Synthesis of nanocrystalline TiC reinforced W nanocomposites by high-energy mechanical alloying: Microstructural evolution and its mechanism

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A B S T R A C T
High-energy mechanical alloying (MA) of a micrometer-sized W and TiC powder mixture was performed to prepare TiC/W nanocomposites. X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), and laser particle size analysis were used to study the morphological change and microstructural evolution occurred during MA process. It showed that the powder particles experienced a continuous refinement during 0–35 h milling; on increasing the applied milling time up to 45 h, the particles had a tendency to coarsen. The 35 h milled powder had a considerably refined particle morphology, showing a narrow size distribution ($D_{25} = 0.47 \mu m$, $D_{50} = 0.61 \mu m$, $D_{75} = 0.74 \mu m$ and $D_{90} = 0.86 \mu m$) and a significantly elevated specific surface area of 4154.86 m$^2$/kg. The TEM results revealed that the particles of 35 h milled product consisted of a large number of ultrafine crystallites of W and TiC with sizes less than 20 nm and the nanometer-sized TiC particles were dispersed uniformly throughout the W matrix. The analysis of XRD spectra by Scherrer equation indicated that the average crystallite sizes of the W and TiC constituents in the 35 h milled powder were 8.5 nm and 13.6 nm, respectively, showing a good agreement with the experimental results. On further increasing the milling time up to 45 h, the partial amorphization of W constituent occurred in the milled powder. Formation mechanisms and theoretical basis for microstructural development and phase change in the milled powders were elucidated.

1. Introduction

Tungsten (W) and its alloys are very promising for the use as high heat flux components and high-power density structural materials in radiation environments, because of their high melting points, low thermal expansion coefficients, excellent compatibility with liquid metals, and low sputtering yield [1–3]. However, they typically exhibit serious embrittlement in several situations [4], which limits the structural applications of W materials. The following two microstructural factors may exert detrimental effects on the ductility of W: (i) the heterogeneity in grain size and its distribution; and (ii) the grain growth and coarsening by recrystallization [4].

Grain size refinement of metallic materials to a nanometer size range is of interest in recent years, since the preparation of such nanostructured materials is expected to enhance the mechanical properties [5–7]. It is revealed that the room-temperature ductility of W materials is strongly dependent on grain size and can be elevated significantly with decreasing the grain size [8]. Grain refinement effect in nanocrystalline W materials, either in the form of films and coatings for surface applications [9,10] or as the bulk-form parts [11,12], is accordingly a crucial methodology to enhance the mechanical properties of the corresponding coarse-grained conventional W materials. On the other hand, it is known that when heated above the recrystallization temperature, the microstructure of W is altered due to grain growth, which reduces strength and hardness and, in turn, causes brittleness [4]. The strengthening of the W matrix with ceramic phases, which are typically in the discontinuous form of particulates dispersed in matrix, is a promising method to decrease the brittleness [13]. A throughout microscopic distribution of the ceramic particles at grain boundaries tends to handicap the grain growth and grain boundary migration at higher temperatures, thereby increasing the recrystallization temperature and resultant toughness [14].

Therefore, in order to overcome the embrittlement of W, a promising alternative method is to synthesize W materials having nanostructured fine grains and homogeneously dispersed particles of ceramics (e.g., transition metal carbides). Based on this strategy, abundant research efforts have been focused on the design and synthesis of high-performance metal matrix composites (MMCs), which is regarded as attractive alternative to the traditional and newer generation of unreinforced metallic materials [15,16]. Typically, the particle size of the reinforcement has a strong influence

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on the strength, ductility, and failure mode of MMCs [17]. Large ceramic particles tend to crack during mechanical loading, resulting in low ductility and premature failure of MMCs. Recent studies have approved that the preparation of metal matrix nanocomposites by decreasing the ceramic particle size to a nanometre scale can lead to a substantial improvement in the mechanical performance of the final products [18,19]. For the W-based nanocomposites being studied, the formation of a significantly refined nanostructured W matrix and a uniform dispersion of the nanoscale ceramic phase within the matrix contribute to the improvement of the mechanical properties.

Mechanical alloying (MA), as a non-equilibrium, low temperature, and solid state powder processing technique, involves repeated cold-welding, fracturing, and re-welding of powder particles in a high-energy ball mill [20–22]. It has demonstrated a high capability in producing equilibrium and non-equilibrium structures, including solid solution [23,24], nanocrystallites [25,26], metastable compounds [27], and amorphous solids [28]. Nevertheless, a homogeneous dispersion of nanometer-scaled particles within the matrix cannot be easily achieved, since nanoparticles generally possess an extremely large specific surface area and the attendant enhanced kinetics of aggregation [29,30]. For MA preparation of W-based nanocomposites, the prevention of the reinforcement clusters or agglomerates in the matrix and the formation of a uniform dispersion of the nanoscale reinforcing particles is accordingly a primary consideration. Secondly, the development of the constitution phases and microstructural features (e.g., particle morphology, particle size and its distribution, and interior grain size and nanostructures) of the nanocomposites powder during MA process requires a comprehensive investigation.

In this work, nanocrystalline TiC particulate reinforced W-based nanocomposite powders were synthesized by MA of a mixture consisting of micrometer-sized W and TiC components. TiC is widely used as reinforcing phase for MMCs, due to its low density, high strength and hardness, and chemical inertness and stability with a number of metallic matrixes [31]. The phases, microstructures, and physical properties (e.g., particle size distribution and specific surface area) of the milled powders were studied and the reasonable mechanisms for the microstructural development during MA process were elucidated.

2. Experimental procedures

2.1. Powder materials

The starting powder components included 99.9% purity W powder with an equiaxed structure and an average particle size of 5 μm (Zhuzhou Kete Industries Co., Ltd., China) and 99.8% purity TiC powder with an irregular shape and an average particle size of 1.5 μm (Zhuzhou Cemented Carbides Group Co., Ltd., China). Powder mixtures containing 24.625 g W and 0.375 g TiC were weighed and mixed, in which the weight fraction of the TiC component was 1.5 wt.%. The TiC component content used in this study was determined based on the previous literatures on powder metallurgy (PM) processing of W-based composites [32,33].

2.2. MA processing

MA was performed in a high-energy Pulversitte 6 planetary mono-mill (Fritsch GmbH, Germany). A hardened chromium-steel grinding bowl was used, whose useful capacity was 250 ml. Stainless steel grinding balls (the number of 010 mm balls was 40 and the number of Ø6 mm balls was 133, with a total weight of 200 g) and 25 g powder mixture to be ground were charged into the grinding bowl, with the ball-to-powder weight ratio of 8:1. MA treatment was under the protection of argon atmosphere to avoid oxidation of the powders. Five different milling times, 10, 25, 30, 35, and 45 h, were set periodically, while the rotation speed of the main disc was fixed at 300 rpm. In order to avoid excessive temperature rise within the grinding bowl, 20 min ball milling duration was followed by an interval of 10 min.

2.3. Microstructural characterization

Phase transformation of the milled powders was identified by a D8 Advance X-ray diffractometer (XRD) (Bruker AXS GmbH,

![Fig. 1. XRD patterns obtained over a wide range of 2θ degrees showing diffraction peaks of the milled powders at different milling times (a). XRD spectra in the vicinity of the strongest diffraction peak of W showing change of W peak during milling (b). The underlying relatively smooth spectra are obtained by XRD scan at a faster rate.](image-url)
Germany) with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA, using a continuous scan mode. A quick scan at 4°/min was primarily performed within a wide range of 2θ = 30–105° to give a general exhibition of diffraction peaks. A slower scan rate of 1°/min was further used over 2θ = 39.0–41.5° to give a more accurate determination of peaks. The Scherrer equation was used to estimate the average crystallite size (Dc) of the milled powder [34]:

\[ D_c = \frac{0.89\lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the wavelength of X-ray, \( \beta \) is the full width at half maximum of diffraction peak, and \( \theta \) is the diffraction angle. The microstructural features of the powders were characterized using a HITACHI S-4800 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 3.0 kV. The particle size distributions and specific surface areas of the milled powders were determined using a BT-9300H laser particle size analyzer (Bettersize Instruments Ltd., China). The accuracy error of as-used laser particle size analyzer was less than 1%. The interior nanostructures of powders such as constitution phases, grain size, and crystal structure were investigated using a Tecnai G2 20 S-TWIN transmission electron microscopy (TEM) (FEI Company, The Netherlands).

3. Results and discussion

3.1. Phases and crystallite sizes

Fig. 1 depicts the XRD spectra of the milled powders at various milling durations (10, 25, 30, 35, and 45 h). As revealed in Fig. 1(a), the visible phases were detected as W and TiC, while no other phases were observed. As shown in Fig. 1(b), XRD spectra in the vicinity of the standard 2θ location of W phase (2θ = 40.264°) indicated the change in W peaks during milling. On increasing the milling time, the strongest diffraction peaks of W became apparently broadened, which implied the formation of considerably small-sized crystallites in the powders underwent a long-time milling. Also, as the milling prolonged, the 2θ locations of the diffraction peaks for W generally shifted to higher 2θ degrees (Fig. 1(b)). According to the Bragg’s law [34]:

\[ 2d \sin \theta = n\lambda \quad (n = 1, 2, 3, \ldots) \]  

the observed increase of 2θ at a higher milling time indicated a decrease in the lattice plane distance \( d \). The average crystalline sizes of the W and TiC constituents at different milling times are revealed in Fig. 2. It showed that the calculated crystallite sizes of both W and TiC components decreased in the early stage of milling and, then, changed slightly at the longer milling times. On prolonging the milling time from 10 to 25 h, the W average crystalline size decreased gradually from 10.1 to 8.7 nm, while the TiC average crystalline size decreased rapidly from 19.3 to 14.2 nm. As the milling time extended from 30 to 35 h, the W average crystalline size remained unchanged at 8.5 nm, and the TiC average crystalline size changed slightly from 13.6 to 13.4 nm. However, as the milling time further increased to 45 h, the mean crystalline sizes of the

![Image](image_url)
W and TiC constituents both became coarsened, rather than being continued to reduce. The mean crystalline size of W showed a slight coarsening to 8.9 nm, while the average crystalline size of TiC was elevated apparently to 13.9 nm after 45 h milling.

The nanocrystallization process and underlying mechanisms in the present TiC/W composite system during milling were proposed as follows. In the early stages of milling (up to 25 h), the work hardening of the milled powder occurred and the dislocation density within the particles increased [35]. The interaction of these dislocations generated sub-boundaries within particles, which in turn resulted in the decomposition of the initial large-sized grains into smaller ones. In addition, with the presence of hard small-sized TiC particles in the milling system, the hindering of the dislocation movement by Orowan bowing mechanism led to an increase in the dislocation density [35], thereby accelerating the grain refining progress. In the middle stages of ball milling (from 25 to 30 h), the fractured powder particles underwent severe deformation repeatedly and, consequently, the local dislocation density increased continuously. The grain refinement effect continued to prevail, leading to the formation of the favorable nanostructure. With ball milling continued (30–35 h), the lattice dislocation density tended to become saturated and its influence on the grain fracturing was insignificant. In this stage, the average crystalline sizes of the powder reached a smallest level and, meanwhile, remained almost unchanged. However, on increasing the milling time up to 45 h, the average crystalline sizes of W and TiC constituents generally increased. According to the traditional grain growth theory, the Gibbs–Thomson equation, the driving force for a grain growth process is inversely proportional to the grain size [36]. The grain growth force is therefore extremely large in a nanocrystalline material. As a consequence, the continuous microscopic action of the mechanical force by the repeated ball–powder–ball collisions increased the driving force for the coarsening of nanocrystallites after 45 h long-term milling.

3.2. Powder morphology and particle size evaluation

The microstructural development of the milled powders with the applied MA times is shown in Fig. 3. Fig. 4 illustrates the particle size distribution of the corresponding powders. The influence of the applied milling time on the particle size and specific surface area is depicted in Fig. 5. After 10 h milling, the starting powder particles underwent a preliminary fracturing (Fig. 3(a)) and the average particle size $D_{50}$ reached 1.4 μm (Fig. 5). The distribution of particle sizes in this case, however,

![Fig. 4. Particle size distributions of the milled powders at various milling times: (a) 10 h; (b) 25 h; (c) 35 h; (d) 45 h.](image)

![Fig. 5. Effect of milling time on average particle size and specific surface area of the milled powders.](image)
showed a certain degree of non-uniformity, i.e., \(D_{25} = 1.03\ \mu m\), \(D_{75} = 1.89\ \mu m\), and \(D_{90} = 2.31\ \mu m\) (Fig. 4(a)). The particles had a relatively coarsened ellipsoidal shape (Fig. 3(a)), and the specific surface area, 1908.97 m\(^2\)/kg, was lowest in this instance (Fig. 5). On increasing the milling time to 25 h, the milled powder was fractured intensively to form a refined near-spherical shaped particles (Fig. 3(b)), resulting in a sharp decrease in the average particle size \(D_{50}\) to 0.81 \(\mu m\) and an apparent increase in the specific surface area to 3064.16 m\(^2\)/kg (Fig. 5). In this instance, the particle size distribution became narrow, i.e., \(D_{25} = 0.64\ \mu m\), \(D_{75} = 0.97\ \mu m\), and \(D_{90} = 1.11\ \mu m\) (Fig. 4(b)). On further increasing the milling time to 35 h, the milled powder exhibited a considerably refined particulate morphology with an almost equiaxed particle shape (Fig. 3(c)). The particle size distribution, \(D_{25} = 0.47\ \mu m\), \(D_{75} = 0.74\ \mu m\), and \(D_{90} = 0.86\ \mu m\), was very narrow (Fig. 4(c)). The average particle size \(D_{50}\) showed a sharp decrease to 0.61 \(\mu m\) and the specific surface area was elevated significantly to 4154.86 m\(^2\)/kg (Fig. 5). Differently, after 45 h milling, the coarsened powder particles having an irregular structure were formed (Fig. 3(d)). The powder did not have a tendency to further fracture; instead, the average particle size \(D_{50}\) increased apparently to 0.87 \(\mu m\), thereby lowering the specific surface area to 1293.01 m\(^2\)/kg (Fig. 5). The resultant

Fig. 6. FE-SEM images showing high-magnification particle morphologies of milled powders after (a) 10 h, (b) 25 h, (c) 35 h, and (d) 45 h milling.

Fig. 7. Schematic of microstructural development during MA of TiC/W nanocomposite powders.
particle size distribution became much broader, i.e., $D_{25} = 0.53 \mu m$, $D_{75} = 1.30 \mu m$, and $D_{90} = 1.75 \mu m$ (Fig. 4(d)).

As revealed in Figs. 3–5, the powder particles experienced a continuous refinement during 0–35 h milling. However, a further increase in the milling time to 45 h increased the average particle size. The high-magnification characteristics of the milled powder particles are provided in Fig. 6. As the W and TiC being milled both had a brittle nature, the milled powders got fragmented in the initial stage of ball milling and, therefore, the average particle size decreased continuously. Whereas, on increasing the milling time above 35 h, the refined particles tended to get cold-welded to each other, resulting in an increase in the average particle size. Fig. 7 depicts a reasonable mechanism for the formation of the TiC nanoparticle reinforced W matrix nanocomposite powder by high-energy ball milling.

(i) In the initial stage of milling (0–10 h), powder particles got trapped between the grinding balls and received the impact forces from the grinding medium. The fracturing mechanism thus predominated in this situation, decreasing the average particle size. Furthermore, the hard TiC particles acted as a milling agent and promoted the fracturing of the W particles, producing the smooth and compact surface of particles (Fig. 6(a)).

(ii) On increasing the milling time (10–25 h), the W and TiC particles, due to their brittle nature, became fragmented continuously during milling and their particle sizes decreased gradually to a nanometer scale (Fig. 6(b)). Normally, the harder (more brittle) component tended to get fragmented and embedded in the softer (less brittle) component [35]. Therefore, the fragmented and harder (more brittle) TiC (HV3230) nanoparticles got trapped and included within the softer (less brittle) W (HV700) matrix, yielding the TiC/W composite powder.

(iii) With further milling above 25 h, the average particle size of the nanocomposite powder continued to decrease, due to the domination of the fracturing mechanism. Meanwhile, the cold welding process also started in the milling system. For a milling time of 35 h, a dynamic balance was maintained between fracturing and cold welding of particles and the milled TiC/W nanocomposites demonstrated the most homogeneous and refined particle morphology (Fig. 6(c)).

(iv) With ball milling prolonged to 45 h, the average particle size increased and high-magnification FE-SEM micrograph revealed that the particle surface was considerably rough and consisted of a large number of ultrafine particles (Fig. 6(d)). This phenomenon implied the prevailing of cold welding mechanism in this case, which was mainly ascribed to the following two factors. Firstly, the starting TiC component that facilitated the fracturing mechanism was included in the W matrix as TiC/W nanocomposites after 35 h milling. Secondly, the significantly refined particles after 35 h milling had a considerably high specific surface area and attendant enhanced kinetics of aggregation via the inter-particle collisions during long-term milling.

3.3. Interior nanostructures

TEM characterization was performed to study the interior nanostructure of the 35 h milled powders. The characteristic microstructures (e.g., grain size, grain structure and its homogeneity) and the corresponding selected area diffraction pattern (SADP) of the 35 h milled nanocomposite powders are provided in Fig. 8. As revealed in Fig. 8(c), the rings in the SADP allowed us to identify the W and TiC phases, confirming the formation of TiC/W composites powder. The particles of the milled product consisted of a large number of ultrafine crystallites of W and TiC with sizes less than

![Fig. 8. TEM micrographs (a and b) and corresponding SADP (c) showing interior nanocrystalline microstructures and constitution phases of the TiC/W nanocomposite powders after 35 h milling.](image-url)
that the nanometer-sized TiC particulates, as selectively indicated by arrows in Fig. 8(b), were dispersed uniformly throughout the W matrix. Combined with the XRD and TEM results (Figs. 1, 2 and 8), it was reasonable to conclude that the 35 h milled product was the typical nanocomposite powder featured by the nanocrystalline W matrix reinforced with the uniformly dispersed TiC nanoparticles.

The bright-field TEM images and the corresponding SADP of the TiC/W composite powder after 45 h milling are provided in Fig. 9. It showed that as relative to the 35 h milled powder, the crystallite size of the powder particles increased slightly, although it was still in a nanometer scale (Fig. 9(a)). High-magnification TEM image showed that the nanoscale TiC reinforcing particles were dispersed homogeneously within the W matrix (Fig. 9(b)). Interestingly, as revealed in Fig. 9(c), a broad and diffused halo suggested the presence of amorphous phase in the selected area of the powder. The TEM characterization, accordingly, revealed that in the TiC/W nanocomposite powder after 45 h milling, the nanocrystalline TiC phase coexisted with a fraction of amorphous W phase. A reasonable explanation for the amorphous phase formation of W constituent during ball milling is proposed as follows. The continuous severe deformation and fracturing of the milled powders will generate a large number of point and lattice defects (e.g., vacancies, interstitials, and dislocations) within the W matrix, which tends to induce the amorphization of a fraction of W constituent in the milled powders. A basic premise for the amorphous phase formation is that a critical defect concentration introduced by severe deformation will promote the spontaneous transformation to the amorphous state. At this defect concentration, it requires that [37]:

\[ G_c + \Delta G_d > G_a \]  

where \( G_c \) is the free energy of the crystalline phase, \( \Delta G_d \) is the increase in free energy due to the defects produced by ball milling, and \( G_a \) is the free energy of the amorphous phase. \( G_c \) can be further expressed by the Gibbs–Thomson equation [38]:

\[ G_c = \frac{4\gamma V_m}{D_c} \]  

where \( \gamma \) is the interfacial energy and \( V_m \) is the molar volume. On increasing the milling time up to 45 h, a significant reduction in \( D_c \) and the attendant increase in \( V_m \) may result in a significant increase in \( G_c \). On the other hand, as the applied milling time prolonged, the continuous severe deformation of the milled powder inevitably produces a large amount of point and lattice defects, which further increases \( \Delta G_d \). The combined effect of these two aspects, consequently, elevates the free energy of the W constituent above that of the amorphous phase (\( G_a \)), resulting in the partial amorphization of W phase after long-time milling treatment.

4. Conclusions

High-energy ball milling of a micrometer-scaled W and TiC powder mixture was performed to prepare TiC/W nanocomposite powders. The main conclusions were drawn as follows:

(1) The milled products were typically nanocomposite powders featured by the nanocrystalline W matrix reinforced with the uniformly dispersed TiC nanoparticles. The average crystalline sizes of the W and TiC constituent were 8.5 nm and 13.6 nm, respectively, in the 35 h milled crystalline state powder.

(2) The powder particles experienced a continuous refinement during 0–35 h milling, due to the operation of a fracturing mechanism. For a milling time larger than 35 h, the particles had a tendency to coarsen, as a cold welding mechanism predominated.

(3) The 35 h milled powder had a considerably refined particle morphology, showing a narrow size distribution (\( D_{25} = 0.47 \mu m \),
$D_{50} = 0.61 \mu m, D_{75} = 0.74 \mu m, \text{and } D_{90} = 0.86 \mu m$ and a significantly elevated specific surface area of 4154.86 m$^2$/kg. (4) On increasing the milling time up to 45 h, the partial amorphization of W constituent occurred in the milled powders. An operative mechanism was that the continuous severe deformation of the milled powders generated a large number of point and lattice defects and elevated the free energy of W phase.

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References