Determination of Crystallite Size, Lattice Strain and Amorphization of Mechanically Alloyed \(W-VC-C\) Powder Composites

Abstract

Effects of TiC additions on physical properties of \(W-VC-C\) nano powder composites during different mechanical alloying (MA) time were investigated. \(W-2\text{wt.\%VC-1\text{wt.\%C}}\) and \(W-2\text{wt.\%VC-2\text{wt.\%TiC-1\text{wt.\%C}}\) composite powders were mechanically alloyed (MA’d) for 1h, 6h, and 24h by high energy ball mill. The effect of TiC content and MA duration on the effective lattice parameter, crystallite size, lattice strain and amorphization rate of the powder composite. Moreover, morphological analyzing of powders after various MA were studied. Addition of TiC declined particle size decreasing rate and powder densities after 24h. Up to 6h, the lattice strain values increases rapidly and from 6-24h lattice strain values enhancement occurs slowly in W-H method, while lattice strain values obtained by Gaussian method approximately increased linearly. The crystallite size of \(W-2\text{wt.\%VC-1\text{wt.\%C}}\) and \(W-2\text{wt.\%VC-2\text{wt.\%TiC-1\text{wt.\%C}}\) composite powders decreased to the 3.317nm and 3.066nm for 24h in Williamson-Hall (W-H) method like Gaussian method respectively.

1. Introduction

Due to Tungsten (W) high melting point its fabrication is extremely difficult. Recently, powder metallurgy (PM) is one of the most interesting methods for W powder production since there is a potential field of applications in aerospace, chemical, transportation, structural and automotive industries [1-4]. High energy ball milling technique broadly used in PM processing for attaining a homogeneous distribution and fine grained matrix [4-5].

MA process give rise to uniform dispersion for the fine reinforcements and grain size of the matrix. Reinforcing of the ductile W matrix with hard particles such as carbides and oxides provides an improvement of physical and mechanical properties of composites [2-9]. While MA’d powders characterization, measurements of crystallite size and lattice strain is very important because of the phase constitution and transformation characteristics that critically dependent on them [6]. The contributions of crystallite size and lattice strain to the broadening of XRD peaks can be calculated by using extrapolated W-H method and Gaussian rule [10, 11].

One theoretical model was proposed in which amorphization was assumed to be realized through interstitial impurity formation during MA [6, 12]. It was reputed that amorphization occurred when impurity atoms penetrated into interstitial sites and distorted the lattice locally. When the local distortions achieved some critical value, the long-range order of the lattice was destroyed and an amorphous phase formed [6].

As dispersion strengtheners, refractory carbide, nitride and oxide phases, such as TiC, ZrC, TiN, ThO\(_2\), ZrO\(_2\), etc. have been mainly used to improve the mechanical properties of tungsten and its alloys [13]. Furthermore, there is no literature about powder characterization which reports on tungsten matrix composites reinforced with VC and TiC. The objectives of the present study are phase and morphological characterization of MA’d W composite powders and investigate the effects of MA time and titanium carbide (TiC) content on the effective lattice parameter, crystallite size, lattice strain and amorphization rate of the \(W-2\text{wt.\%VC-1\text{wt.\%C}}\) and \(W-2\text{wt.\%VC-2\text{wt.\%TiC-1\text{wt.\%C}}\) composite powders. Moreover, morphological analyzing of MA’d powders were studied.

2. Materials and Experimental Procedure

\(W-2\text{wt.\%VC-1\text{wt.\%C}}\) and \(W-2\text{wt.\%VC-2\text{wt.\%TiC-1\text{wt.\%C}}\) powder composites were used in this study. The nano powder composites were produced by MA method.

2.1 Materials

Elemental tungsten (W) powders (99.9% purity, 17 \(\mu\text{m}\) average particle size) as the matrix of the powder composite and vanadium carbide (VC) powders (99.9% purity, 7 \(\mu\text{m}\) average particle size), titanium carbide (TiC) powders (99.9% purity, 15 \(\mu\text{m}\) average particle size) as reinforcement. Moreover, 1 wt% graphite powders (99.9% purity, 21 \(\mu\text{m}\) average particle size) were added to each batch as a process control agent (PCA) to eliminate cold welding between powder particles and thereby to prevent agglomeration.

2.2. High energy ball milling

W, VC, TiC and C powders were blended to constitute compositions of \(W-2\text{wt.\%VC-1\text{wt.\%C}}\) and \(W-2\text{wt.\%VC-2\text{wt.\%TiC-1\text{wt.\%C}}\)
2wt.%TiC-1wt.%C (thereafter referred to as W-2VC-1C and W-2VC-2TiC-1C) which were MA’d for 1h, 6h and 24h. High-energy milling experiments were carried out in a Spex™ Mill 8000D using a tungsten carbide (WC) vial and WC balls (6.35mm in diameter) as milling media. The ball-to-powder weight ratio (BPR) was 10:1. To avoid oxidation during MA, the vials were sealed in a glove box under Ar gas (99.995% purity).

2.3. Morphological and powder density analysis

Morphological characterizations were carried out using a Jeol™ Scanning Electron Microscope attached with Jeol™ EDS. Particle distribution, size and morphologies were investigated by using SEM images. Powder particle size measurements were carried out in Malvern™ Laser particle size analyzer and Microtrac™ NANO-flex. Moreover, bulk densities of MA’d nano-sized powder composites were measured using a Micromeritics AccuPyc™ helium pycnometer.

2.4. Structural evolutions

X-ray diffraction (XRD) measurements were carried out in a Bruker™ X-Ray Diffractometer ($\lambda=1.5405$ Å) at 35 kV and 40 mA settings in the 2$\theta$ range from 30º to 110º at a scanning speed of 2º min$^{-1}$. To eliminate equipment effects the LaB$_6$ crystal was used as a standard sample. The crystallite size and lattice strain were estimated using the Williamson–Hall method [14].

$$\cos \Theta = K \lambda D + 4 E \sin \Theta$$

(1)

where $\beta_s$ is the full-width at half-maximum of the diffraction peak, $\Theta$ is the diffraction angle, $\lambda$ is the X-ray wavelength, $D$ is the crystallite size and $E$ is the lattice strain and $K$ is constant equal 0.9. $\beta_s$ can be given as

$$\beta_s = \beta_e + \beta_i$$

(2)

where $\beta_i$ is the width at half-maximum of the LaB$_6$ powder peaks used for calibration and $\beta_e$ is the evaluated width. It is clear that when $\beta_s \cos \Theta$ is plotted against $\sin \Theta$, a straight line with slope(E) and intercept $K \lambda / D$ is obtained [15]. Lattice parameters were determined by using three major diffraction peaks {(110), (200) and (211)} in order to increase the precision of the measurements. Meanwhile, lattice strain and crystallite size were measured by Gaussian methods via TOPAS 3 (BRUKER AXS). Besides, the percent of crystallization rate were calculated by using EVA Bruker™ software.

3. Results and Discussion

3.1 Morphology

Fig 1 illustrates the SEM micrographs of different milled times (1h, 6h, 24h) for W-2VC-1C and W-2VC-2TiC-1C nanocomposite powders fabricated by MA. It is appointed that the particle size is changing with MA time, because of the two opposing phenomena of cold welding and fracturing of powders [6]. 1 h MA, the powders exhibit large irregular shapes, see Fig. 1a and 1c, and then were dramatically changed in particle sizes after 6 h MA. After 24 h MA time, more fine and homogeneous particle size distribution were shown in Fig. 1b and 1d. It suggests that with continued plastic deformation the particles were work hardened and fracture by fatigue failure or fragmentation [16]. As shown in fig 1, MA’d W-2VC-2TiC-1C powders have some greater particles than W-2VC-1C at same MA durations. It means that, TiC declined particle size decreasing rate. This phenomena was approved by particle size distribution which measured in nano-sizer. It should be established that the MA process not only refines the powder but also causes significant lattice strain and hence increases the dislocations in the powder crystals [17]. Such results are in agreement with those reported in different papers concerning the production of powders by high energy ball milling [6, 7].

Powder theoretical densities of W-2VC-1C and W-2VC-2TiC-1C composites are 17.18 and 16.40 g/cm$^3$, respectively, which decreased to 13.30 and 13.62 g/cm$^3$ after 24 MA respectively. After 24h MA, $d_{50}$ particle size measured as ~228nm and ~174nm for W-2VC-1C and W-2VC-2TiC-1C respectively. This is supported with SEM analysis in Fig. 1b-1d, W-2VC-2TiC-1C powder composites have smaller particle size than W-2VC-1C.

3.2 Structure analysis

X-ray diffraction patterns of W-2VC-1C and W-2VC-2TiC-1C powder composites for different MA times are shown in Fig 2-3. In these figures the XRD patterns of powders reveal the presence of the characteristic peaks of the W phase which has a b.c.c. Bravais lattice and Im3m space group with the lattice parameter of a=0.316nm.
Only W peaks were seen, while characteristic peaks of VC, TiC and C were not appeared because of their low amounts. By increasing the MA time, whole appeared peaks intensity reduced drastically due to the reduction of powders particles to submicron sizes and/or the low volume fraction of the MA’d powders [18, 19].

The clear shift of the W peaks toward lower 2θ due to the solution of the C atoms into the W matrix and lattice strain created by MA impaction [7]. Further increase in MA duration results in further broadening of the peaks of both phases as a result of grain refinement and build up strain during MA. Moreover, increasing the MA time, leads to broadening of the W peaks and decreasing of their intensities, which demonstrate reduction in crystallite size and accumulation of strain in the materials [8,9].

The effect of MA time on the lattice strain of composite powders is presented in Fig. 4. As shown in this figure, lattice strain of W-2VC-1C and W-2VC-2TiC-1C calculated via W-H and Gaussian methods were increased by increasing MA time. Up to 6h for W-2VC-1C and W-2VC-2TiC-1C powder compositions, the lattice strain values (0.651 and 0.652 respectively) increases rapidly and from 6-24h lattice strain values (1.323 and 0.884 after 24h respectively) enhancement occurs slowly in W-H method. While, lattice strain values obtained by Gaussian method approximately increased linearly. Crystal defects such as dislocations and point defects were increased via MA [15]. The formed defects increase lattice strain and energy so it becomes unstable. The dislocations rearrange themselves to a lower energy state leading to the formation of sub-grain. At longer times of MA and therefore, higher plastic deformation and generation of more dislocations, the misorientations between sub-grains at their boundaries increase and finally they convert to high angle boundaries and become grains with nano sizes [8].

Crystallite size variations of W-2VC-1C and W-2VC-2TiC-1C matrix versus MA time are offered in Fig. 5. For W-2VC-1C and W-2VC-2TiC-1C MA’d powder composites, up to 6 h, the crystallite size decreases rapidly (5.614nm and 12.700nm respectively) and then diminishes slowly (3.317nm and 3.066nm respectively for
24h) in W-H method. Meantime, crystallite size amounts measured by Gaussian method like W-H method.

In Fig. 6, crystallization rate and lattice parameter versus MA time for W-2VC-1C and W-2VC-2TiC-1C powder composites were illustrated. The crystallization rate of W-2VC-1C and W-2VC-2TiC-1C powder composites linearly decreased to 82% and 80% respectively MA time increment.

TiC addition increased decrystallization (amorphization) rate of the W-2VC-1C powder composites. During MA, destabilization of the crystalline phase is thought to occur by the accumulation of structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. These defects raise the free energy of the system to a level higher than that of the amorphous phase and accordingly, it becomes possible for the amorphous phase to form [15]. This phenomena were shown in Fig. 2-3. These figures illustrate that (200), (220) and (310) peaks were disappeared after 24h MA time. That approve amorphization rate increment by MA.

Fig. 6a-6b show that a values increase by MA time increment. It means that, lattice parameter expanded and lattice interplaner distances increased. This fact relate XRD peaks slipping toward the lower $\theta$ due to MA period increment. As shown in Fig. 6, with up to 24h MA, lattice parameter (a) increases due to interstition of C atoms into W lattice [6] and grain refinement [9]. This was inferred by the clear shift of the W peaks toward lower angles (Fig. 2-3).

4. Conclusion

MA process not only refines the W-2VC-1C and W-2VC-2TiC-1C composite powder but also causes significant lattice strain and hence increases the dislocations in the powder crystals. Lattice strain values obtained by Gaussian method approximately increased linearly. For W-2VC-1C and W-2VC-2TiC-1C compositions, up to 6 h, the crystallite size decreases rapidly and then diminishes slowly in W-H method. The characteristic W peaks (200), (220) and (310) were disappeared after 24h MA time. In both compositions, lattice parameter expanded and lattice interplaner distances increased due to MA period increment. TiC addition increased amorphization rate of the W-2VC-1C powder composites.

References