

## Structural Evaluation of Mechanically Alloyed W-50at%C Powders

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**Abstract.** Tungsten carbide is potentially attractive for development of catalysts and widely used for fabrication of cutting tools due to its high hardness and wear resistance while the ball milling can improve the mechanical properties from the metastable structures and nanomaterials. The aim of this work was to evaluate the phase transformations during milling of the W-50at%C elemental powder mixture under argon atmosphere in a planetary P-5 ball mill using WC-Co balls (10 mm diameter) and vials (225 mL), 200 rpm, and a ball-to-powder weight ratio of 10:1. Samples were collected into the vial after different times: 20, 60, 300 and 600 min. The as-milled W-50at%C powders were characterized by X-ray diffraction (XRD). Only peaks of W were identified in W-50at%C powders milled up to 600 min, which were broadened and moved to the direction of smaller diffraction angle. In addition, the lattice parameter and cell volume of W were reduced during ball milling of W-50at%C powders, indicating that the C atoms dissolved into the W lattice in order to form metastable structures. Carbon atoms were interstitially dissolved into the W lattice during the initial milling times, and its preferential substitutional dissolution was identified for longer times due to the larger amounts of crystallographic defects during ball milling.

### Introduction

The use of hard metal has shown a sharp growth mainly due to its use as cutting tools, medical devices, nuclear reflectors and sporting components, which are produced by different routes. It well known that metal carbides (W, Mo, Ti, V, Ta, Nb and Cr) present high hardness, toughness and wear resistance [1-4]. According to the phase diagram of the C-W system, the WC compound is stable at room temperature and it is formed by the peritectic reaction  $[L+C \leftrightarrow WC]$  at  $2785 \pm 5^\circ\text{C}$  [5].  $W_2C$  is formed by congruent transformation at  $2785 \pm 10^\circ\text{C}$  and itself decomposes at  $1250^\circ\text{C}$  by eutectoid reaction  $[W_2C \leftrightarrow W+WC]$ . W dissolves negligible C amounts at equilibrium conditions.

In the powder metallurgy process, the hard metal is produced by liquid phase sintering, which is a non-equilibrium thermodynamic process that transform the aggregated powder into a solid structure [1]. In this way, the tungsten carbide with a cobalt binder phase (WC-Co) is the most used composite for high-performance cutting tools and wear-resistant parts [2-4].

Nanotechnology may contribute to produce nanostructured and metastable materials (extended solid solutions and/or amorphous structure) with superior chemical and mechanical properties than those others processed by conventional melting and powder metallurgy techniques [6,7]. High-energy ball milling are widely used for producing the iron- and nickel-based super alloys for high-temperature structural applications [7]. Depending on the starting powders, type of mill and milling parameters, the nanosized and metastable structures can be achieved.

In work recent, it was reported that the use of stoichiometric W-50at%C composition has contributed for producing the WC compound faster than in compositions with higher C amounts, while the  $W_2C$  compound was formed in compositions with higher carbon content milled at low speed and ball-to-powder ratio, as well as in carbon-deficient composition milled for shorter milling times [8]. This work aims to evaluate the phase transformations during milling of the W-50at%C elemental powder mixtures at different times.

## Experimental Procedure

The commercial raw materials used in this work were W (granules with purity of 99.5%) and C (graphite with purity of 99.8%) powders. These materials were processed at room temperature following the stoichiometric W-50at%C composition in a planetary Fritsch P-5 ball mill under argon atmosphere using WC-Co vial (500 mL) and balls (10 mm diameter), 200 rpm, and a ball-to-powder ratio of 10:1. In order to understand on the phase transformation during milling of the W-50at%C mixture the materials were milled at different times: 20, 60, 180 and 600 min.

Samples were characterized by X-ray diffraction in a Rigaku Ultima IV equipment using Cu-K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ), 40 kV, and 30mA. The Powdercell computer program [9] and JCPDS files [10] were used for indexing the phases, as well as to refine and determine the lattice parameter of W in XRD patterns of mechanically alloyed W-C powders. The full-width at height maximum (FWHM) values of the major W peak were calculated using the Gauss function, and crystallite sizes of W were determined by the Scherrer equation.

## Results and discussion

X-ray patterns of W, C, and the W-50at%C mixtures at different milling times are presented in Fig. 1. Only peaks of C and W were identified in XRD pattern of the W-50at%C powders milled for 20 min. Initially, the main C peak was more intense than the peak of W. After milling for 20 min, it can be noted a change of the relative intensity of these main W and C peaks. Peaks of C disappeared after milling for 60 min of W-50at%C powders, suggesting that carbon atoms were dissolved into the W lattice to form an extended solid solution. Unexpectedly, the intensity of W peaks have increased during milling up to 180 min of W-50at%C powders. This fact can be related with the severe plastic deformation and the preferential C dissolution in W during milling, which have favored the occurrence of fracture mechanisms and X-ray scattering of W. Following, the intensity of W peaks were reduced in W-50at%C milled for 600 min. No tungsten carbide peak was identified in mechanically alloyed W-50at%C powders. However, the energy provided during milling could be released during further sintering and contribute for the consolidation of WC-based devices.

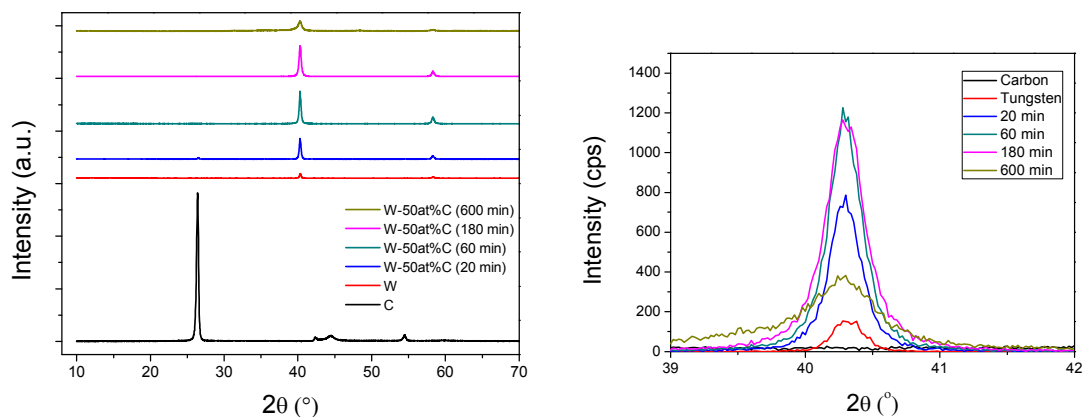


Fig. 1: X-ray diffractograms of the W-50at%C powder mixture at different milling times: 20, 60, 180 and 600 min. Details on the changed intensity of major W peak with milling time is also illustrated.

Fig. 2 shows the effect of milling time on the diffraction angle ( $2\theta$ ) and FWHM values of the main (110) W peak. Results have indicated that the (110) W peak was shifted toward the direction of smaller diffraction angles, and the peak of W has broadened continuously during milling up to 600 min. Errors of the measured diffraction angles and FWHM values were lower than 3% and 0.1 % respectively.

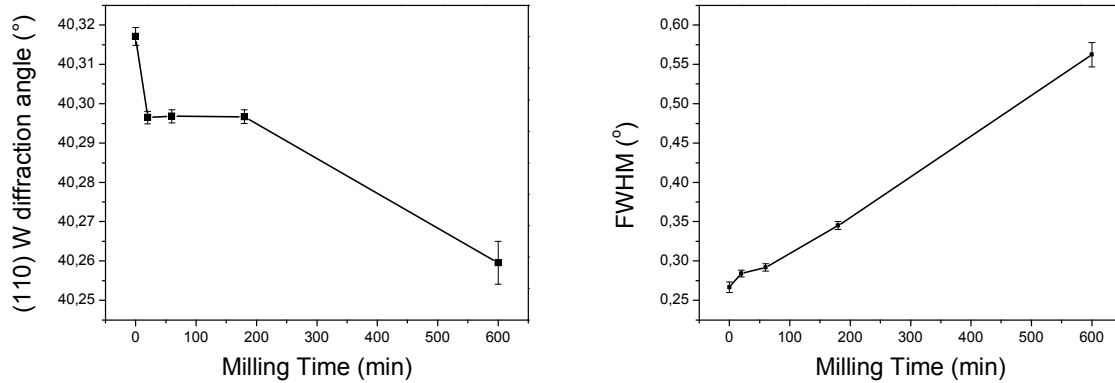


Fig. 2: Effect of milling time on the diffraction angle and FWHM values of the (110) W peak in W-50at%C powders.

The effect of milling time on the lattice parameters and cell volume of  $W_{ss}$  (ss – solid solution) in W-50at%C powders are presented in Fig. 3. Tungsten and carbon possess atomic radii of 1.37 Å and 0.71 Å, respectively. The lattice parameter ( $a=b=c$ ) and of cell volume of W are 3.16 Å and 31.55 Å<sup>3</sup>, respectively. Results have indicated that the lattice parameter and cell volume of W has initially increased in powders milled for 20 min, suggesting that the interstitial C dissolution occurred preferentially during the initial milling time. Following, these values have decreased continuously during milling up to 600 min. The higher amount of crystallographic imperfections provided during milling of W granules contributed for substitutional C dissolution into the W lattice in order to form an extended W solid solution.

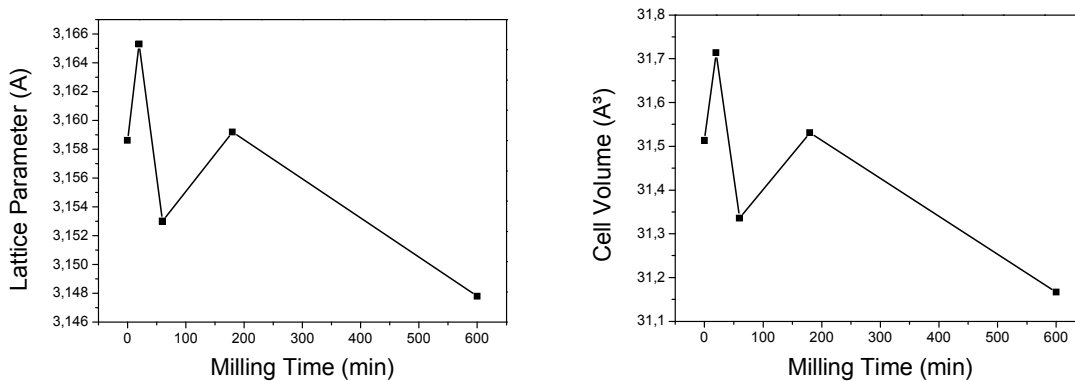


Fig. 3: Effect of milling time on the cell volume and lattice parameter of  $W_{ss}$  in the W-50at%C powders.

Fig. 4 displays the effect of milling time on the crystallite size of  $W_{ss}$  in the W-50at%C powders. Results have indicated that the sizes of crystallite were reduced continuously during milling up to 600 min, indicating that the milling parameters produced nanosized and metastable structures, which can contribute to reduce the sintering temperature and produce materials with finer microstructures and superior mechanical properties.

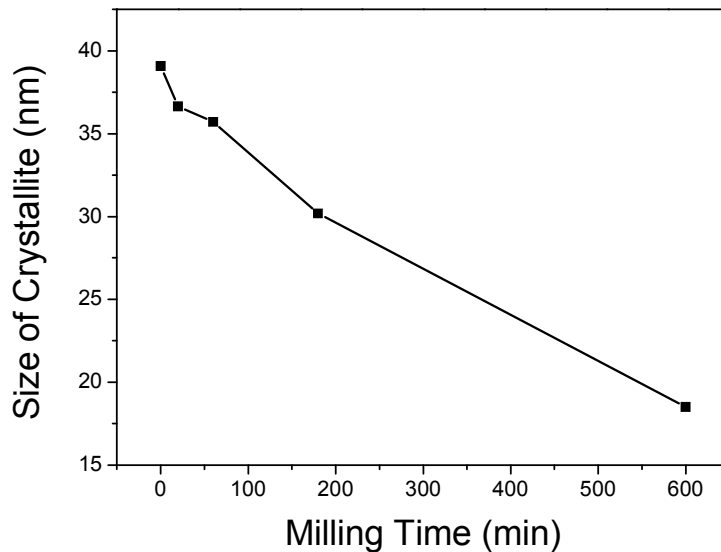


Fig. 4: Effect of milling time on the crystallite size of  $W_{ss}$  in the W-50at%C powders.

### Summary

Only peaks of W were identified in W-50at%C powders milled up to 600 min, which were broadened and moved to the direction of smaller diffraction angle.

The lattice parameter and cell volume of W were reduced during ball milling of W-50at%C powders, indicating that the C atoms were dissolved into the W lattice in order to form metastable structures.

Carbon was interstitially dissolved into the W lattice during the initial milling time, and its substitutional dissolution was identified for longer times due to the higher amounts of crystallographic imperfections during ball milling.

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