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Structural Properties of TiC obtained by Mechano-synthesis

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Mechanical alloying (MA) of the titanium carbide (TiC) compound from high purity elemental powders has been studied. The powders were mechanically milled in a vibratory ball mill at room temperature for different milling times from 8 to 20 h. The mechanical alloying experiments were conducted using two milling tools; tungsten carbide container and balls, and tungsten carbide (WC) container with hardened steel balls. The as-milled powders were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The use of WC container and balls contaminate the Ti+C mixture powders. However, the combined use of WC vials and hardened steel balls minimizing the powders contamination. Rietveld refinement revealed that the cubic carbide phase presents C vacancies. Therefore, the TiC phase obtained by MA process is not a stoichiometric phase. XRD and HREM observations indicate a heavy deformation in the TiC structure as a consequence of high-energy ball-milling.

Keywords: Titanium carbide; mechanical alloying; microstructure; structure refinement; X-Ray diffraction.

Se estudio a partir de polvos elementales de alta pureza, la posibilidad del aleado mecánico del compuesto de carburo de titanio. Los polvos fueron mecánicamente aleados empleando un molino vibratorio de bolas a temperatura ambiente y usando diferentes tiempos de molienda desde 8-20 horas. Los experimentos de molienda mecánica fueron realizados empleando dos tipos de herramientas de molienda: contenedor y bolas de carburo de tungsteno y contenedor de carburo de tungsteno y bolas de acero endurecido. Los polvos obtenidos después de la molienda fueron caracterizados usando difracción de rayos X y microscopia electrónica de transmisión. El uso de contenedores y bolas de carburo de tungsteno contamina los polvos de Ti y C. Sin embargo, el uso combinado de carburo de tungsteno y bolas de acero endurecido minimiza la contaminación de los polvos. Las mediciones de las características estructurales obtenidas mediante refinamiento Rietveld indicaron que, la fase cúbica del carburo presenta vacancias de carbón y como consecuencia de esto, no es estequiométrica. Los resultados tanto de DRX como de HREM, indican una alta deformación en la fase cerámica como consecuencia del estado nanocristalino.

Descriptores: Carburo de titanio; aleado mecánico; microestructura; refinamiento de estructura; difracción de rayos X.

PACS: 07.85.Jy; 81.20.Ev; 61.10.Nz; 61.50.Nw; 81.05.Je; 68.37.Lp

1. Introduction

Titanium carbide (TiC) is a high temperature ceramic material widely used as abrasive [1], grinding wheels, cutting tools [2] and coated cutting tips [3]. This is due to the excellent properties such as high strength and hardness combines with high melting point and low density. In recent years, different methods have been used to produce micro or nanometric TiC. Among them we found, carbothermal reduction [4], conventional melting and casting [5], combustion synthesis [6], electron beam radiation/laser surface melting/plasma spray synthesis [7-10], and mechanical alloying, MA [11-14]. MA is a very powerful technique that can be used to produce all kinds of materials. Through this technique, materials can be manufactured to produce nanostructures. Other advantages of this technique include the relatively low costs and the possibility of production in large quantities. However, an important problem during the ball-

milling is the powders contamination from the milling media (vials and balls) [15]. The use of different types of milling media is able to overcome this problem to a certain extent [16]. Based on previous works of the TiC production by MA, the present paper reports the results of an investigation aimed to minimize the powder contamination from milling tools and provide different data about the TiC formation by MA process.

2. Experimental procedure

TiC ceramic material was prepared by mechanical alloying from a mixture of elemental powders Ti (99.99%), particle size $\approx 100 \mu\text{m}$ and C (99.99%), particle size $\approx 50 \mu\text{m}$, to give the stoichiometric composition ($\text{Ti}_{50}\text{C}_{50}$). The MA was performed using a vibratory SPEX 8000 mixer and mill, with vials and balls of tungsten carbide or vials of tungsten car-

bide and balls of hardened steel. The WC balls hardness was 70 HRC and the steel balls hardness was 80 HRC.

The materials were milled for 4, 8, 10, 12 and 20 hours in the presence of methanol (0.05 ml/g) in order to prevent excessive agglomeration. The milling media size diameters were 0.5 in and the weight ratio of ball-to-powder was 10:1. The powders were characterized by X-ray diffraction (XRD) using a Siemens D5000, Cu $k\alpha$ radiation with a counting time of 10 s per step (0.02°), and transmission electron microscopy (FEG Philips Tecnai F20 and JEOL 2010). The TEM observations were carried out using powder samples deposited on carbon-coated copper grids.

3. Results and discussion

Figure 1 shows XRD patterns for powders as-received and after different MA times. The powders were initially milled by 20 h using vial and balls of tungsten carbide WC. After

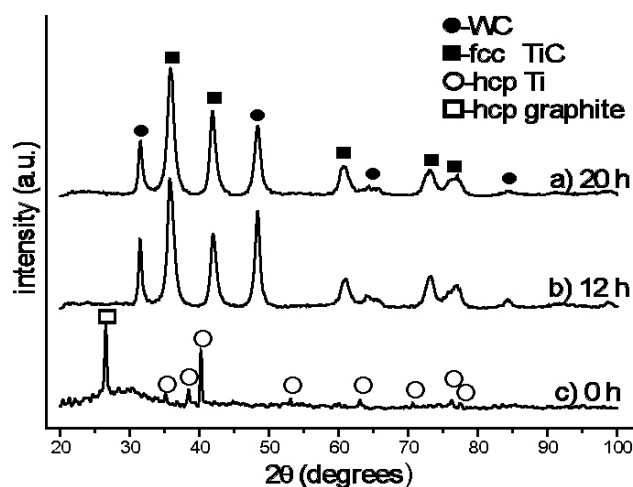


FIGURE 1. XRD patterns of TiC powders milled for different MA times, using vial and balls of WC.

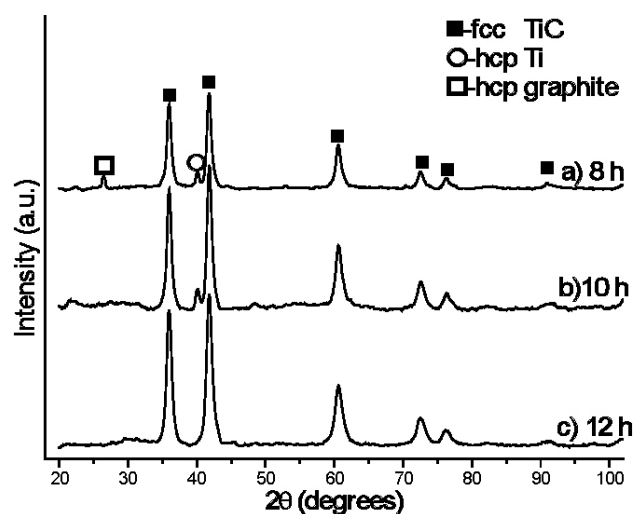


FIGURE 2. XRD patterns of TiC powders milled for different MA times, using WC vial and hardened steel balls.

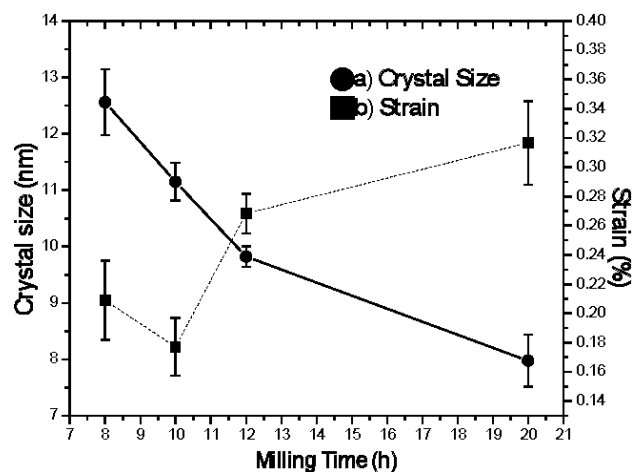


FIGURE 3. MA time for TiC samples as a function on crystal size and strain.

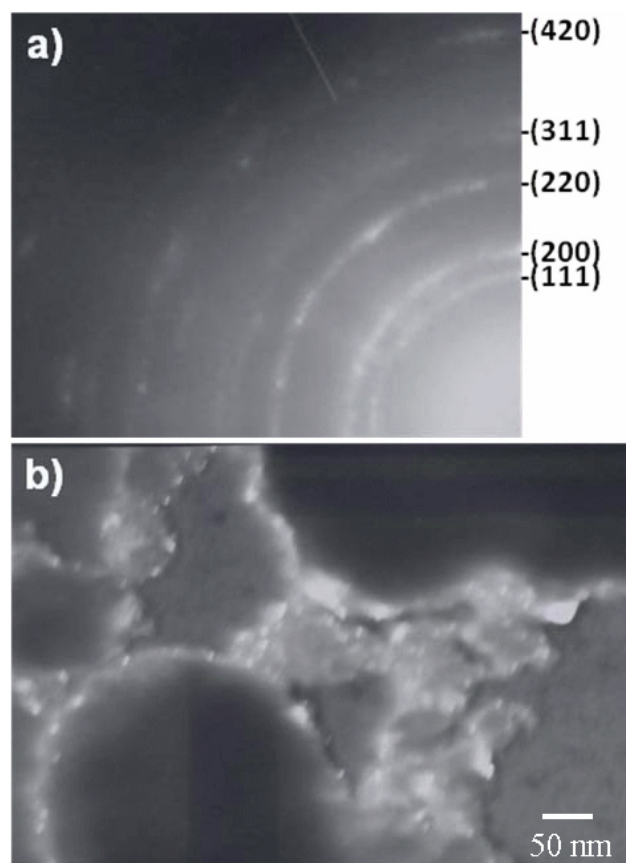


FIGURE 4. TEM images of TiC powders for 12 h of MA time specimen, (a) SAD Pattern, and (b) Dark field image.

this MA time the TiC formation was evident. However, it can be seen that the milled powders are seriously contaminated with WC. Thus, in order to know the optimum milling time of the TiC formation and to reduce the contamination, the milling time was diminished. The XRD pattern which corresponds to 12 h of MA time also show the presence of

the TiC phase, however, these powders even appear contaminated with WC. As is seen, peaks for both phases are broadened significantly with the milling time. This indicates that after TiC formation, the milling energy is now used for the reduction of crystal size and increment of the internal strain of carbide.

In order to avoid the powder contamination, hardened steel balls and WC vial were used. Figure 2 shows the diffractograms of the samples prepared with hardened steel balls for 8, 10 and 12 h of milling time. TiC phase is already observed after 8 h of the MA time. However, reflections related to Ti and C elemental powders are also present. These elemental reflections are vanishes gradually and then disappears totally for 12 h of milling time, which TiC cubic phase only appear. Thus, during the mechanical milling process we find that the dissolution of hcp-C into Ti hcp-lattice is given to form TiC cubic fcc [11]. It is important to note that there is no evidence of reflections related with milling media (steel) and container (WC). Therefore, the powders contamination from milling media was reduced to the minimum; at least it was not detected by the XRD technique.

Figure 3 shows the crystal size and lattice strain variation of TiC compound with MA time. The reduction of crystal size is accompanied by the increase slight of the lattice strain. The data for the 12 h of MA sample indicate that the crystal size refinement is to be around 10 nm. For the same specimen, the contribution of internal strain is smaller about 0.3%.

Transmission electron microscopy studies for the 12 h of MA sample are shown in Fig. 4a and 4b. Selected area diffraction (SAD) pattern (Fig. 4a) indicates the polycrystalline nature of the sample with the (111), (200), (220), (311) and (420) reflection planes of the fcc-cubic TiC phase. SAD pattern reveals some texture of the planes. It is important to note that there are no reflections which corresponding to the starting elements (Ti,C) and no traces of compounds incoming from milling tools (WC vial or Fe balls) were observed. This suggests that we found the TiC phase without any signal of contamination from the vial and balls. The dark-field image (Fig. 4b) confirms the crystal nanometric size ranges, which are similar to those obtained by XRD measurements.

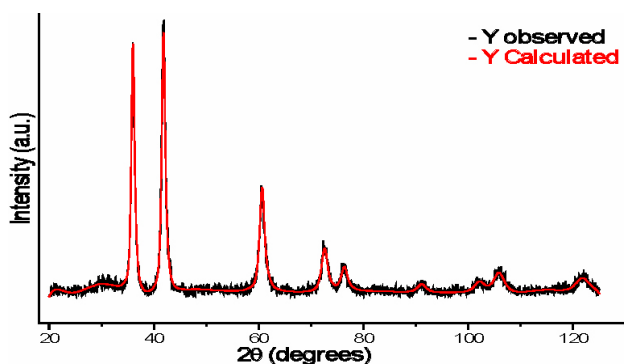


FIGURE 5. Rietveld-refinement patterns (observed and calculated) for 12 h of MA time specimen.

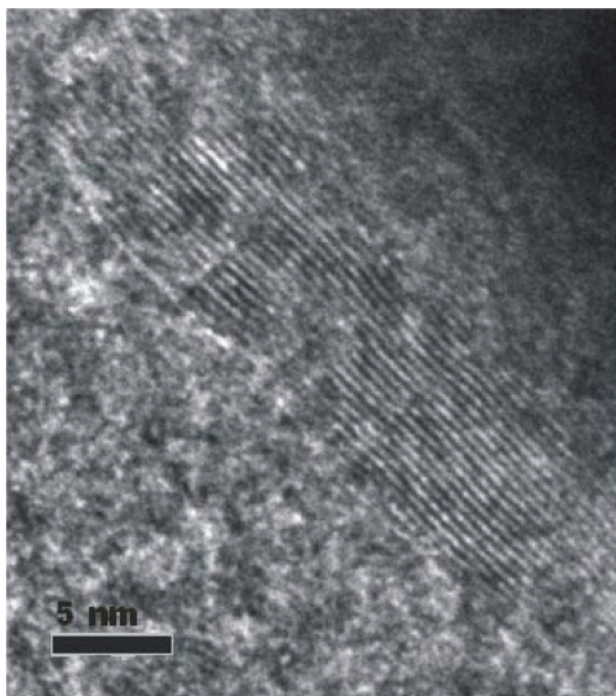


FIGURE 6. HREM micrograph of TiC powders milled for 12 h using hardened steel balls.

Rietveld structure refinement [17] of TiC ceramic compound from X-ray diffraction data were carried out as shown in Fig. 5. The lattice parameter of the fcc-TiC phase was evaluated to be 0.4323 nm, being smaller than the reported value 0.4326 nm [11]. Additionally, it has been noted that the lattice parameter increases slightly with the increment of milling time from 8 to 12 h. These parameter measurements suggest that the increment in milling time leads to the C and Ti solubility in the fcc-TiC crystalline phase, resulting in a gradual TiC formation. The value of the atomic occupation factor for C element was 0.9936. This value is smaller in comparison of Ti (1.0). This result suggests an important C vacancies concentration in the TiC structure and therefore, a non-stoichiometric phase [18]. The presence of crystalline defects could be a consequence of the heavy deformation which is introduced into the powders through MA process.

Nanometric crystal size, internal strain, lattice parameter and occupation factor values suggests that in the ceramic compound, some crystalline defects are induced after MA process. Figure 6 shows a high-resolution electron microscopy image which correspond to 12 h of MA. Important planar deviations of crystal lattice can clearly be observed. Crystalline defects and internal strain are observed through XRD and TEM, indicating heavy deformation in the ceramic compound at nanometric scale regime. This mechanical behavior is commonly observed in based carbon nanocrystals [19].

4. Conclusions

Mechanical alloying from binary equiatomic Ti-C powders was investigated using XRD, SEM and TEM. After 12 h of MA time the TiC phase appeared as a monophase. No signal of any contamination from milling tools was detected. Some structural information of the TiC phase formation during MA process has been obtained. The XRD-data for the 12 h of MA sample indicate that the crystal size refinement is to be around 10 nm. Rietveld refinement revealed that the cubic

carbide phase presents C vacancies. Therefore, the TiC phase obtained by MA process is not a stoichiometric phase. XRD and HREM observations indicate a heavy deformation in the TiC structure as a consequence of high-energy ball-milling.

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