https://doi.org/10.2298/SOS2203305M

## UDK: 621.926.087; 549.2

## Mechanosynthesis of β-Cr<sub>2</sub>N using BN as the Nitrogen Source

# A. Martinez-Garcia<sup>1,2</sup>, K. Navarro-Mtz<sup>3</sup>, E. Lopez-Vazquez<sup>2</sup>, M. Valera-Zaragoza<sup>1</sup>, E. A. Juarez-Arellano<sup>1\*)</sup>

<sup>1</sup>Instituto de Química Aplicada, Universidad del Papaloapan, Circuito Central 200, Parque Industrial, 68301, Tuxtepec, Oaxaca, México.

<sup>2</sup>Tecnológico Nacional de México, Instituto Tecnológico de Oaxaca, Av. Víctor Bravo Ahuja 125, 68030, Oaxaca, México.

<sup>3</sup>Instituto de Biotecnología, Universidad del Papaloapan, Circuito Central 200, Parque Industrial, 68301, Tuxtepec, Oaxaca, México.

#### Abstract:

The mechanosynthesis of hexagonal chromium nitride ( $\beta$ -Cr<sub>2</sub>N) is explored by the high-energy ball-milling of Cr and h-BN. The  $\beta$ -Cr<sub>2</sub>N onset formation is observed after 20 min of milling, although the complete reaction is achieved at 100 min of milling. Two different 1Cr:1BN and 2Cr:1BN molar ratios were evaluated, observing that the molar ratio plays an essential role in the end products during mechanosynthesis. The products were characterized by XRD, FTIR and Raman spectroscopy, thermal analysis (TGA and DSC), SEM, and surface area (BET). A preliminary phase stability map vs. accumulative energy ( $\Delta E_{vaccum}$ ) has been constructed. The accumulative energy needed for the complete  $\beta$ -Cr<sub>2</sub>N formation is  $\Delta E_{vaccum} > 720$  kJ/g.

**Keywords**:  $\beta$ -Cr<sub>2</sub>N phase; Chromium nitride; High-energy ball-milling; Accumulated energy.

## **1. Introduction**

Transitions metal nitrides have gained considerable attention because of properties such as high hardness, high-temperature chemical stability, high-temperature electrical conductivity, or high abrasion resistance [1-3]. These properties make them ideal materials in applications where friction reduction, wear resistance, and corrosion resistance properties are needed [4,5]. In particular, chromium nitrides ( $Cr_xN_y$ ) have shown superior chemical and physical properties than TiN, the most used material in the industry [6-8]. In addition, recent studies have shown that chromium nitrides possess promising characteristics as coating materials, like good oxidation resistance, corrosion resistance, and lower friction coefficient [9-13].

The chromium-nitrogen system is relatively simple, although, to this day, there is only an early stage phase diagram [14,15]. There are only two known thermodynamic stable chromium nitride phases:  $\gamma$ -CrN ( $Fm\overline{3}m$ , NaCl-type) and  $\beta$ -Cr<sub>2</sub>N ( $P\overline{3}1m$ , CdI<sub>2</sub>type). The  $\gamma$ -CrN phase is usually synthesized industrially at temperatures around 1000°C for extended periods (2-3 weeks) by reacting: 1) chromium hydrides with ammonia or a mixture of nitrogen-hydrogen gas, or 2) metallic chromium powder with ammonia [16,17]. Another method used in the production of  $\gamma$ -CrN powders is through

<sup>\*)</sup> **Corresponding author:** eajuarez@unpa.edu.mx

ammonolysis reactions [18]. Multiple reports have shown that  $\gamma$ -CrN can be obtained by a combination of short milling times and a subsequent thermal treatment [19,17] or by prolonged (25 hours) high-energy ball-milling treatment [20,21].

The  $\beta$ -Cr<sub>2</sub>N phase is obtained by the direct chromium conversion in a nitrogen atmosphere. However, this method regularly leads to a mixture of  $\beta$ -Cr<sub>2</sub>N and  $\gamma$ -CrN phases [17,22,23]. Other methodologies used in the synthesis of the  $\beta$ -Cr<sub>2</sub>N phase are: thermal decomposition of  $\gamma$ -CrN above 1100°C [24-26], self-propagating hightemperature synthesis [27], and solid-state metathesis reactions of chromium at elevated temperatures [28]. Mechanical milling has been used as an activation mechanism, but the final product is a mixture of Cr,  $\beta$ -Cr<sub>2</sub>N, and  $\gamma$ -CrN [17,19].

Chromium nitrides have very similar properties, such as hardness ( $\gamma$ -CrN - 13-17 GPa,  $\beta$ -Cr<sub>2</sub>N - 18.5 GPa) and bulk modulus ( $\gamma$ -CrN - 243 (10) GPa,  $\beta$ -Cr<sub>2</sub>N - 275 (23) GPa) [29-32]. Both phases are used in hard coatings and thermoelectric materials. They are also important as secondary metallurgical phases in refractory alloys, special steels, and dispersion strengtheners [28,33,34]. Nevertheless, the  $\gamma$ -CrN phase decomposes to  $\beta$ -Cr<sub>2</sub>N between 1150-1300°C [25,26]. Therefore, the  $\beta$ -Cr<sub>2</sub>N phase has grown in importance in the hardening processes of chromium-containing steel work pieces due to its thermal stability [35,36].

As previously described, the synthesis of chromium nitrides involves long periods. Therefore, the search for new methodologies is of great importance. High-energy ball-milling has proven to be a powerful technique for obtaining materials such as nitrides, carbides, borides, intermetallic and metastable phases [37-44]. Ball-milling has advantages such as easy operation, easy to scale industrially, short processing times, and that it could produce nanostructured powders. However, the search for new methods should not be limited to synthesis methods, but it also explores different alternatives of nitrogen sources instead of N<sub>2</sub> and ammonia, customarily used. Besides, the strong N  $\equiv$  N triple bond results in the difficulty of converting N<sub>2</sub> into other compounds. Thus, the use of new nitrogen sources during mechanical milling could improve the synthesis of chromium nitrides. For example, Sun *et al.* reduced the c-ZrN synthesis time using LiN as a nitrogen source [45], or Garcia-Mendoza *et al.* demonstrated the formation of the metastable  $\delta$ -TaN phase by a combination of high-energy ball-milling and the use of BN as nitrogen source [44].

Therefore, this study evaluates the combination of high-energy ball-milling and h-BN, as a nitrogen source, for chromium nitrides mechanosynthesis. To ensure the formation of  $\gamma$ -CrN and  $\beta$ -Cr<sub>2</sub>N phases, two different Cr:BN ratios were explored (1Cr:1BN and 2Cr:1BN). The products of the milling process were identified and characterized by X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), and surface area analysis by the Brunauer-Emmett-Teller (BET) method. A milling energy map was also built using Burgio's mathematical model [46].

## 2. Materials and Experimental Procedures 2.1 High energy ball milling

Chromium (Sigma-Aldrich, 99.9 %) and hexagonal boron nitride (h-BN, Sigma-Aldrich, 98 %) powders in the molar ratio of 1Cr:1BN, and 2Cr:1BN, were homogenized in an agate mortar and placed in the milling vials.

The mechanosynthesis was carried out in a planetary ball-mill (Pulverisette 7 premium line, FRITSCH). Vials (80 ml) and balls (15 of 1 cm) of tungsten carbide were used as a milling material. A main disk rotation rate of 600 rpm, a ratio of transmission

between bowls and main disk of -2:1, a ratio between the mass of the balls and the mass of the sample (ball to powder ratio, BPR) of 115:1, and different milling times were used. The milling vials were hermetically sealed with an N<sub>2</sub> atmosphere (N<sub>2</sub>, Infra, 99.99 %) to avoid chromium oxidation from the O<sub>2</sub> or H<sub>2</sub>O present in the air during the milling. The milling was done in cycles of 5 min milling and 10 min pause for cooling to evade overheating.

#### **2.2 Characterization**

## 2.2.1. Powder X-Ray Diffraction (XRD)

Powder X-ray diffraction patterns were collected in air and at room temperature in a Bruker D-8 Advance diffractometer with Cu  $K_{\alpha 1}K_{\alpha 2}$  radiation. A sodium iodide (NaI) scintillation detector and flat polymer sample holder were used. The  $2\theta$  interval explored was  $10^{\circ} - 90^{\circ}$  with  $0.1^{\circ}$  step size, 4 s counting time, continuous mode, and spinning of 30 rpm. Rietveld refinement has been done using the program FULLPROF [47]. Linear interpolation between approximately 28 manually selected points for the background and a pseudo-Voigt profile function has been used.

#### 2.2.2. Spectroscopies (FTIR and Raman)

Infrared spectra were obtained from a standard infrared spectrometer model 100FT-IR (ATR, Perkin Elmer). The characterization was carried out by scanning the mid and near-infrared range (4000 - 600 cm<sup>-1</sup>). Raman spectra were obtained on equipment constructed and operated at Geosciences Institute from Frankfurt University. An argon laser with a wavelength of 532.12 nm was used. Also, between 10 and 20 mg of sample was placed on glass slides and covered with glass coverslips.

#### 2.2.3. Thermal Analysis

Thermogravimetric curves were obtained using a Perkin Elmer STA 6000 simultaneous thermal analyzer. The sample (10-20 mg) was placed in an open alumina pan at room temperature using a heating rate of 10 °C/min in temperature intervals between 30 and 800°C with constant  $N_2$  flow. The calorimetric analysis was carried out using a Discovery brand DSC 250 calorimetric analyzer. The samples (1-2 mg) were placed in closed alumina capsules to be treated at room temperature using a heating rate of 100 °C/min in temperature intervals between 30-400°C with constant  $N_2$  flow.

#### 2.2.4. Scanning Electron Microscopy (SEM)

SEM observations were made using a Phenom-World Pro X Desktop scanning electron microscope using a 10 kV voltage. The uncoated samples were mounted on double-sided sticking carbon tape.

#### 2.2.5. Surface area (BET)

Adsorption/desorption isothermal was obtained at  $-196^{\circ}$ C in BELSORP-mini equipment. Samples were degassed at 300°C with a constant (N<sub>2</sub>) flow for 2 hours. BET method was used to calculate the surface area [48].

#### 2.3. Mathematical model

The accumulated energy supplied for the planetary ball-mill  $\Delta E_{vaccum}$  to the powder mixtures during the milling is calculated with the mathematical model described by Burgio *et al.* and Martinez-Garcia *et al.* [43,46,49]. However, accumulated energy supplied  $\Delta E_{vaccum}$  equation can be simplified as a function of the experimentally controlled variables such as the density of the milling material ( $\rho_b$ ), the speed of the ball mill main disk ( $W_d$ ), the milling time (*t*), and the sample mass ( $m_s$ ), Equation 1. The advantage of using this simplified equation is that once the accumulated energy supplied is known, and different milling conditions can be compared only as a function of energy.

$$\Delta E_{vaccum} = 3.93097 \times 10^{-14} \left(\frac{\rho_b W_d^3 t}{m_s}\right)$$
(1)

A chromium nitride milling-energy map was built using the  $\Delta E_{vaccum}$  and the experimental results from XRD, FTIR, and TGA. The map was set up as described by Martinez-Garcia *et al.* [43,49].

## **3. Results and Discussion 3.1. Mechanosynthesis**

The powder diffraction patterns showing the phase evolution of the 1Cr:1BN and 2Cr:1BN stoichiometric mixtures during high-energy ball-milling can be seen in Fig. 1.



Fig. 1. Powder X-ray diffraction patterns of the milling products of 1Cr:1BN and 2Cr:1BN mixtures at different milling times.

The starting mixtures can be identified as a mechanical mixture of metallic Cr (PDF-00-006-0694) and h-BN (PDF-01-079-675). The diffraction patterns from the samples up to 20 min of milling show broad chrome's reflections while the h-BNs' reflections are no longer observed. Similar behavior is observed in both stoichiometric mixtures (Fig. 1). This effect is due to the formation of structural defects promoted by the milling. However, from 20 min of milling, a new reflection at around 42.8° in 2 $\theta$  is observed. This reflection is associated with the  $\beta$ -Cr<sub>2</sub>N (111) plane (PDF-00-051-0939). Although the intensity of  $\beta$ -Cr<sub>2</sub>N reflections increases with prolonged milling time, the intensity of WC reflections (PDF-00-051-0939) from the milling material also increases. Thus, the presence of WC is very prominent after 60 min of milling.

The hardness of WC (22-28 GPa [1]) is higher than  $\beta$ - Cr<sub>2</sub>N (18.5 GPa [32]). However, some authors have shown that the particle size reduction (Hall-Petch effect) and decrease of metal vacancies increase the hardness of metallic nitrides [44,50,51]. Sanjinès reported 27 GPa of microhardness and 22 GPa of nano hardness in  $\beta$ -Cr<sub>2</sub>N thin films deposited by magnetron sputtering [52]. Therefore, the hardness of the mechanosynthesized  $\beta$ -Cr<sub>2</sub>N phase obtained in this study may have increased due to structural micro-deformation promoted by high-energy ball-milling.

This increment in hardness could be responsible for WC's presence in the samples after the onset of formation of the  $\beta$ -Cr<sub>2</sub>N phase (20 min of milling).

It has been reported that the hardness of metal transition nitrides decreases with the increment of metal vacancies. For example, the hardness of  $\delta$ -TaN,  $\delta$ -Ta<sub>0.82</sub>N, and  $\delta$ -Ta<sub>0.67</sub>N are 26 GPa, 18.2 Gpa, and 14.7 GPa, respectively [44]. Thus, although there are no similar reports regarding the  $\beta$ -Cr<sub>2</sub>N phase, from Fig. 2, it can be seen that the products from the 1Cr:1BN and 2Cr:1BN stoichiometric mixtures behave differently. The reflections of the  $\beta$ -Cr<sub>2</sub>N phase observed in 2Cr:1BN show more broadening with milling than the phase obtained in 1Cr:1BN. Thus, in the experiments with a 1Cr:1BN molar ratio is very likely to have the formation of stoichiometric  $\beta$ -Cr<sub>2</sub>N with hardness similar or greater than the milling material, while in the experiments with 2Cr:1BN molar ratio is very likely to have the formation of non-stoichiometric  $\beta$ -Cr<sub>2-x</sub>N with metal vacancies. Nevertheless, further investigations are needed to corroborate this observation.



**Fig. 2.** Riveted tenement of the powder X-ray diffraction pattern of the 1Cr:1BN sample after 100 min of milling.

The Rietveld refinement of the 1Cr:1BN sample after 100 min of milling is shown in Fig. 2, while the lattice parameters and crystal structure are shown in Tab. I. The lattice parameters values obtained here agrees with what is reported:  $\beta$ -Cr<sub>2</sub>N (a = 4.80 Å,

c = 4.47 Å, V = 89.19 Å<sup>3</sup>; PDF-00-035-0803) and WC (a = 2.90 Å, c = 2.83 Å, V = 20.76 Å<sup>3</sup>; PDF-00-051-0939). The quantitative phase analysis using the Rietveld refinement of the X-ray diffraction pattern shows that the 1Cr:1BN sample after 100 min of milling is a mixture of ~73%  $\beta$ -Cr<sub>2</sub>N and ~27% WC (Tab. I).

**Tab. I** Lattice parameters and crystal structure of  $\beta$ -Cr<sub>2</sub>N and WC (milling material), obtained from Rietveld refinement of the XRD pattern of the 1Cr:1BN sample after 100 min of milling (Fig. 2).

Parameter	β-Cr <sub>2</sub> N	WC
Lattice Parameter		
a / Å c / Å V / Å <sup>3</sup>	4.801(1) 4.480(1) 89.46(3)	2.903(1) 2.836(1) 20.70(1)
Crystal Structure		
Space Group	$P\overline{3}1m$	$P\overline{6}m2$
Atoms	Cr // N	W // C
Wyckoff Position	6k // 1a ; 2d	1 <i>a //</i> 1 <i>f</i>
Positions	$0.348(1), 0, 0.262(1) - 0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$	$0,0,0-\frac{1}{3},\frac{2}{3},,\frac{1}{2}$
Fract. / %	73.3 (1)	26.7 (1)
Reliability Factors		
$R_p = 2.38; R_{wp} = 3.10; R_{exp} = 2.97; X^2 = 1.09$		

Although the formation of  $\beta$ -Cr<sub>2</sub>N was observed in the XRD patterns, the doubt that emerges is whether  $\beta$ -Cr<sub>2</sub>N is actually formed or whether a Cr-BN phase or Cr<sub>x</sub>B<sub>y</sub> phase is obtained instead during the mechanosynthesis. So far, the formation of ternary Cr-B-N phases has not been reported. Ma et al. deposited Cr-B-N coats on stainless steel and Si disks using closed field unbalanced magnetron sputtering; they reported that the coats were a mixture of  $\gamma$ -CrN, CrB<sub>2</sub>, and h-BN. Besides [53], there are no reports of chromium borates forming isostructural phases to  $\beta$ -Cr<sub>2</sub>N [54]. Therefore, to evaluate the status of boron and h-BN in the samples after 100 min of milling, spectroscopic analysis was carried out (Fig. 3).

#### 3.2. Spectroscopy analysis

Infrared spectra of the 1Cr:1BN and 2Cr:1BN samples milled during 100 min are shown in Fig. 3. Although the chromium nitrides and chromium borides do not show characteristic signals in the mid and near-infrared spectra [55-57], the h-BN does. The FTIR absorption spectrum of h-BN has distinctive bands at 1352 and 798 cm<sup>-1</sup> corresponding to B-N bond stretching vibration and B–N–B out-of-plane bending vibration, respectively [44,57]. In Fig. 3, it can be seen that none of the samples show

these bands. Thus there are no B-N and B-N-B bonds of h-BN in the samples after 100 min of milling. Garcia-Mendoza *et al.* showed similar behavior during the mechanosynthesis of  $\delta$ -TaN using h-BN as a nitrogen source [44].



Fig. 3. FTIR and Raman spectra of the 1Cr:1BN and 2Cr:1BN samples after 100 min of milling.

Iizumi *et al.* reported the mechanosynthesis of CrB and CrB<sub>2</sub> starting from the elements after 10 hours of milling [59]. Consequently, Cr-B phases need more mechanical energy than Cr-N phases to form. Such energies are not reached in this study. Besides, according to the Cr-B equilibrium diagram, 1400°C is the minimum temperature necessary to trigger the reaction [60], while for the Cr-N system is 700°C [14]. This difference can be attributed to the enthalpy of formation ( $\Delta H_{f(298)}^0$ ) of  $\beta$ -Cr<sub>2</sub>N (-125.5 kJ mol<sup>-1</sup>),  $\gamma$ -CrN (-117.5 kJ mol<sup>-1</sup>), CrB (-78.9 kJ mol<sup>-1</sup>) and CrB<sub>2</sub> (-119.5 kJ mol<sup>-1</sup>) [59, 61, 62]. Therefore, since the  $\beta$ -Cr<sub>2</sub>N phase has a slightly more negative enthalpy of formation, it is considered that its production is more favorable during the mechanosynthesis of Cr-BN mixtures.

Raman spectra of the 1Cr:1BN and 2Cr:1BN samples milled during 100 min are shown in Fig. 3.  $\beta$ -Cr<sub>2</sub>N belongs to the  $D_{3d}^1$  group symmetry presenting five active modes in Raman scattering: 2A<sub>1g</sub> + 3E<sub>g</sub> (at 215, 267, 284, 385 and 490 cm<sup>-1</sup> and bands due to second-order combination at 586, 667, 760, 943 and 1050 cm<sup>-1</sup>) [63]. In the 1Cr:1BN and

2Cr:1BN samples (Fig. 3), the first-order active modes could not be observed due to the low intensity and widening of the peaks in the spectra. However, considering that XRD demonstrated the formation of the  $\beta$ -Cr<sub>2</sub>N phase, it could be that the broad peak observed around 200-600 cm<sup>-1</sup> is the sum of the scattering of the first-order active modes of  $\beta$ -Cr<sub>2</sub>N. The second-order active modes are observed. Boron (827 and 1166 cm<sup>-1</sup>) and WC (267, 716, and 805 cm<sup>-1</sup>) active modes were not observed or are overlapped with other signals [63-66].

In Raman spectroscopy, several factors could affect the width, intensity, or displacement of the peaks due to reduced vibration modes. Some of the more critical factors are particle size, non-stoichiometry, amorphization, or structural defects [63,67, 68]. Refractory materials such as chromium nitride are known to contain many structural defects [56]. Besides, high-energy ball milling promotes non-stoichiometric compounds and a high concentration of structural defects during milling [69]. These factors influence the Raman spectrum results in our study since the 2Cr:1BN sample is less crystalline and has more structural defects than the Cr:1BN sample (Fig. 1), leading to a less intense and more broad Raman spectrum (Fig. 3).

#### 3.3. Thermal analysis

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on the 1Cr:1BN sample after 100 min of milling to determine its thermal stability (Fig. 4). This sample was selected since it was the one that shows the highest content of  $\beta$ -Cr<sub>2</sub>N (Fig. 1). The thermogravimetric curve shows two-weight losses and one weight gains up to 800°C (Fig. 4).



Fig. 4. Thermogravimetric and Differential Scanning Calorimetric curves of 1Cr:1BN after 100 min of milling.

The first weight loss of ~1.8 wt% is observed between 30-200°C, and it is associated with humidity evaporation. The second weight loss of ~0.8 wt% observed at 200-400°C could be related to the decomposition of metastable phases of chromium oxides or hydrated chromium oxides [70,71]. These phases could be formed by exposing the sample to the environment. The weight gain of ~2.7 wt% is observed between 400-800°C, and it is associated with the interaction of boron with the N<sub>2</sub> gas (buoyancy and drag) used in TGA measurements. Mirkarimi *et al.* reported that the CVD process's optimal temperature to form c-BN thin films is between 427 and 527°C [72]. This temperature region agrees with the B-N phase diagram reported by Mujica *et al.* [73]. Thus, the boron from the h-BN phase remains unreacted and amorphous in the sample after the high-energy ball milling, and during the TGA measurements, it reacts with the N<sub>2</sub> gas used.

The temperature-dependence of the heat flow for the 1Cr:1BN sample after 100 min of milling up to 400°C is shown in Fig. 4 where two signals are observed. The first one is an endothermic signal at  $\sim$ 75°C, associated with the evaporation of the sample's humidity adsorbed. The second is an exothermic signal that starts at 275°C and continues after 400°C, related to the decomposition of metastable phases of chromium oxides and hydrated chromium oxides [70,71]. These results complement and strengthen the thermogravimetric analysis results.

## 3.4. Morphological and surface analysis

The reported  $\beta$ -Cr<sub>2</sub>N morphology is homogeneous agglomerate particles, without specific geometry and wide particle size distribution, where the size is related to the synthesis method. For example, nitriding of Cr in ammonia gives particle sizes between 200-300 nm [74], while self-propagating high-temperature synthesis provides agglomerates of 1.5  $\mu$ m [27].



Fig. 5. SEM micrographs of the 1Cr:1BN and 2Cr:1BN samples after 100 min of milling.

The morphology and topography of 1Cr:1BN and 2Cr:1BN samples after 100 min of milling are shown in Fig. 5. The micrographs show agglomerate particles of heterogeneous appearance, without specific geometry and particle size below 30  $\mu$ m. These agglomerates were partially sintered during the high-energy ball-milling process (Fig. 5). Although, no significant difference was observed among the 1Cr:1BN and 2Cr:1BN samples.



Fig. 6. Nitrogen adsorption/desorption isotherm and surface area, by the BET method, of 1Cr:1BN after 100 min of milling.

There are very few reports of the surface area of  $\beta$ -Cr<sub>2</sub>N. Jiang *et al.* and Michalsky and Pfromm reported surface areas of 0.61 m<sup>2</sup>/g and 0.4 m<sup>2</sup>/g, respectively [75,76]. Measurements of the specific surface area of 1Cr:1BN and 2Cr:1BN samples after 100 min of milling gives surface areas of 1.75 m<sup>2</sup>/g and 1.71 m<sup>2</sup>/g, respectively. No significant difference was observed among the 1Cr:1BN and 2Cr:1BN adsorption isotherms. Fig. 6 shows the characteristic adsorption isotherm of 1Cr:1BN after 100 min of milling. According to the IUPAC classification, the adsorption isotherm is type III; no inflection point is observed. Therefore, the adsorption is giving by capillary condensation [77]. This type is characteristic of nonporous or macroporous solid materials with relatively weak adsorbate-adsorbent interactions. The adsorbed molecules are clustered around the most favorable sites on the particles [77,78]. The hysteresis loop is Type H3, where the lower limit of the desorption isotherm indicates that the desorption is cavitation-induced. The origin of the loop behavior could be the particle's shape [79]. Thus, the isotherm curve shape suggests that the particles are nonporous and that the specific surface areas depend only on the particles' surface.

## **3.5.** Phase stability map vs. accumulative energy ( $\Delta E_{vaccum}$ )

A phase stability map vs. accumulative energy ( $\Delta E_{vaccum}$ ) was constructed (Fig. 7). The map shows three different regions. In the first region (0-175 kJ/g), the starting materials (Cr and h-BN) are only amorphized. The second region (175-720 kJ/g) corresponds to the partial formation of the  $\beta$ -Cr<sub>2</sub>N phase. While the third region, >720 kJ/g, corresponds to a mixture of  $\beta$ -Cr<sub>2</sub>, WC (contamination from the grinding material), and amorphous boron (from the BN). Usually, the optimization of a high-energy ballmilling synthesis process requires many experiments due to a large number of variables in the process. However, knowing the  $\Delta E_{vaccum}$  needed for the complete formation of  $\beta$ -Cr<sub>2</sub>N, different milling conditions (rpm, time, sample mass, density, etc.) could be used.



Fig. 7. Phase stability map vs. accumulated energy ( $\Delta E_{vaccum}$ ) for the mechanosynthesis of  $\beta$ -Cr<sub>2</sub>N from Cr and h-BN.

#### 4. Conclusion

The mechanosynthesis of  $\beta$ -Cr<sub>2</sub>N, starting from Cr and h-BN, is observed after a short milling time. Compared with previous studies, in this study, only the  $\beta$ -Cr<sub>2</sub>N phase is obtained. Even though the system Cr-N is simple, the starting *x*Cr:*y*BN molar ratio plays an essential role in the end products during mechanosynthesis. Although the complete reaction was observed at 100 min of milling, the obtained sample shows low crystallinity and high structural defects in a mixture of ~73%  $\beta$ -Cr<sub>2</sub>N and ~27% WC (contamination from the grinding material). Nevertheless, knowing the  $\Delta E_{vaccum}$  needed for the entire  $\beta$ -Cr<sub>2</sub>N formation (>720 kJ/g), different milling conditions could be used to reduce the milling time, reducing the deformation and strains in the sample and reducing or eliminating the contamination from the grinding material.

#### Acknowledgments

AMG acknowledges the scholarship granted by CONACyT (279527) and thanks to Prof. Björn Winkler (Institut für Geowissenschaften, Frankfurt University) for all the support given during the research stay. CONACyT supported this work (INFRA-2015-01-252013, LN-2015-01-252013, and LN-2016-271911).

#### 5. References

- 1. Friedrich, B. Winkler, E. A. Juarez-Arellano, L. Bayarjargal, Materials., 4(10) (2011) 1648-1692.
- 2. H. O. Pierson, Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps, William Andrew, 1996.
- C. Wang, S. A. Akbar, W. Chen, V. D. Patton, Journal of Materials Science., 30 (7) (1995) 1627-1641.
- 4. A. T. Santhanam, Application of transition metal carbides and nitrides in

industrial tools, in: The chemistry of transition metal carbides and nitrides, Springer, 1996.

- 5. S. T. Oyama, Introduction to the chemistry of transition metal carbides and nitrides, in: The chemistry of transition metal carbides and nitrides, Springer, 1996.
- 6. F. D. Lai, J. K. Wu, Surface and Coatings Technology., 88 (1-3) (1997) 183-189.
- 7. Navinšek, P. Panjan, A. Cvelbar, Surface and Coatings Technology., 74 (1995) 155-161.
- 8. W. Herr, B. Matthes, E. Broszeit, M. Meyer, R. Suchentrunk, Surface and Coatings Technology., 60 (1-3) (1993) 428-433.
- 9. B. Navinšek, P. Panjan, Thin Solid Films., 223 (1) (1993) 4-6.
- P. Ballhause, B. Hensel, A. Rost, H. Schüssler, Materials Science and Engineering: A., 163 (2) (1993) 193-196.
- 11. A. Tricoteaux, P. Y. Jouan, J. D. Guerin, J. Martinez, A. Djouadi, Surface and Coatings Technology., 174 (2003) 440-443.
- 12. Z. P. Huang, Y. Sun, T. Bell, Wear., 173 (1-2) (1994) 13-20.
- L. Cunha, M. Andritschky, K. Pischow, Z. Wang, A. Zarychta, A. S. Miranda, A. M. Cunha, Surface and Coatings Technology., 153 (2-3) (2002) 160-165.
- 14. K. Frisk, Calphad., 15 (1) (1991) 79-106.
- J. W. Seok, N. M. Jadeed, R. Y. Lin, Surface and Coatings Technology., 138(1) (2001) 14-22.
- 16. L. E. Toth, Transition Metal Carbides and Nitrides, Elsevier, 2014.
- 17. R. Ren, Z. Yang, L. L. Shaw, Nanostructured materials., 11 (1) (1999) 25-35.
- X. Q. Li, K. M. Wang, S. S. Gao, W. L. Huan, H. B. Jia, Preparation of chromium nitride nanopowders using high pressure gas-solid reaction bed, in: Materials Science Forum, Vol. 809, Trans Tech Publ, 2015, pp. 74-77.
- 19. A. Calka, J. S. Williams, Synthesis of nitrides by mechanical alloying, in: Materials Science Forum, Vol. 88, Trans Tech Publ, 1992, pp. 787-794.
- Y. Ogino, T. Yamasaki, N. Atzumi, K. Yoshioka, Materials Transactions, JIM., 34 (12) (1993) 1212-1216.
- 21. C. Real, M. A. Roldan, M. D. Alcala, A. Ortega, Journal of the American Ceramic Society., 90 (10) (2007) 3085-3090.
- 22. R. Blix, Zeitschrift für Physikalische Chemie., 3 (1) (1929) 229-239.
- 23. M. Widenmeyer, E. Meissner, A. Senyshyn, R. Niewa, Zeitschrift für Anorganische und Allgemeine Chemie., 640 (14) (2014) 2801-2808.
- 24. H. Ono-Nakazato, K. Taguchi, T. Usui, K. Tamura, Y. Tomatsu, Metallurgical and Materials Transactions B., 32 (6) (2001) 1113-1118.
- 25. R. Sakaguchi, M. Nagao, Y. Maruyama, S. Watauchi, I. Tanaka, Journal of CrystalGrowth., 546 (2020) 125782.
- 26. Y Tsunekawa, M. Okumiya, T. Kobayashi, M. Okuda, M. Fukumoto, Journal of Thermal Spray Technology., 5 (2) (1996) 139-144.
- 27. K. Hirota, Y. Takano, M. Yoshinaka, O. Yamaguchi, Journal of the American Ceramic Society., 84 (9) (2001) 2120-2122.
- 28. M. D. Aguas, A. M. Nartowski, I. P. Parkin, M. MacKenzie, A. J. Craven, Journal of Materials Chemistry., 8 (8) (1998) 1875-1880.
- Rivadulla, M. Bañobre-López, C. X. Quintela, A. Piñeiro, V. Pardo, D. Bal-domir, M. A. López-Quintela, J. Rivas, C. A. Ramos, H. Salva, Nature materials., 8 (12) (2009) 947-951.
- W. K. Grant, C. Loomis, J. J. Moore, D. L. Olson, B. Mishra, A. J. Perry, Surface and Coatings Technology., 86 (1996) 788-796.
- 31. Soignard, O. Shebanova, P. F. McMillan, Physical Review B., 75 (1) (2007) 014104.

- 32. M. A. Gharavi, G. Greczynski, F. Eriksson, J. Lu, B. Balke, D. Fournier, A. Le Febvrier, C. Pallier, P. Eklund, Journal of Materials Science., 54 (2) (2018) 1434-1442.
- 33. T. Aizawa, H. Kuwahara, M. Tamura, Journal of the American Ceramic Society., 85 (1) (2002) 81-85.
- 34. A. Le Febvrier, N. Van Nong, G. Abadias, P. Eklund, Applied Physics Express., 11 (5) (2018) 051003.
- 35. T. H. Lee, S. J. Kim, E. Shin, S. Takaki, On the crystal structure of Cr<sub>2</sub>N precipitates in high-nitrogen austenitic stainless steel. iii. neutron diffraction study on the ordered Cr<sub>2</sub>N superstructure, Acta Crystallographica Section B: Structural Science, 62 (6) (2006) 979-986.
- D. Zeng, S. Yang, Z. D. Xiang, Applied surface science., 258 (12) (2012) 5175-5178.
- E. A. Juarez-Arellano, M. Kakazey, M. Vlasova, G. Urquiza-Beltran, M. Aguilar-Franco, X. Bokimi, E. Martinez, E. Orozco, Journal of Alloys and Compounds., 492 (1-2) (2010) 368-372.
- M. Kakazey, M. Vlasova, M. Dominguez-Patiño, E. A. Juarez-Arellano, Bykov, I. Leon, A. Siqueiros-Diaz, Journal of Magnetism and Magnetic Materials., 323 (20) (2011) 2429-2435.
- S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepi- oni, K. D. M. Harris, G. Hyett, W. Jones, Chemical Society Reviews., 41 (1) (2012) 413-447.
- 40. M. G. Granados-Fitch, E. A. Juarez-Arellano, J. M. Quintana-Melgoza, M. Avalos-Borja, International Journal of Refractory Metals and Hard Materials., 55 (1) (2016) 11-15.
- 41. M. Kakazey, M. Vlasova, E. A. Juarez-Arellano, T. Torchynskac, V. A. Basiukd, RSC Advances., 6 (2016) 58709.
- 42. M. G. Granados-Fitch, J. M. Quintana-Melgoza, E. A. Juarez-Arellano, M. Avalos-Borja, Journal of the American Ceramic Society., 101 (7) (2018) 3148-3155.
- 43. A. Martinez-Garcia, A. K. Navarro-Mtz, C. Neun, L. Bayarjargal, W. Morgenroth, E. Lopez-Vazquez, M. Avalos-Borja, B. Winkler, E. A. Juarez-Arellano, Journal of Alloys and Compounds., 810 (2019) 151867.
- T. Garcia-Mendoza, A. Martinez-Garcia, I. G. Becerril-Juarez, E. Lopez-Vazquez, M. Avalos-Borja, M. Valera-Zaragoza, E. A. Juarez-Arellano, Ceramics International., 46 (14) (2020) 23049-23058.
- 45. Y. Sun, B. Yao, Q. He, F. Su, H. Z. Wang, Journal of alloys and compounds., 479 (1-2) (2009) 599-602.
- N. Burgio, A. Iasonna, M. Magini, S. Martelli, F. Padella, Il nuovo cimento D., 13 (4) (1991) 459-476.
- 47. J. Rodríguez-Carvajal, Physica B., 192 (1-2) (1993) 55-69.
- 48. S Brunauer, P. H. Emmett, E. Teller, Journal of the American chemical society., 60 (2) (1938) 309-319.
- 49. A. Martinez-Garcia, A. K. Navarro-Mtz, A. Aparicio-Saguilan, M. Valera-Zaragoza, M. Avalos-Borja, E. A. Juarez-Arellano, Inorganic Chemistry: An Indian Journal 10 (2) (2015) 34-40.
- 50. R. Oganov, A. O. Lyakhov, Q. Zhu, Comprehensive Hard Materials, Elsevier, 2014,
- 51. Y. H. Yang, D. J. Chen, F. B. Wu, Surface and Coatings Technology., 303 (2016) 32-40.
- 52. R. Sanjinès, P. Hones, F. Lèvy, Thin Solid Films., 332 (1-2) (1998) 225-229.
- 53. Q. Ma, F. Zhou, S. Gao, Z. Wu, Q. Wang, K. Chen, Z. Zhou, L. K. Y. Li, Applied

Surface Science., 377(2016) 394-405.

- 54. E. Campbell, U. R. Kattner, Calphad., 26 (3) (2002) 477-490.
- 55. S. Khan, A. Mahmood, A. Shah, Q. Raza, M. A. Rasheed, I. Ahmad, International Journal of Minerals, Metallurgy, and Materials., 22 (2) (2015) 197-202.
- 56. G. Mangamma, T. N. Sairam, S. Dash, M. Rajalakshmi, M. Kamruddin, V. K. Mittal, S. V. Narasimhan, A. K. Arora, C. S. Sundar, A. K. Tyagi, Journal Nanoscience and Nanotechnology., 7 (3) (2007) 970-976.
- 57. R. A. Nyquist, R. O. Kagel, Handbook of infrared and Raman spectra of inorganic compounds and organic salts: infrared spectra of inorganic compounds, Academic press, 2012.
- 58. L. Zhai, Z. Liu, C. Li, X. Qu, Q. Zhang, G. Li, X. Zhang, B. Abdel-Magid, RSC advances., 9 (10) (2019) 5722-5730.
- 59. K. Iizumi, K. Kudaka, D. Maezawa, T. Sasaki, Journal Of The Ceramic Society Of Japan., 107 (1245) (1999) 491-493.
- 60. Q. Zhai, J. Xu, T. Lu, Y. Xu, Journal of Materials Science and Chemical Engineering., 2 (09) (2014) 12.
- 61. M. W. Chase, Journal of Physical and Chemical Reference Data., 25 (4) (1996) 1069-1111.
- 62. L. Topor, O. J. Kleppa, The Journal of Chemical Thermodynamics., 17 (2) (1985) 109-116.
- 63. A. Barata, L. Cunha, C. Moura, Thin solid films., 398 (2001) 501-506.
- 64. H. Werheit, V. Filipov, U. Kuhlmann, U. Schwarz, M. Armbrüster, A. Leithe-Jasper, T. Tanaka, I. Higashi, T. Lundström, V. N. Gurin, Science and Technology of Advanced Materials., 11 (2) (2010) 023001.
- Y. Yan, B. Xia, X. Qi, H. Wang, R. Xu, J. Y. Wang, H. Zhang, X. Wang, Chemical communications., 49 (43) (2013) 4884-4886.
- 66. R. K. Abbas, K. M. Musa, Petroleum., 5 (3) (2019) 329-334.
- 67. H. Campbell, P. M. Fauchet, Solid State Communications., 58 (10) (1986) 739-741.
- 68. T. Xing, L. H. Li, L. Hou, X. Hu, S. Zhou, R. Peter, M. Petravic, Y. Chen, Carbon., 57 (2013) 515-519.
- 69. C. Suryanarayana, Mechanical alloying and milling, Progress in materials science., 46 (1-2) (2001) 1-184.
- H. Ye, Q. Zhang, F. Saito, B. Jeyadevan, K. Tohji, M. Tsunoda, Journal of applied physics., 93 (10) (2003) 6856-6858.
- 71. S. Labus, A. Malecki, R. Gajerski, Journal of thermal analysis and calorimetry., 74 (1) (2003) 13-20.
- 72. P. B. Mirkarimi, K. F. McCarty, D. L. Medlin, Materials Science and Engineering., 21 (1997) 47-100.
- 73. A. Mujica, A. Rubio, A. Muñoz, R. J. Needs, Reviews of Modern Physics., 75 (2003) 863-912.
- 74. L. Li, Q. Zhen, R. Li, International Journal of Minerals, Metallurgy, and Materials., 22 (3) (2015) 319-324.
- 75. T. Jiang, W. I. Odnevall, G. Herting, and chromium nitride powders compared with chromium metal in synthetic biological solutions, ISRN Corrosion 2012.
- 76. R. Michalsky, P. H. Pfromm, Solar Energy., 85 (11) (2011) 2642-2654.
- 77. M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, Rouquerol, K. S. W. Sing, Pure and Applied Chemistry 87 (9-10) (2015) 1051-1069.
- 78. S. J. Gregg, K. S. W. Sing, H. W. Salzberg, Journal of The Electrochemical Society., 114 (11) (1967) 279C-279C.

79. K. S. W. Sing, R. T. Williams, Adsorption Science & Technology., 22 (10) (2004) 773-782.

**Сажетак:** Механохемијска синтеза хексагоналног хром нитрида ( $\beta$ -Cr<sub>2</sub>N) је истражена високо-енергетским млевењем Cr и h-BN. Почетак формирања  $\beta$ -Cr<sub>2</sub>N је примећен након 20 тіп млевења, иако је целокупна реакција завршена после 100 тіп. Проучавана су два различита молска односа 1Cr:1BN и 2Cr:1BN, и закључено је да молски односи имају кључну улогу у финалним продуктима механохемијске реакције. Продукти су испитивани уз XRD, FTIR и Раман спектроскопију, термијске анализе (TGA и DSC), SEM, и специфичну површину (BET). Направљена је пелиминарна мапа стабилности фаза у функцији акумулативне енергије ( $\Delta E_{vaccum}$ ). The Aкумулативна енергија потребна за комплетирање реакције формирања  $\beta$ -Cr<sub>2</sub>N је  $\Delta E_{vaccum} > 720$  kJ/g. **Кључне речи**:  $\beta$ -Cr<sub>2</sub>N фаза, хром нитрид, високо-енергетско млевење, акумулативна енергија.

© 2022 Authors. Published by association for ETRAN Society. This article is an open access article distributed under the terms and conditions of the Creative Commons — Attribution 4.0 International license (<u>https://creativecommons.org/licenses/by/4.0/</u>).

