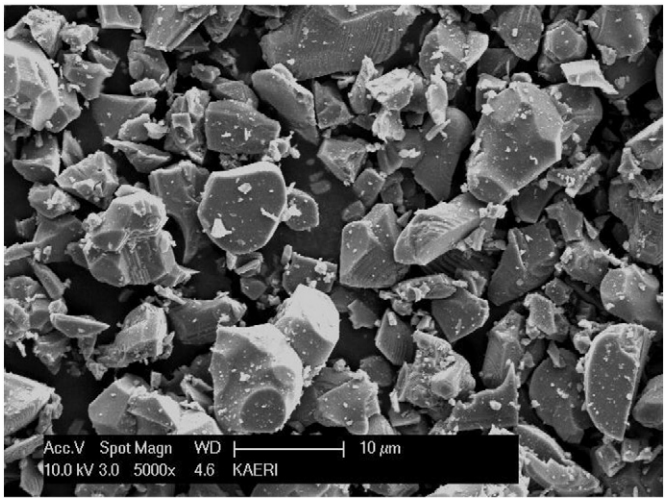

Fig. 1. SEM image for the TiC starting powder.

Table 1
Experimental parameters for the very high speed planetary ball milling process.

Specifications of the milling machine (PM300)		
Max. rotation speed of disk, rpm		850
Max. rotation speed of jar, rpm		2065
Jar volume, cm^3		300
Grinding ball		Steel (AISI 52100)
Cooling system		Water cooling
Milling atmosphere		Argon
Milling conditions		
Ball to powder weight ratio		40:1
Ball weight, g		400
Powder weight, g		10
Milling time, min		3, 10, 20, 60, 120
Ball size, mm		10, 8, 5, 3
Amount of PCA	Stearic acid, wt.%	2.5, 5
	Toluene, ml	0.5, 5, 10

2.2. Characterization of the milled TiC powders

The size and surface morphology of the milled TiC powders were first examined using field emission scanning electron microscopy (FE-SEM, FEI Sirion) coupled with energy dispersive spectroscopy (EDS). The detailed particle morphology has been further investigated using high-resolution transmission electron microscopy (HR-TEM, JEOL 2100F). The crystal structure of the milled powders was identified by X-ray diffraction (XRD, Rigaku D/MAX-2500) with Cu Kα radiation operating at 40 kV and 300 mA. The particle size distribution was evaluated using an acoustic particle size analysis (APSA, MATEC zeta-APS). For the APSA measurement, the milled TiC particles were dispersed ultrasonically in the ethanol solvent. The specific surface area and average particle size of the milled TiC powders were also measured by a Brunauer–Emmett–Teller (BET, Micromeritics ASAP2020) technique using a nitrogen adsorption method. Prior to the characterization, the TiC powders milled with the toluene were fully dried at 120 °C for 7 h in a vacuum chamber ($<10^{-3}$ Torr), while the stearic acid in the milled powders was eliminated by heating at 400 °C for 3 h. The amount of impurities was measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo Elemental ICP-MS X-7).

3. Results and discussion

3.1. Effect of the milling time on the milling behavior of the TiC powders

Fig. 2 shows the SEM morphologies for the milled TiC powders prepared as a function of the milling time (milling speed: 850 rpm, ball size: 5 mm). In milling for 3 min (Fig. 2(a)), a large portion of the TiC powders was fragmentized considerably, but their size distribution was quite inhomogeneous. Their irregular shape and faceted surface morphology were maintained as it was in Fig. 1, indicating that the fragmentation was predominant over the agglomeration in this early milling stage. When the milling time increased to 10 min, several large powders were produced by an enhanced agglomeration of fragmentized small particles as indicated by the arrows in Fig. 2(b). At this milling time, the individual particles grew much finer by the pulverizing effect, but easily adhered to each other owing to the increased fresh surface. As the milling time increased further, the agglomerated particles started to disaggregate, simultaneously showing a gradual decrease in the particle size, as noted from the powders milled for 20 min (Fig. 2(c)). This particle refinement progressed more by a prolonged ball milling, and eventually the finest TiC particles were obtained at the milling time of 60 min without any noticeable agglomeration. For this milling time, the milled powders showed a relatively homogeneous size distribution, as shown in Fig. 2(d). After reaching the critical size, the TiC particles were coarsened again by the excessive milling, as evidenced