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*Research Article*

# Influence of Milling Media on the Mechanical Alloyed W-0.5 wt.% Ti Powder Alloy

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The effects of milling atmosphere and mechanical alloying (MA) duration on the effective lattice parameter, crystallite size, lattice strain, and amorphization rate of the W-0.5 wt.% Ti powders were investigated. W-0.5 wt.% Ti powders were mechanically alloyed (MA'd) for 10 h and 20 h in a high energy ball mill. Moreover, morphology of the powders for various MA was analyzed using SEM microscopy. Their powder density was also measured by helium pycnometer. The dry milled agglomerated powders have spherical particle, while wet milled powders have layered morphology. Milling media and increasing of milling time significantly reduce the crystallite size. The smallest crystallite size is 4.93 nm which belonged to the dry milled powders measured by Lorentzian method after 20 hours' MA. However, after 20 hours, MA'd powders show the biggest crystallite size, as big as 57.07 nm, measured with the same method in ethanol.

## 1. Introduction

Tungsten (W) alloys are attractive candidate materials for various high temperature structural applications due to their excellent properties such as high melting point, high modulus, high resistance of thermal shock, and low coefficient of thermal expansions (CTE) [1, 2]. However, alloying of monolithic W is mandatory for applications which require high strengths at elevated temperatures since mechanical properties of monolithic W decrease significantly with increasing temperatures [3–11]. Small amounts of nickel (Ni) added as a transition element during mechanical milling (MM) and/or mechanical alloying (MA) activate sintering and enable the fabrication of fully dense W-based alloys and composites at lower temperatures than the usual sintering temperatures of W [7–13]. Similar to Ni, titanium (Ti) is probably a good candidate in triggering activated-sintering mechanism in W; however, its role as an activator in W has not been investigated yet. MM and MA are complex processes which involve the optimization of a number of variables to achieve a desired phase or microstructure. Milling media, milling time, ball to powder ratio, milling speed, and starting powder size range influence both the stages of milling and the quality of milled product [14–16].

MA and MM in different milling media result in changing of powder properties and consequently alter mechanical, physical, and thermal properties of the final products. During the MA/MM process, the flattened layers overlap and form cold welds for soft powders which results in the formation of layered composite powder particles consisting of various combinations of the starting ingredients. On the other hand, the work-hardened elements or composite powder particles might be fractured at the same time. These competing events of cold welding (with plastic deformation and agglomeration) and fracturing (size reduction) continue repeatedly throughout the milling period [17–19]. Finally, a refined and homogenized microstructure will be obtained while the composition of the powder particles is of the same proportion of the starting constituent powders [20, 21]. Occasionally, metal powders are milled in a liquid medium also named as wet milling. However, if there is no liquid used during the milling process it is called dry milling [22, 23]. During wet milling, due to the low efficiency such as retarding crystallite

refinement attributes to the decrease of the ball's impact force on powders [17, 18, 23].

Currently, there is no available information in the literature regarding W-Ti alloys MA'd in various media such as Ar, ethanol, and isopropyl alcohol (IPA). Moreover, no investigations have been reported on the measurement of the lattice parameter, crystallite size, and lattice strain of the MA'd W-0.5 wt.% Ti in different medium. The aim of the present study is to investigate the combined effects of mechanical alloying (MA) and various milling media on the W-0.5 wt.% Ti powder alloy.

## 2. Experimental Procedure

Elemental tungsten (W) (Eurotungstene™, 99.9% purity, 45 $\mu$m average particle size) and titanium (Ti) (Alfa Aesar™, 99.9% purity, 45 $\mu$m average particle size) powders were used in the current study. W powders were premilled for 10 h in a Spex™ Duo Mixer/Mill 8000D with a speed of 1425 rpm in a tungsten carbide (WC) vial with 6.35 mm diameter (1/4 inches) WC balls. Loading and unloading of vials were carried out inside a Plaslabs™ glove box under purified Ar gas (99.995% purity) to prevent oxidation during MA. The ball to powder weight ratio (BPR) was 10 : 1.

The premilled W and elemental Ti powders were blended to constitute the W-0.5 wt.% Ti composition and the powder blends were mechanically alloyed (MA'd) in argon atmosphere (dry milling media), in ethanol and isopropyl alcohol (wet milling media) for 10 and 20 h in a Spex™ Duo Mixer/Mill 8000D using the same conditions used for premilling: loading and unloading of vials were carried out inside a Plaslabs™ glove box under purified Ar gas (99.995% purity) and BPR was 10 : 1.

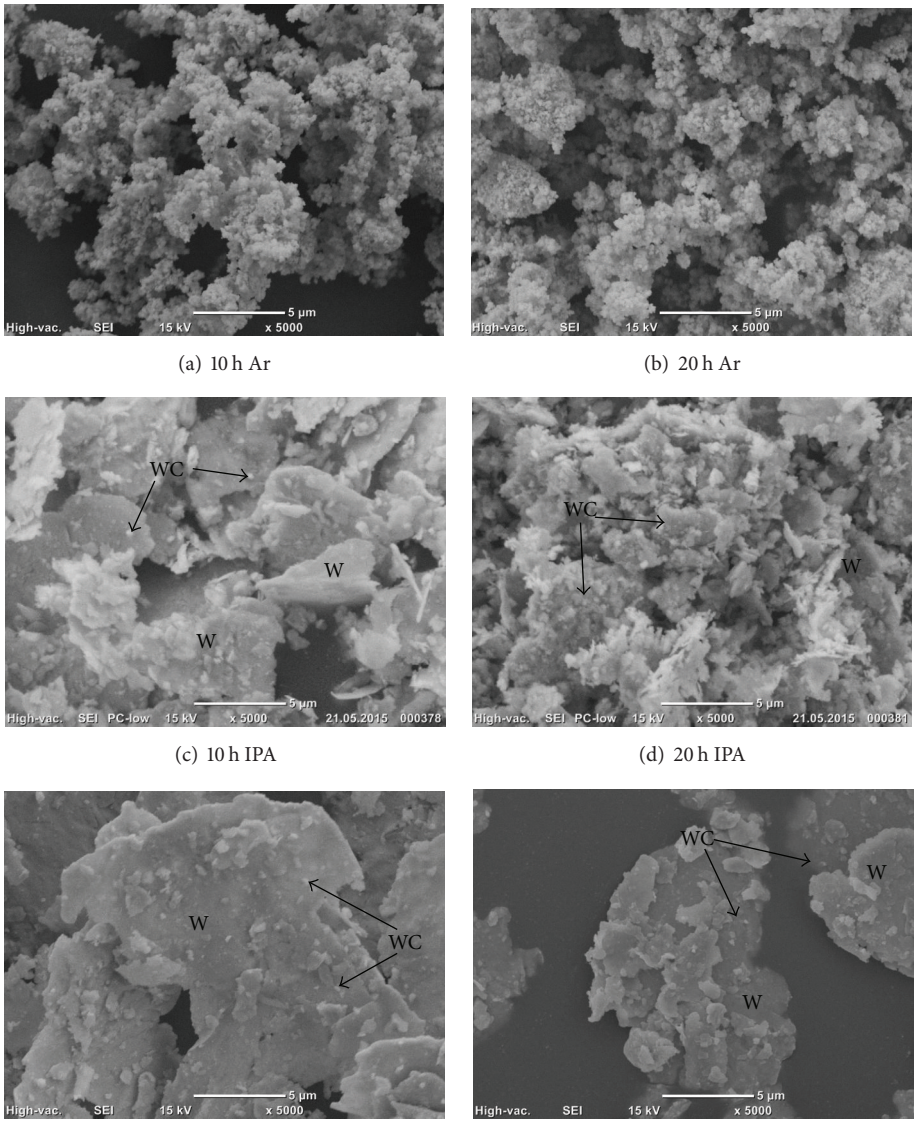
Morphological characterizations of MA'd W-0.5 wt.% Ti powders were carried out in a Jeol™ JCM-6000 Benchtop Scanning Electron Microscope attached with a Jeol WX-36210DPP EDS unit (Energy Dispersive Spectrometer) using an accelerating voltage of 15 kV. Microstructural characterizations of MA'd W-0.5 wt.% Ti powders were performed using a Bruker™ D8 Advance X-ray diffractometer (XRD) ($CuK_\alpha$ radiation, $\lambda = 1.542$ Å). Crystallite size and strain rates were measured and calculated using TOPAS 5 (Bruker AXS) software using Lorentzian and Gaussian methods. Powder particle size measurements were performed in a Malvern™ Master-sizer Laser particle size analyzer and in a Microtrac™ NANO-flex in situ particle size analyzer. True densities of MA'd W-0.5 wt.% Ti powders were measured in a helium Pycnometer Micromeritics AccuPyc™ II 1340.

## 3. Results and Discussions

Figures 1(a)–1(f) are the SEM micrographs showing the morphologies of W-0.5 wt.% Ti powders MA'd for 10 h and 20 h in different milling media: (a) in Ar (dry milling, Figures 1(a) and 1(b)), (b) in isopropyl alcohol (wet milling, Figures 1(c) and 1(d)), and (c) in ethanol (wet milling, Figures 1(e) and 1(f)). As seen in Figures 1(a) and 1(b), powders MA'd in Ar using dry milling conditions are in the form of agglomerates comprising nearly spherical or spheroidal shaped powder particles having a maximum particle size about 400 nm. Further, MA duration in dry milling conditions has hardly had any effect on the morphology and size of the particles as can be clearly observed in Figures 1(a) and 1(b). On the other hand, as seen in Figures 1(c) and 1(e), during wet milling, layered morphologies formed after MA for 10 h. When MA duration increased to 20 h, particles were shattered into smaller fragments and consequently the particle sizes were reduced (Figures 1(d) and 1(f)). It is interesting to note that the powder particles fabricated during MA in IPA are smaller than those milled in ethanol. Energy dispersive spectroscopy (EDS) spectral analyses revealed the presence of WC regions and/or WC particles in the wet milled powders. In addition, EDS mapping analyses showed homogeneous Ti distributions within W particles in all MA'd powders.

XRD patterns of MA'd W-0.5 wt.% Ti powders are illustrated in Figure 2. The XRD patterns of all MA'd W-0.5 wt.% Ti powders revealed the presence of the characteristic peaks of the W (Ti) solid solution phase denoted as the $Ti_xW_{(1-x)}$ phase (Bravais lattice: b.c.c.; S.G.: Im-3m (229); $a = 0.316$ nm; ICDD #49-1440) and small amounts of the WC phase (Bravais lattice: h.c.p.; S.G.: P-6m2 (187); $a = 0.290$ nm, $c = 0.283$ nm; ICDD #57-0939).

It is evident from Figure 2 that mechanical alloying, regardless of the milling conditions (wet or dry milling and milling duration), caused the decrease of the peak intensities of W (Ti) solid solution phase and increased peak line broadening. MA'd powders underwent deformation and cold welding caused by continuous collision and fracturing between balls and powders. Thus, the intensity of the diffraction peaks decreased with increasing milling time and became wider due to severe lattice distortion and grain size refinement. However, peak broadening of the W-0.5 wt.% Ti powders MA'd in dry milling conditions (in Ar) is much more than those MA'd in wet milling conditions (in both IPA and ethanol). This is an expected observation since conditions employed during dry milling are more severe than those during wet milling. In other words, most of the kinetic energy generated by the ball-to-ball and ball-to-vial collisions is absorbed by the liquid media during wet milling as opposed to dry milling where almost all kinetic energy is directly transferred to the powders. As a consequence, it is expected that the crystallite sizes of the dry milled powders are to be much smaller and their lattice deformation amounts are higher than those milled in wet conditions. It is also seen in Figure 2 that, due to the effects of MA, intensive WC contamination appeared after MA [8]. Presumably, these peaks arose from the milling media (vial and balls) owing to the excessive impact energy accumulated during mechanical alloying at a longer duration of 20 h [13]. Comparing wet and dry MA shows that WC peaks are more intense in wet milling, particularly in IPA [8]. In Ar atmosphere, powders covered whole surface of WC balls and they became smaller. However, in wet milling, the surfaces of the WC balls were clean and during colliding these balls were eroded probably leading to WC contamination in the powders. As shown in Figure 1, small particles of WC are seen in wet MA'd powders and EDS results supported the WC contamination in the long-time




(a) 10 h Ar (b) 20 h Ar

(c) 10 h IPA (d) 20 h IPA

(e) 10 h ethanol (f) 20 h ethanol

Figure 1: SEM micrographs of MA'd W-0.5 wt.% Ti powders in different milling media: (a) MA'd for 10 h and (b) MA'd for 20 h in Ar, (c) MA'd for 10 h and (d) MA'd for 20 h in isopropyl alcohol (IPA), and (e) MA'd for 10 h and (f) MA'd for 20 h in ethanol.

Table 1: Crystallite size and lattice strain values of MA'd W-0.5 wt.% Ti powders in different milling media.

| Milling media | Pure W | Ethanol | | IPA | | Ar | |
|---|---|---|---|---|---|---|---|
| MA time (h) | | 10 | 20 | 10 | 20 | 10 | 20 |
| Crystallite size L (nm) | 510.47 | 61.00 | 57.07 | 41.30 | 17.27 | 6.53 | 4.93 |
| Crystallite size G (nm) | 436.90 | 31.17 | 30.13 | 20.67 | 13.30 | 5.73 | 5.57 |
| Lattice strain L | 0.0029 | 0.0357 | 0.3409 | 0.3402 | 1.4823 | 2.1784 | 3.4140 |
| Lattice strain G | 0.0024 | 0.0436 | 0.6308 | 0.4636 | 1.8015 | 2.5255 | 3.5669 |

milling. Interestingly, these particles were not found in the SEM micrographs of dry milled powders.

Crystallite size and lattice internal strain determination are the most two important applications in powder X-ray diffractometry for materials characterization. Table 1 shows the variation of the crystallite sizes with milling time (10 and 20 h) in three different milling media calculated by Lorentzian and Gaussian methods. High speed ball milling powders result in peak intensity reduction as well as a broadening in full width at half maximum (FWHM). This happens due to a reduction in the crystallite size and an accumulation of the lattice strain. These changes were prominent with variation of

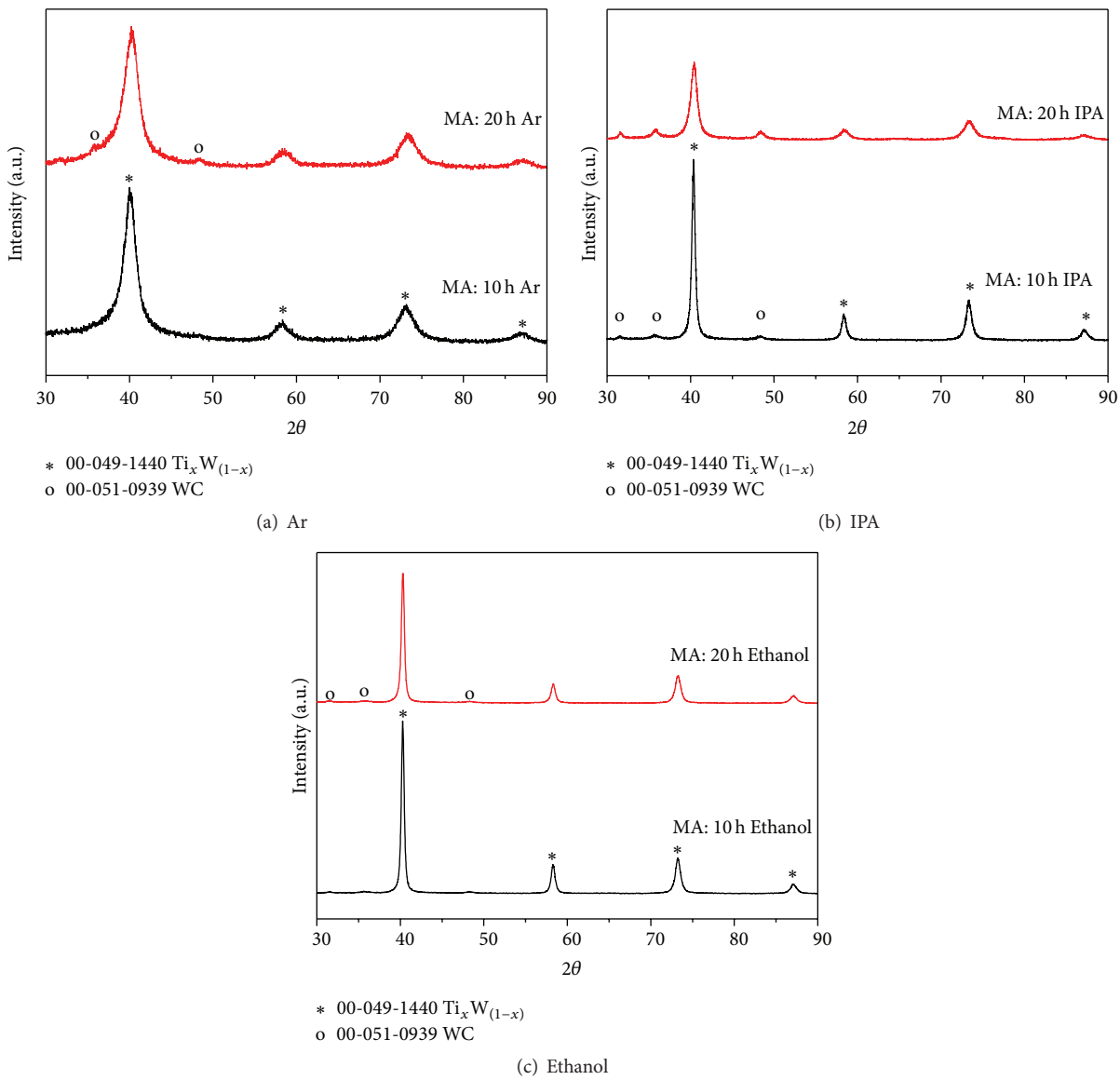



Figure 2: XRD patterns of MA'd W-0.5 wt.% Ti powders in different milling media after 10 h and 20 h MA.

milling time and milling media. There was a rapid decrease in crystallite size of W-0.5 wt.% Ti powders that occurs from the blended powders and powders mechanically alloyed for 10 h. However, after 10 h of MA, only a slight further reduction in crystallite size occurs. According to Zuhailawati and Mahani [24] crystallite size measurement in this study was performed using Lorentzian and Gaussian methods. The results indicate that selected MA media were highly effective in reducing crystallite size by increasing milling time. As shown in Table 1, the smallest crystallite sizes belong to the dried milled powders, whereas powders MA'd in ethanol have the largest crystallite sizes. This can be also confirmed with peak broadening shown in Figure 1. Interestingly, Gaussian method shows slightly smaller crystallite sizes compared to Lorentzian method. However, the strain values calculated by Gaussian method are slightly higher than those measured by Lorentzian method.

Figure 3 shows that lattice parameter of the W (Ti) solid solution phase, that is, "$a$" values, is maximum after 10 h MA. Maximum lattice parameters are 3.175, 3.163, and 3.158 nm, respectively, for the W (Ti) solid solution phase of the powders MA'd for 10 h in Ar, ethanol, and IPA. Also shown from Figure 3 is that the crystallization rate decreased linearly with increment of MA time from 10 h to 20 h. The maximum and minimum crystallite rates were measured as 65% and 91% after 20 h MA, respectively, in Ar and ethanol media.

Pycnometer densities (true densities) MA'd W-0.5 wt.% Ti powders are presented in Table 2. The MA'd W-0.5 wt.% Ti powders milled in ethanol have the highest densities. This can be also explained with sharp XRD peaks shown in Figure 2(c). On the contrary, the powders MA'd in IPA have the lowest densities. This can be attributed to collisions between vial and balls resulting in continuous increment of WC impurities,

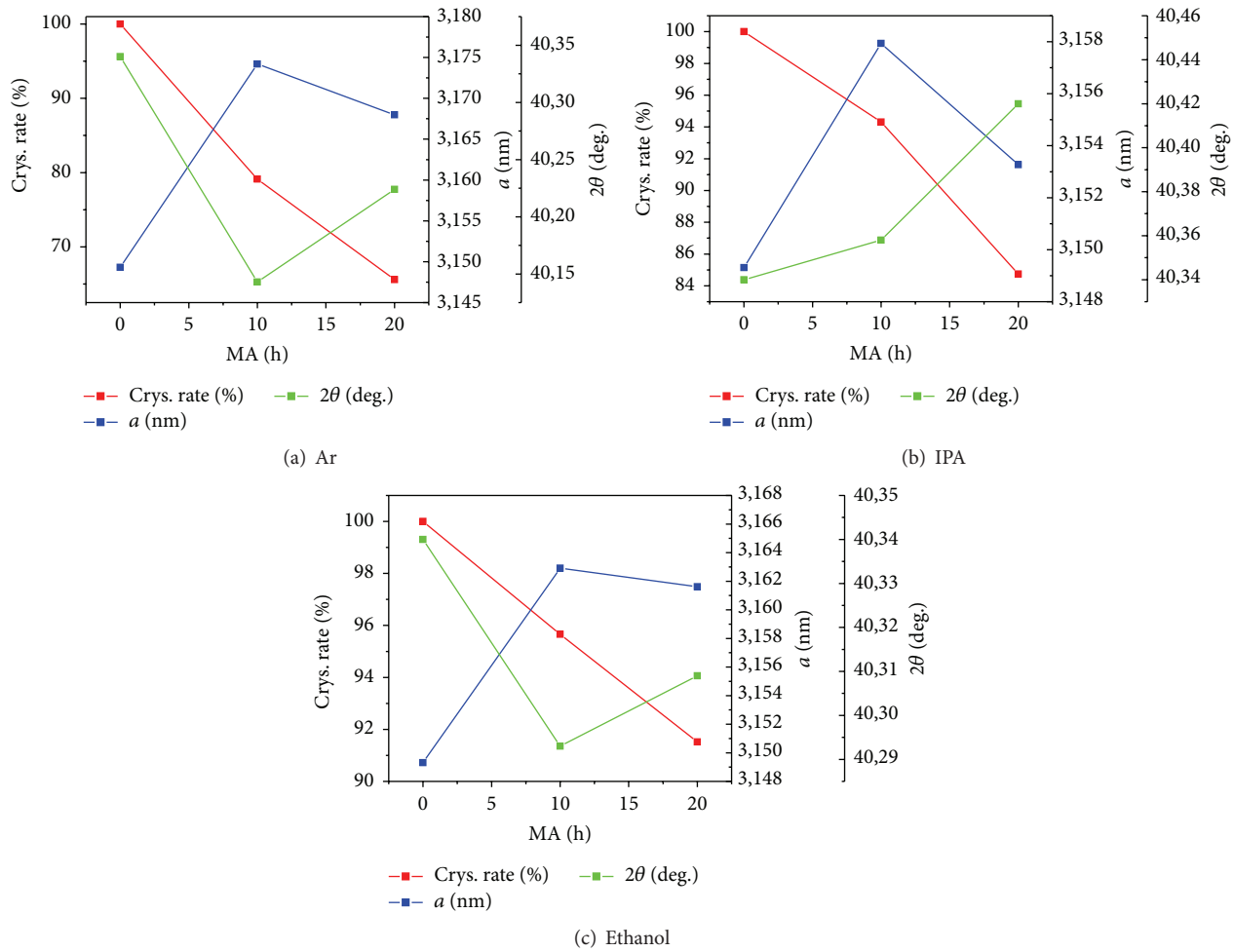



Figure 3: Crystallization rates, lattice parameters, and $2\theta$ (110) degrees of MA'd W-0.5 wt.% Ti powders in different milling media after 10 h and 20 h MA.

Table 2: Pycnometer powder densities of the MA'd W-0.5 wt.% Ti powders.

| Milling media | Milling time | |
|---|---|---|
| | 10 h | 20 h |
| Ethanol | 18.23 ± 0.020 | 18.15 ± 0.032 |
| Argon | 15.38 ± 0.026 | 14.87 ± 0.022 |
| IPA | 12.88 ± 0.025 | 12.24 ± 0.020 |

relative to MA time. This is particularly true for the powders milled in IPA media and confirmed by Figure 2 which shows that powders MA'd in IPA have more intense WC peaks than the others. Probably, increment of the WC particles might decrease density of the MA'd W-0.5 wt.% Ti powders [17, 18, 25].

## 4. Conclusions

The morphological and structural changes of MA'd W-0.5 wt.% Ti powders were studied. From this study the following conclusions can be drawn:

(1) The powders MA'd produced by dry milling method for both 10 h and 20 h have spherical particle, while wet milling results in layered morphology. Particles which MA'd powders in IPA have are smaller than the ones milled in ethanol. On the other hand, the MA'd powders in argon have the smallest particles.

(2) There was a rapid reduction in crystallite size of W-0.5 wt.% Ti powders between the as-blended powders (0 h) to 10 h of MA, while after 10 h of MA only a slight further reduction in crystallite size was measured by Lorentzian and Gaussian methods.

(3) Milling media were highly effective in reducing crystallite size by increasing milling time. The smallest crystallite size belonged to the dried milled powders. Meanwhile, powders MA'd in ethanol have the largest crystallite sizes.

(4) Crystallization rate decreased linearly with MA time. The maximum and minimum crystallite rates measured were 65% and 91%, respectively, in Ar and ethanol media after MA for 20 h.

(5) MA'd W-0.5 wt.% Ti powders milled in ethanol have the highest densities, and the powders MA'd in IPA have the lowest.

## Competing Interests

The authors declare that they have no competing interests.

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