Fast and efficient approach to synthesis of ultra-fine TiC powder

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Abstract
A fast and large scalable process to produce TiC powder was obtained using a horizontal rotary ball mill within 60 min via a mechanically induced self-propagating reaction (MSR). The as-synthesized TiC particles have well-defined crystals structure and the median diameter of ~1 μm with less impurity due to short duration of milling. The mechanism for the acceleration of MSR was investigated in detail. The graphene nano-platelets are exfoliated from graphite by ultra-high-energy of the horizontal rotary ball mill after less than 30 min of milling, which plays a crucial role in formation of leaf-like nanoplatelets with Ti lamella by ball collision. At the same time, the ultra-high-energy of ball milling can boost self-prorogating reaction in a short duration of milling.

1. Introduction

As an outstanding nonoxide ceramic material, titanium carbide (TiC) has desirable properties such as high melting point, low density, superior hardness, high Young’s modulus, excellent electronic and thermal conductivity, which have made it as a remarkable material for extensive applications in cutting tools, grinding wheels, wear-resistant and heat shields coatings, turbine seals and a reinforcing phase in composites and superalloys [1–3].

Traditionally, carbothermal reduction has been used to obtain TiC powder from TiO2 and carbon at temperatures above 2073 K thanks to cost effectiveness of raw materials and large-scale production [4–6]. A further process of ball milling is usually necessary to obtain the fine TiC powder [7]. As the routes mentioned above required expensive high temperature equipment, several other synthetic techniques have been developed including: self-propagating high-temperatures synthesis (SHS) from Ti and C [8–10], metallic thermal reduction [11], post milling solid synthesis [3, 12], sonochemical [13], melting-casting [2], improved carbothermal reduction [14–19], thermal plasma [16, 20], vapor deposition [21], a thermo-chemical reaction [22–24] and mechanical alloying (MA) [25–27] etc. Traditional mechanical alloying (MA) is a promising method to produce TiC powder with ultra-fine size and convenient process at room temperature. In addition, the composition of final products is feasibly controlled by the ratio of raw materials. MA is usually performed by high-energy ball milling and often known as mechanically induced self-propagating reaction (MSR) or mechanically induced solid-state diffusion reaction (MDD) [24, 28, 29].

There are a number of reports and published papers about mechano-synthesis of TiC due to technical and scientific reason. In addition, the final product of this synthesis method is a fine, homogeneous nanocrystalline powder, and can be easily used in conventional powder metallurgical processes. Delogu et al [29, 30] reported that the mechanochemistry of Ti + C powder during ball milling depended on the chemical composition, the collision energy and volume of the powder charge. As the composition between Ti20C80 and Ti45C55, or between Ti52C28 and Ti80C20, a gradual kinetics was occurred. An MSR underwent while powder mixtures between Ti45C55 and Ti52C28. Lohse et al [31, 32] also found a minimum carbon content was required to sustain MSR to form TiC, below which TiC was formed via MDR. Wu et al [33] suggested a transitional bonded state (Ti···C) plays an important role in reducing the ignition temperature for a combustion reaction during the mechanosynthesis process. Oghenevweta et al [28, 34] proposed a dual mechanism of MSR involving a rapid
high temperature nucleation of new TiC with local melting of unreacted Ti and the growth of pre-existing nano-TiC.

Note that it usually required some tens of hours to obtain stoichiometric TiC depending on the type of mill [27] such as vibro-mill [30, 35], magneto ball mill [28, 31, 32, 34, 36] and planetary ball mill [6, 37–40]. Specifically, the incubation period before a MSR was 37 h in [28, 34], 70 h in [32] and 71 h in [31, 36]. Up to now, minimum synthesis time in planetary ball mill is within 35 min [39]. The long duration of ignition of combustion reaction was due to the impact energy of the mill. By increasing the impact energy, the ignition time decreased exponentially [29, 41]. The critical power intensity at which the transition from gradual to MSR occurs was 2.7 W g⁻¹ [38] or 0.027 J [29]. Therefore, increasing velocity of balls or collision energy would benefit MSR and shorten the incubation time.

This study aims at synthesizing ultra-fine TiC powders at a fast and efficient method using a horizontal rotary ball mill (CM01-2L, Zoz GmbH), which could supply much larger ball energies than typical planetary devices. The maximum velocity of the horizontal rotary ball mill was ~15 m s⁻¹ and about 3 times faster than that of planetary ball mills [41, 42]. The detail of the evolution of TiC was investigated at high impact energy during MA for the first time to the best of our knowledge.

2. Experimental

2.1. Materials

High purity elemental Ti powder (99.5 % purity, –500 mesh) was purchased from Beijing Xing Rong Yuan Technology Co., Ltd. and synthetic graphite powder (MBG-M1, 99.9 % purity) with a median diameter of 10.2 µm was supplied by Huizhou Chuangya Power Battery Materials Co., Ltd. n-Octadecanoic acid was purchased from the Sinopharm Group Co. Ltd. and used as a process control agent (PCA) to avoid sticking of the powders to the vial and balls during ball milling. All materials were used as-received without further treatment.

2.2. Preparation of TiC powder

A horizontal rotary ball mill (CM01-2L) from Zoz GmbH (Germany) equipped with a hardened steel container and bearing balls was employed. The volume of the milling chamber was 2 L and the #3 ball was chosen with a diameter of 2.38 mm. Total weight of filled balls was 2 kg and the ratio of the weight of the balls to the powder (BPR) was 20:1. Milling speed was 900/1000 rpm. Elemental titanium and graphite were 100 g and mixed at the composition of Ti₅₀C₅₀ (1:1 atomic ratio). 0.75 g PCA was utilized during milling. Argon atmosphere was used to protect powder from oxidation during milling. The wall of the chamber was under a continuous water cooling at an ambient temperature. Small aliquots of the sample were taken out to detect the structural evolution of powder at different milling time.

2.3. Characterization

X-ray diffraction (XRD, D/Max 2200, Rigaku) using a Cu Kα (1.54056 Å) target was carried out with a scanning rate of 8° min⁻¹ and a step of 0.02°. The morphology of the powder was acquired using scanning electron microscopy (SEM, XL30ESEM, Philips), and field-emission transmission electron microscopy (Nova Nano SEM 450, FEI). The atomic structure was conducted by the high angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and high-resolution transmission electron microscope (HRTEM, Tecnai G² TT30, FEI). The particle size distributions and median diameters of powder were processed by a laser diffraction particle size analyzer (Winner2000, WEINA).

3. Results and discussion

Figure 2 presents XRD patterns of raw materials and mechanically alloyed Ti₅₀C₅₀ powders as a function of milling time. The un-milled powders demonstrated the sharp diffraction peaks of both elemental Ti and C in accordance with the PDF cards of #04-003-714 and #01-089-848 respectively. The (002) graphite peaks with extremely oriented disappeared into the background after only 15 min of milling, while the Ti peaks slightly broadened and shifted to lower Bragg angles due to high density of lattice imperfections produced by MA. No evidence of TiC was demonstrated prior to ignition of MSR. The grain sizes of Ti were estimated according to the Scherrer equation [43], \(D = \frac{K \lambda}{B \cos \theta},\) decreased from ~400 nm to 178 nm. During the initial stage, dissolution of C in Ti phase resulted to planar imperfections [6, 25, 37], like stacking faults, and expansion of the d-spacing (d) and small decrease of Bragg angles (θ) as a consequences of Bragg equation, \(2d \sin \theta = n \lambda.\) The relative intensities of the (002) Ti peaks over other peaks increased. It was suggested that Ti particles were embedded on the graphite layer and aligned along the (002) direction due to the similar texturing effect [39]. The
results are well consisted with the 3–10 h of milling in [6, 25, 28, 40, 44]. After 30 min of milling comparing with 37 h in [28] or 19 h in [33, 40], MSR was ignited and XRD pattern (figure 2 (30 min)) showed sharp peaks indexed with PDF card # 65-8808 which matched the fcc TiC phase (Fm-3m (225)) with a slight shift to lower Bragg angles, meaning the increase of TiC lattice parameters. All the Ti peaks disappeared, suggesting complete reaction obtained immediately. While 60 min of milling, the position of TiC peaks made no shift and the large bump peak disappeared. The continuous dissolution of C to TiCx lattice decreased with the lattice parameter of TiCx crystal, and thus the Bragg diffraction angle will be increased to the standard position of TiC phase. With further milling time up to 210 min, the TiC peaks became slightly broadened, indicating the decrease of crystallite sizes of TiC. These also confirmed that the formed TiC phase was very stable. The grain sizes of TiC were estimated at 30 min, 60 min and 210 min as 25.2 nm, 16.5 nm and 12.7 nm respectively. The decrease of grain size was attributed to the repeated actions of collision that balls impacted on the particles [25]. It was revealed that the nanocrystalline TiC particles with narrow size distribution could be fabricated by MA within a very short duration of milling.

Figure 3 illustrates average diameters (D_{50}) and particle size distributions of Ti50C50 mixture sampled at different milling time and raw materials. The median diameters of graphite and Ti powder are 8.91 μm and 20.2 μm respectively. After 15 min of milling, the median diameter increased to 27.61 μm owing to the deformation of titanium particles to flake/platelet shape resulting from the impact of balls [25]. After ignition at ~30 min, the diameter decreased rapidly to 5.61 μm which indicated the TiC powders were formed as small particles. The diameter became 0.98 μm while continually milling and reacting. After long duration of milling up to 210 min, aggregation of TiC with a diameter of 2.75 μm were formed and two peaks in figure 3(b) suggested rod-shaped particles.

Figures 4(a) and (b) show FESEM morphologies of as-milled products of Ti50C50 mixture after milling for 30 min. The metallic Ti particles were typically deformed as plates (figure 4(a)), and many leaf-like flakes (figure 4(b)) were stacked on the surface of the particle. The composition of the particle in spot A (red circle) in
Figure 4(a) was Ti$_{73}$C$_{27}$ and that in spot B was Ti$_{31}$C$_{69}$ based on the quantitative analysis of EDS in figure 4(c). It was suggested that C was dissolved into Ti plates under collision of balls. When the content of C in Ti particle approached to saturation, the TiCx mixture flakes were formed and exfoliated, which made the extra heterogeneous mixture of C and Ti at micro- or nanometer size. Oghenevweta et al. [28] also proposed that the formation of thin-plated TiC multilayers was a unique step of growth sequence of TiC nuclei at the start of MSR.

Graphene nanoplatelets obtained from graphite by ball milling are given in figure 5. It was shown that graphene was delaminated from graphite as large as several hundred nanometers and self-assembled into nanoplatelets, which was also confirmed by EDS in figure 5(b). Although there were many reports about large-scale production of graphene or amorphous graphite from graphite via ball milling [45–49], it was the first time to find that the formed graphene played an important role in acceleration of MSR to the best of our knowledge. The formation of graphene could elucidate both the disappearance of the XRD peaks associated with graphite after a very short duration of milling [6, 38] and the presence of Raman spectroscopy peaks corresponding to graphite which were no longer detected by XRD analysis. In addition, another reason was the mass absorption coefficient of Ti for Cu K$_\alpha$ was more than 45 times higher than that of C [6].

Figure 6 shows TEM images and the selected-area electron diffraction pattern (SAED) of Ti$_{50}$C$_{50}$ mixture sampled at 30 min of milling. The diameter of the particle in figure 6(a) was in good agreement with figure 3. Along the edge of the particle, graphene mounted into the Ti powders, as shown in figure 6(b). During milling, C atoms gradually diffused into and reacted with Ti to form TiC under the heavy collision of balls. Sharp diffraction spots and rings in the SAED pattern (inserts) matched the d-spacing of (001), (101) of Ti and (200), (220) and (020) of TiC, as presented in figure 6(c). Both of two phases were close together. The SAED pattern (insert) in figure 6(d) was indexed with (006) and (0014) of TiC$_x$. The difference of composition of C in the grains was due to the diffusivity of C atoms during ball milling. The formation of TiC$_x$ could decrease the ignition temperature [10, 31] and induced the successive formation of TiC [6, 12]. The formation of nonstoichiometric
TiC$_x$ prior to MSR has been found by Raman spectroscopy in the previous study [36]. The activation energy for the chemical diffusion of carbon in TiC$_x$ was constant, but its rate increased exponentially with the carbon vacancy fraction (x) [50]. At the initial time, the distribution of C in Ti powder was non-uniform and different non-stoichiometric TiC$_x$ compound were formed. Nevertheless, stoichiometric TiC would be in the end after milling via either MSR or MSD.

TEM and HRTEM images of end product of TiC after 60 min of milling are shown in figure 7. There were no excess starting raw materials (Ti and/or C atoms) in the alloy powders, as shown in figures 7(a) and (b). Sharp spot pattern was detected in the SAED rings corresponding to fcc TiC. Figure 7(c) displays the HRTEM of a near-edge zone of the particle. The lattice fringe spacing in figure 7(d) matched well with the interplanar spacing of TiC. The internal structure of the particles was marked by a single phase and well-defined crystalline features (figure 7(b)), which agreed well with other literatures [25, 26, 44]. A small part of TiC$_x$ with several nanometers was also observed on the surface of the particle. Due to a very short duration of milling (60 min), O element wasn’t determined in the as-synthesized TiC powders indicating avoiding oxidation of Ti and other impurity.

Figure 3. (a) Particle size distributions of Ti$_{50}$C$_{50}$ mixture sampled at different milling time and (b) average diameters of raw materials and Ti$_{50}$C$_{50}$ mixture.

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\begin{align*}
\text{Volume distribution} / \% & \\
\text{Particle Size / \(\mu m\)} & \\
15 \text{ min} & \\
30 \text{ min} & \\
60 \text{ min} & \\
210 \text{ min}
\end{align*}
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associated with dissolving of Fe from the wastage of the grinding mill ball/chamber according to the quantitative analysis of EDS in figure 7(f) [7, 37, 38].

The MSR process of TiC and structural evolution have been discussed by many researchers [25, 29, 31, 32, 36, 38, 39]. MSR of Ti + C depended on two main factors. One was to reduce the particle size with accumulated deformation or chemical energy and mix of the raw materials which could propagate the reaction by self-exothermic process, another was the ignition temperature to trigger SHS. That was the reason why the incubation period played a crucial role in chemical diffusion of C into Ti by deformation during ball milling. Otherwise, local MSR ignited by an individual collision could not propagate across the entire powder, and extinguished due to heat loss. For Ti + C powder mixtures with lower carbon contents, TiC was formed via

Figure 4. FESEM micrographs (a), (b) marked with red circles indicating the selected spots of interest for EDS acquisition and the corresponding EDS (c) of milled powders of Ti50C50 mixture sampled after 30 min of milling.
MDR instead of MSR due to the rate-limiting factor of the availability of carbon [31, 32, 41]. Wu et al. [33, 40] indicated the ignition temperature of TiC decreased by several hundred degrees with the increase of milling time. In our case, graphene was firstly formed by high-energy ball milling from graphite, and reacted with Ti by repeated cold welding and fracture to form leaf-like nano-platelets of non-stoichiometric TiCx, which mixed the elemental Ti with C in nanometer scale to heterogeneous composite. It was found that when TiC nanocrystallites embedded into amorphous carbon, charge transfer from the Ti 3d eg orbitals at the interface to the C 2p orbitals in the amorphous C phase would increase [51] and benefited the formation of TiC. Normally, the ignition temperature for a combustion reaction of Ti + C was about 2720 K [10], and a adiabatic temperature of 1800 K was necessary for the occurrence of combustion during the mechano-synthesis process thanks to lower activation energies resulting from the accumulation of lattice defects [33, 37]. Nevertheless, the local temperature of ball milling was as high as 2773 K [35]. Previous studies have shown that Ti + C powder started to nucleate at 150–250 °C after 36 h of milling [34]. This was an indication that the rate-controlling step was chemical diffusion of C during milling prior to combustion [6, 31, 52]. Therefore, the detailed sequence of formation of TiC under our conditions was the following: At beginning of milling, Ti particles were stretched as thin plates and graphite became graphene nano-platelets. Small non-stoichiometric TiCx layers were exfoliated from Ti to form heterogenous Ti + C mixture plates at nanometer level due to collision of balls. Once the activation energy of the mixture decreased to that under colliding temperature of MA, MSR occurred and TiC layers were instantaneously generated.

Figure 5. TEM observations (a) and the corresponding EDS (b) of graphene nanoplatelets obtained from graphite by ball milling.
4. Conclusions

A fast and large scalable approach to produce TiC powder was obtained by high-energy ball milling within 60 min, which could result in significant capital expenditure savings. The as-synthesized TiC particles had a highly crystalline phase and the median diameters of $\sim 1 \mu m$. The mechanism for the acceleration of MSR was
investigated in detail by SEM and TEM. The graphene nano-platelets were exfoliated from graphite by ultra-high-energy of the horizontal rotary ball mill. The graphene reacted with Ti lamella by collision of balls to form leaf-like nanoplatelets of Ti + C mixture. At the same time, MSR was boosted by the ultra-high energy in a short duration. Conclusively, the present method signified the great potential of the high-speed horizontal rotary ball milling for fabricating fine and homogeneous ceramic powders.

Figure 7. Milled products of Ti50C50 mixture sampled at 60 min of milling: (a) TEM overview; (b) SAED pattern obtained on the overall region in (a); (c)–(e) HRTEM image with SAED (insert) displaying spots that matched the d-spacing of TiC and (f) EDS of the overall region in (a).
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References

[1] Rasaki S A, Zhang B, Anbalagam K, Thomas T and Yang M 2018 Synthesis and application of nano-structured metal nitrides and carbides: a review Prog. Solid State Chem. 50 1–15
[2] Wang X, Ding H, Qi F, Liu Q, Fan X and Shi Y 2017 Mechanism of in situ synthesis of TiC in Cu melts and its microstructures J. Alloys Compd. 695 3410–8
[3] Mostaan H, Mehrizi M Z, Rafiei M, Beygi R and Abbassian A R 2017 Contribution of mechanical activation and annealing in the formation of nanopowders of Al(Cu)/TiC-Al2O3 hybrid nanocomposite Ceram. Int. 43 4680–5
[4] David J, Trolillard G and Maître A 2013 Transmission electron microscopy study of the reaction mechanisms involved in the carbothermic reduction of anatase Acta Mater. 61 5414–28
[5] Sen W et al 2011 Preparation of TiC powders by carbothermal reduction method in vacuum Trans. Nonferrous Met. Soc. China 21 185–90
[6] Ye L L and Quan M X 1995 Synthesis of nanocrystalline TiC powders by mechanical alloying Nanostruct. Mater. 5 25–31
[7] Hong S-M et al 2015 Fabrication of titanium carbide nano-powders by a very high speed planetary ball milling with a help of process control agents Powder Technol. 274 393–401
[8] Song M S et al 2009 Growth of TiC octahedron obtained by self-propagating reaction J. Cryst. Growth 311 378–82
[9] Nersisyan H H, Lee J H and Won C W 1998 Mechanosynthesis mechanism of TiC powders Mater. Sci. Technol. 14 4726–35
[10] Chen X, Fan J and Lu Q 2018 Synthesis and characterization of TiC nanopowders via sol-gel and subsequent carbothermal reduction process J. Soli. State Chem. 262 44–52
[11] Yuan X, Cheng L, Kong L, Yin X and Zhang L 2014 Preparation of titanium carbide nanowires for application in electromagnetic wave absorption J. Alloys Compd. 596 132–9
[12] Mohapatra S, Mishra D K and Singh SK 2015 Microscopic and spectroscopic analyses of TiC powder synthesized by thermal plasma technique Powder Technol. 237 41–5
[13] Preis H, Berger L M and Schulzle D 1999 Studies on the carbothermal preparation of titanium carbide from different gel precursors J. Eur. Ceram. Soc. 19 195–206
[14] Koc R and Folmer J S 1997 Synthesis of submicrometer titanium carbide powders J. Am. Ceram. Soc. 80 952–6
[15] Koc R and Folmer J S 1997 Carbothermal synthesis of titanium carbide using ultrafine titania powders J. Mater. Sci. 32 3101–11
[16] Tong L and Reddy R G 2005 Study of titanium carbide nano-powders by thermal plasma Scripta Mater. 52 1253–8
[17] Alexandrescu R et al 1997 Synthesis of TiC and SiC/TiC nanocrystalline powders by gas – phase laser – induced reaction J. Mater. Sci. 32 2629–35
[18] Yuan X, Cheng L and Zhang L 2015 Controlled fabrication of TiC nanocrystal clusters on surface of Ti particles for application in electromagnetic wave absorption J. Alloys Compd. 622 282–7
[19] Lin H, Tao B, Xiong J and Li Q 2013 Using a cobalt activator to synthesise titanium carbide (TiC) nanopowders Int. J. Refract. Met. Hard Mater. 41 363–5
[20] Zhong J et al 2012 Formation of novel mesoporous TiC microspheres through a sol-gel and carbothermal reduction process J. Eur. Ceram. Soc. 32 3407–14
[21] Liu Z G, Guo J T, Ye L L, Li G S and Hu Z Q 1994 Formation mechanism of TiC by mechanical alloying Appl. Phys. Lett. 65 2666–8
[22] EiSakaandarary M S, Konno T J, Sumiyama K and Suzuki K 1996 Morphological and structural studies of mechanically alloyed Ti44C56 powders Mater. Sci. Eng. A 217 265–8
[23] Le Caër G, Bauer-Grosse E, Pianelli A, Bouzy E and Matteazzi P 1990 Mechanically driven syntheses of carbides and silicides J. Mater. Sci. 25 4726–31
[24] Ogohenweta J E, Wexler D and Calka A 2018 Study of reaction sequences during MSR synthesis of TiC by controlled ball milling of titanium and graphite Mater. Charter. 140 299–311
[25] Delogu F and Tacaks L 2014 Mechanochimistry of Ti-C powder mixtures Acta Mater. 80 435–44
[26] Delogu F 2013 Activation of self-sustaining high-temperature reactions by mechanical processing of Ti-C powder mixtures Scripta Mater. 69 233–6
[27] Lohse B H, Calka A and Wexler D 2007 Synthesis of TiC by controlled ball milling of titanium and carbon J. Mater. Sci. 42 669–75
[28] Lohse B H, Calka A and Wexler D 2005 Effect of starting composition on the synthesis of nanocrystalline TiC during milling of titanium and carbon J. Alloys Compd. 394 148–51
[29] Wu N Q, Lin S, Wu J M and Li Z Z 1998 Mechanochemistry of TiC powders Mater. Sci. Technol. 14 287–91
[30] Ogohenweta J E, Wexler D and Calka A 2016 Early stages of phase formation before the ignition peak during mechanically induced self-propagating reactions (MSRs) of titanium and graphite Scripta Mater. 122 93–7
[35] Deidda C, Doppiu S, Monagheddu M and Cocco G 2003 A direct view of the self combustion behaviour of TiC system under milling JNM. 15-16 215–20
[36] Lohse B H, Calka A and Wexler D 2005 Raman spectroscopy as a tool to study TiC formation during controlled ball milling J. Appl. Phys. 97 114912–8
[37] Rahaei M B, Yazdani rad R, Kazemzadeh A and Ebadzadeh T 2012 Mechanochemical synthesis of nano TiC powder by mechanical milling of titanium and graphite powders Powder Technol. 217 369–76
[38] Dorofeev G A, Ladjanov V I, Lubrin A N, Gilmutdinov F Z, Kuzminykh E V and Ivanov S M 2011 Initial stage of mechanochemical synthesis in the Ti-C exothermic system Bull. Russ. Acad. Sci. Phys. 75 1427–34
[39] Ghosh B and Pradhan S K 2010 Microstructure characterization of nanocrystalline TiC synthesized by mechanical alloying Mater. Chem. Phys. 120 537–45
[40] Wu N Q, Wang G X, Wu J M, Li Z Z and Yuan M Y 1997 Investigation of TiC formation during ball-milling of elemental titanium and carbon Int. J. Refract. Met. Hard Mater. 15 289–93
[41] Deidda C, Delogu F, Maglia F, Anselmi-Tamburini U and Cocco G 2004 Mechanical processing and self-sustaining high-temperature synthesis of TiC powders Mater. Sci. Eng. A 375–377 800–3
[42] Boschetto A, Bellusci M, La Barbera A, Padella F and Veniali F 2013 Kinematic observations and energy modeling of a Zoz Simoloyer high-energy ball milling device Int. J. Adv. Manuf. Technol. 69 2423–35
[43] Holzwarth U and Gibson N 2011 The Scherrer equation versus the Debye-Scherrer equation Nature Nanotech. 6 534
[44] El-Eskandarany M S 1996 Synthesis of nanocrystalline titanium carbide alloy powders by mechanical solid state reaction Metall. Mater. Trans. A 27 2374–82
[45] Zhao W, Fang M, Wu F, Wu H, Wang L and Chen G 2010 Preparation of graphene by exfoliation of graphite using wet ball milling J. Mater. Chem. 20 3817–9
[46] Jeon I-Y et al 2012 Edge-carboxylated graphene nanosheets via ball milling Proc. Natl Acad. Sci. 109 5588–93
[47] Jeon I-Y et al 2013 Large-scale production of edge-selectively functionalized graphene nanoplatelets via ball milling and their use as metal-free electrocatalysts for oxygen reduction reaction J. Am. Chem. Soc. 135 1386–93
[48] Jeon I-Y, Bae S-Y, Seo J-M and Baek J-B 2015 Scalable production of edge-functionalized graphene nanoplatelets via mechanochemical ball-milling Adv. Funct. Mater. 25 6961–75
[49] Huang J Y 1999 HRTEM and EELS studies of defects structure and amorphous-like graphite induced by ball-milling Acta Mater. 47 1801–8
[50] van Loo F J J and Bastin G F 1989 On the diffusion of carbon in titanium carbide Metall. Trans. A 20 403–11
[51] Magnusson M, Lewin E, Hultman L and Jansson U 2009 Electronic structure and chemical bonding of nanocrystalline–TiC/amorphous-C nanocomposites Phys. Rev. B 80 235108–14
[52] Forrester J S and Schaffer G B 1993 The chemical kinetics of mechanical alloying Metall. Mater. Trans. A 26 725–30