Effect of ball to powder ratio on the mechanosynthesis of Re_2C and its compressibility

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Abstract

The mechanosynthesis of hexagonal rhenium carbide (Re_2C) from the elements is explored as a function of the balls to powder ratio (BPR). Burgios's equation has been used to calculate the accumulated energy (ΔE_{accum}) and the transferred energy per hit (ΔE_b). To get the complete mechanosynthesis of Re_2C several con-

ditions have to be met: BPR > 115:1, $\Delta E_{accum} > 500 \frac{kJ}{g}$, and $\Delta E_b > 2.656 \times 10^{-14}$ kJ. The reaction is completed after 30 min of milling if a BPR of 230:1 is used. The pressure dependence of the unit-cell volume and the lattice parameters have been evaluated by synchrotron radiation diffraction using a diamond anvil cell up to 61(2) GPa. A fit of a 2^{nd}-order Birch-Murnaghan equation of state results in a bulk modulus of $B_0 = 374(3)$ GPa.

Key words: rhenium carbide, high-energy ball-milling, compressibility, metastable phase, accumulated energy

1 Introduction

It was well accepted until very recently that rhenium does not form stoichiometric carbides at ambient pressure and the phase diagram of the system Re-C shows limited solubility of carbon into rhenium only (Hughes 1959, Kharkova and Velikanova 1987). The earliest reports of the formation of rhenium carbide at high pressure were from Popova et al. (Popova and Boiko 1971, Popova et al. 1972, Popova 1975). They reported the formation of a hexagonal ReC phase above 6 GPa and 1073 K (Popova and Boiko 1971) and a cubic ReC phase above 17 GPa and 1300 K (Popova et al. 1972, Popova 1975). All observations were based on quenched samples at ambient conditions and no further structural details were given. The cell parameters of the hexagonal polymorph were later confirmed by Kharkova and Velikanova on quenched samples (Kharkova and Velikanova 1987), but no further synthesis of cubic ReC has been reported.

Juarez-Arellano et al. (2008; 2009) performed systematic in-situ synchrotron based high-(p,T) studies up to around 70 GPa and 4000 K searching for the cubic polymorph and explored the (p,T)-conditions leading to the formation of

the hexagonal phase. They were unable to synthesize a cubic polymorph and concluded that the hexagonal polymorph is the only phase formed between 10-70 GPa and 1000-4000 K. They also showed that the composition of the hexagonal rhenium carbide phase is always close to Re_2C and that the bulk modulus is B_0 = 379(30) GPa (B′=5.5). It was demonstrated later by Raman spectroscopy that the Re_2C phase has a ReB_2-type crystal structure (Zhao et al. 2010, Friedrich et al. 2012).

Zhao et al. (2010) reported that the Re_2C phase could be partially obtained at 2 GPa and ~1600 K using a cubic-anvil press (Zhao et al. 2010). Below that pressure and temperature the reaction does not occur. They also reported that in order to complete the reaction at least 4 GPa and ~2000 K are needed. Due to the large volume of the sample obtained in the cubic-anvil press, Zhao et al. (2010) could also determine the hardness of Re_2C (H_v = 17.5 GPa). This hardness value shows that Re_2C is a hard material according to Kanyanta (2016) classification. Yasui et al. (2015) synthesized Re_2C from rhenium and home-made amorphous carbon nitride at 10 GPa and 1500 K using a multi-anvil press. They confirmed the hardness value previously reported (H_v = 15.9(7) GPa) and measured the pressure dependence of the unit-cell volume from a quenched sample up to 30 GPa (B_0 = 386(10) GPa). However, due to the lack of hydrostatic conditions, Yasui et al. (2015) reported a peculiar compression behaviour above 10 GPa.

Granados-Fitch et al. (2016) reported for the first time the synthesis of Re_2C at ambient pressure after 640 min of high-energy ball-milling (Granados-Fitch et al. 2016). They also demonstrated that Re_2C is chemically more stable at ambient conditions than WC and that Re_2C could be used also as a catalyst for H_2 production from biomass (Granados-Fitch et al. 2019a;b).

The successful mechanosynthesis opens the possibilities for future Re_2C industrial applications as a refractory compound with a very low compressibility and high hardness. However, the mechanosynthesis conditions need to be further explored in order to reduce the milling time needed to obtain the Re_2C. Thus, if the goal is to obtain the compound at shorter milling times, then increasing the ball-mill energy is the obvious step. Nevertheless, this can be achieved in many ways due to the large number of possible variables in a high-energy ball-mill. Changing the energy as a function of just one variable can be done by increasing the milling speed or changing the balls to powder ratio (BPR). Increasing the milling speed increases the wear of the milling tools (grinding medium and container), which could also lead to an increase of sample contamination. The powder yield may also decrease if the powder gets stuck to the inner walls of the milling container due to increase in the cold welding caused by the higher degree of plastic deformation (Suryanarayana 2004). Thus, changing the balls to powder ratio (BPR), decreasing the powder mass, has been chosen as a variable in this study.

Therefore, in the present study, the balls to powder ratio (BPR) in the mechanosynthesis of Re_2C is explored. Also, the model proposed by Burgio et al. (1990) is used to predict the accumulated energy needed for the mechanosynthesis of Re_2C. A correlation between the accumulated energy at different milling conditions and the phase formation has been constructed. Finally, in order to compare the compression behavior of milled samples with in-situ and quenched high-(p,T) synthesized samples, the equation of state of Re_2C obtained by mechanosynthesis has been obtained up to a pressure of 61(2) GPa.

2 Experimental

2.1 High-Energy Ball-Milling

Granados-Fitch et al. (2016) did not used a fix BPR. They started with 5 g of powder (Re+C) but 1 g of sample was removed from the vial at 40, 80, 160, 320 and 640 min to evaluate the evolution of the reaction. Therefore, from 0-40 min they used a BPR of 23:1, from 40-80 min 29:1, from 80-160 min 38:1, from 160-360 min 65:1, and from 320-640 115:1. In this study, in order to change the energy delivered by the mill different fix BPR were used (33:1, 115:1, 153:1 and 230:1) changing the Re-C powder mass: 3.5, 1, 0.75 and 0.5 g, respectively. Rhenium (Sigma-Aldrich, 99.995%) and carbon (graphite, Sigma-Aldrich, <20 μm) powders in molar ratio of 2:1 were homogenized in an agate mortar. High-energy ball-milling was carried out in hermetically sealed vials in a planetary ball-mill (Pulverisette 7 premium line, Fritsch). WC vials (80 ml) and WC milling balls (15 of 1 cm of diameter) were used. A rotation rate of 600 rpm and different milling times were used. The temperature during milling was not measured, but the vials could be touched directly after milling. In order to avoid overheating the milling was done in cycles of 5 min milling and 15 min pause for cooling.

2.2 Characterization

The evolution of the reaction on the thermally treated pellets has been followed by X-ray diffraction. X-ray powder diffraction (XRPD) patterns were collected in air and at ambient temperature in a Bruker D-8 Advance diffractometer with $CuK_{\alpha 1}K_{\alpha 2}$ radiation. Sodium iodide (NaI) scintillation detector and flat

polymer sample holder were used. The 2θ-interval explored was 10° - 90° with 0.05° step size, 10s counting time, continuous mode and spinning of 15 rpm. The Le Bail fits and Rietveld refinement have been performed using the program FULLPROF (Rodriguez-Carvajal 1993). A linear interpolation between approximately 30 manually selected points for the background and a pseudo-Voigt profile function have been used.

2.3 Mathematical Model

The mechanical milling process in a high-energy ball-mill depends on many variables such as the density of the grinding material, the number and the size of the balls, the grinding speed, the grinding time, the balls to powder ratio, the atmosphere used, etc. Therefore, the optimization of a high-energy ball-milling synthesis requires a large number of experiments. Several mathematical models have been reported to describe the high-energy ball-milling process. Among those, Burgio et al. (1990) reported a simple kinematic model, which considers the role of the geometrical parameters of the mill and the vial, the ball diameter, or diameters ratio between the main disk and the vial. Further information can be found elsewhere (Martinez-Garcia et al. 2015).

In Burgio's model the transferred energy is calculated using an estimate of the total energy released by the balls during collision. This energy is given by the kinetic energy of the balls during the launch and the energy after the impact. The transferred energy for one ball in one impact (ΔE_b) is calculated according to Burgio's equation (Burgio et al. 1990) (equation 1).

$$\Delta E_b = -\frac{\pi \rho_b d_b^3 W_d^2}{24}\left(\frac{D_v - d_b + R_T^2 D_d}{R_T^2}\right)\left(\frac{D_v - d_b}{R_T}\right) \quad (1)$$

Equation 1 considers the density of the milling material (ρ_b: ball and vial), the ball diameter (d_b), the speed of the ball mill main disk (W_d), the vial diameter (D_v), the main disk diameter (D_d), and the transmission ratio between the main disk W_d and the vial W_v and (R_T).

The transferred energy for one ball in one impact (ΔE_b) depends of the free space in the vial. Therefore, a factor (φ_b) is used to describe the degree of filling. A value of "0" represents a completely filled vial with balls (no movement is possible) and a value of "1" represents just one ball in motion. The degree of filling (φ_b) is calculated according to equation 2 based on considerations proposed by Ghayour et al. (2016).

$$\varphi_b = \frac{\frac{1}{6}\pi N_b d_b^3 + \frac{m_s}{\rho_s}}{\pi r_v^2 H_v}\Bigg) \quad (2)$$

The degree of filling (φ_b) depends of the number of balls used (N_b), the ball diameter (d_b), the sample mass (m_s), the sample density (ρ_s), the vial radius (r_v) and the vial height (H_v). Because in this study the initial Re-C powder mass is changed then the value of the degree of filling is also changing. i.e. a BPR of 33:1 (φ_b=0.8960), 115:1 (φ_b=0.8978), 153:1 (φ_b=0.8980), 230:1 (φ_b=0.8982). But because the values are so similar then the average value was used for all the calculations (φ_b=0.897(1)),

The total transferred energy from the mill to the system during collisions is the accumulated energy due to the numerous impacts to the sample. Therefore, the accumulated energy (E_{accum}) during milling can be calculated according to equation 3.

$$\Delta E_{accum} = \left[\left(-\frac{\pi\varphi_b K N_b d_b^3}{24}\right)\left(1-\frac{1}{R_T}\right)\left(\frac{D_v - d_b + R_T^2 D_d}{R_T^2}\right)\left(\frac{D_v - d_b}{R_T}\right)\right]\frac{\rho_b W_d^3 t}{m_s} \tag{3}$$

K is a constant that accounts for the elasticity of collisions, a value of 1 represents perfectly inelastic collisions. Normally K is considered equal to 1.5 (Ghayour et al. 2016, Gotor et al. 2013). The parameters used in equation 3 are: φ_b = 0.897, K = 1.5, N_b = 15, d_b = 0.01 m, R_T = -0.5, D_v = 0.0462 m, D_d = 0.14 m, H_v= 0.0462 m, ρ_b=14.7 gcm^{-3} and t is the milling time in seconds. With these parameters, equation 3 can be simplified as a function of variables only that can be controlled and changed experimentally (equation 4).

$$\Delta E_{accum} = 3.93097 \times 10^{-14}\ \left.\frac{\rho_b W_d^3 t}{m_s}\right) \tag{4}$$

2.4 High-pressure synchrotron X-ray diffraction experiments

Powder diffraction pattern have been collected at the Extreme Conditions Beamline P02.2 at PETRA III synchrotron (DESY Photon Science, Hamburg, Germany). A mechanosynthesized Re_2C sample (115:1) was loaded into

Boehler-Almax type diamond anvil cell (DAC) for the high pressure experiments. Ne was employed as a pressure-transmitting medium. The pressure was determined using the ruby fluorescence method (Mao et al. 1978). The sample was placed in a hole of 110-130 μm in diameter, which had been drilled by a custom-built laser lathe in pre-indented Re gasket (40-50 μm in thickness). The diamond culets had a diameter of 300 μm and an opening angle of 48°. Diffraction patterns have been acquired using a wavelength of 0.2906 Å, a beam focused to 1.5×2.3 μm^2 full width at half maximum using Kirkpatrick-Baez mirrors and a PerkinElmer XRD1621 flat panel detector. The sample-to-detector distance of 391.07 mm was determined employing a CeO_2 reference sample. All the diffraction images were processed, corrected for distortion and integrated using FIT2D (Hammersley et al. 1996). Powder diffraction data were collected from ambient pressure up to 61(2) GPa. Lattice parameters have been obtained from Le Bail fits using FULLPROF (Rodriguez-Carvajal 1993). The bulk modulus was derived using the EoSFit7 program (Gonzalez-Platas et al. 2016).

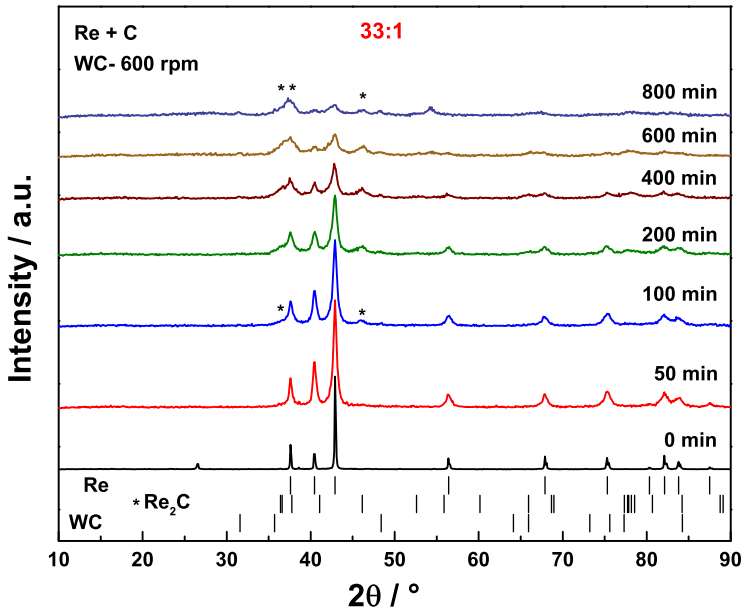
3 Results and Discussion

In this study, we started with a fix BPR of 33:1 (3.5g of Re-C powder). The X-ray diffraction patterns of the evolution of the mechanosynthesis of Re_2C is shown in Figure 1(a). At this BPR, the first signs of Re_2C formation could be observed after 100 min of milling. However, the reaction does not evolve with the milling time up to 800 min of milling. After 800 min of milling the small reflections of Re_2C starts to vanish, which may indicate amorphization. Some contamination due to the grinding material (WC) is observed after 400 min of milling. Using a BPR of 115:1 (1g of Re-C powder), Figure 1(b), the

reaction is completed after 200 min of milling. At this BPR the contamination is observed earlier (80 min of milling).

BPR of 153:1 (0.75g of Re-C powder) and 230:1 (0.5g of Re-C powder) have been also tested, Figure 2. The reaction using a BPR of 153:1 is completed at 45 min, while using a BPR of 230:1 the reaction is completed at 30 min. Contamination is observed at 45 min of milling using 153:1. No evidence for the presence of WC (grinding material) is observed using 230:1. Thus, the BPR has a significant effect on the time required to achieve the Re_2C reaction. Decreasing the milling time is decreasing the wear of the grinding medium and therefore less contamination is observed in the products.

(a)



(b)

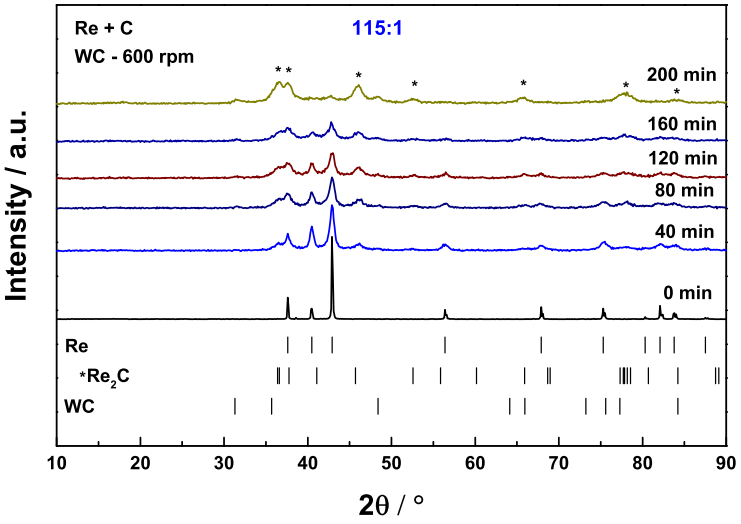
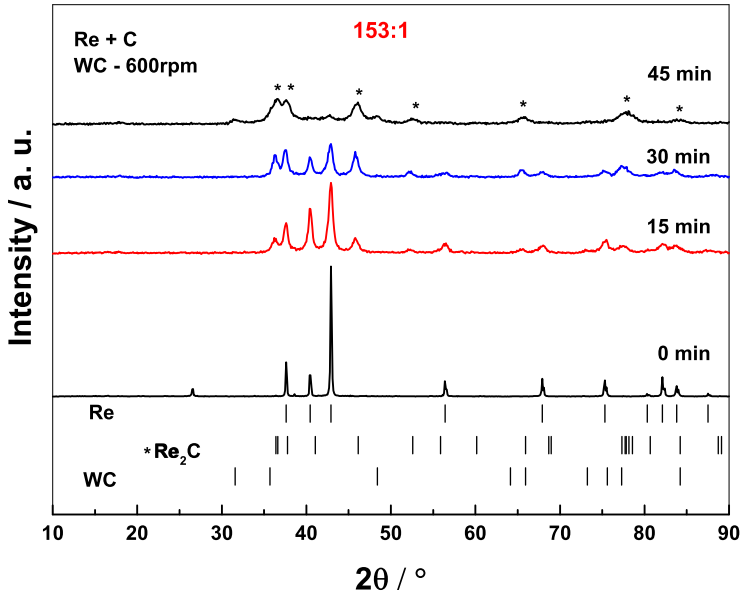


Fig. 1. Evolution of the mechanosynthesis of Re_2C using a ball to powder ratio (BPR) of 33:1 (a) and 115:1 (b). The tick marks are a guide to the eye to highlight the Re_2C reflections.

(a)



(b)

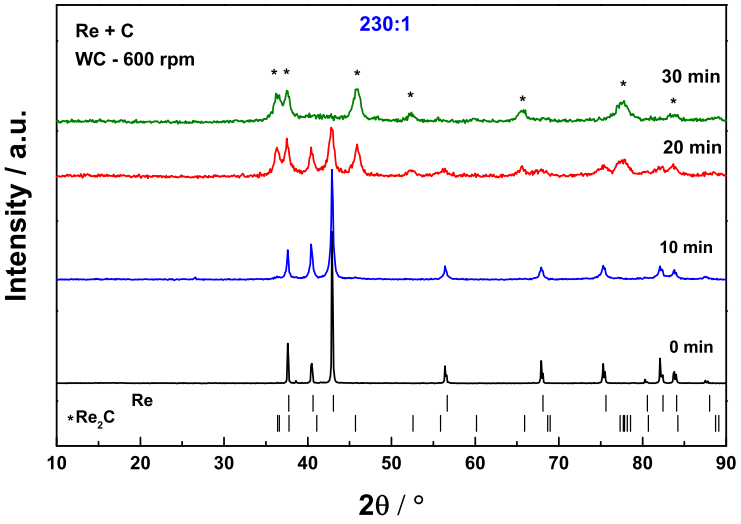


Fig. 2. Evolution of the mechanosynthesis of Re_2C using a ball to powder ratio (BPR) of 153:1 (a) and 230:1 (b). The tick marks are a guide to the eye to highlight the Re_2C reflections.

It has been reported that the higher the BPR, the shorter is the time required for the reaction (Suryanarayana 2004). This behavior is also observed in this study for the complete reaction of Re_2C using 115:1 (200 min), 153:1 (45 min) and 230:1 (30 min). However, at BPR of 33:1 only a partial reaction occurs. From Figures 1 and 2, it is clear that the end products strongly depend on the operative milling conditions and that they have a clear correlation with the input energy. Thus, in order to have an idea of the energy generated during the milling process the Burgios's equation (Burgio et al. 1990) has been used to calculate the accumulated energy (ΔE_{accum}), equation 3. A correlation between the accumulated energy (ΔE_{accum}) at different milling conditions and the phase formation is shown in Figure 3.

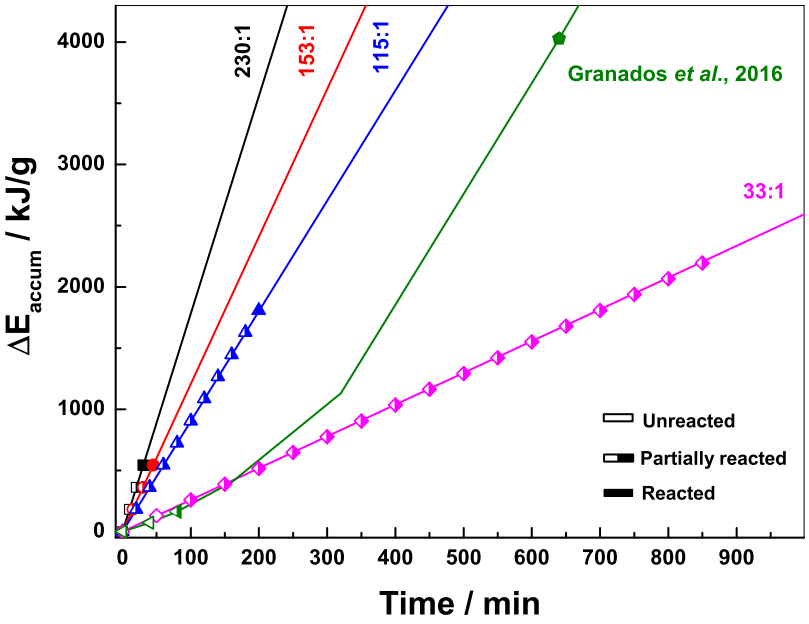


Fig. 3. Accumulated energy map (ΔE_{accum}) showing the mechanosynthesis conditions of Re_2C as a function of the balls to powder ratio (BPR). The ΔE_{accum} was calculated using the model reported by Burgio et al. (1990).

It can be seen in Figure 3 that the accumulated energy does not show a clear tendency regarding the formation of Re_2C. The model of Burgio et al. (1990) gives good approximations if only geometrical parameters of the mill and the vial are considered, as Martinez-Garcia et al. (2015) had shown. However, changing the sample mass, and therefore the BPR, could be affecting the degree of filling (φ_b) and the K constant that accounts for elastic collisions, equation 2. However, we have shown that φ_b does not change much if different sample mass is used. In order to evaluate the effect of K in Figure 4 is shown the transferred energy for one ball in one impact (ΔE_b) as a function of the balls to powder ratio (BPR). The ΔE_b does not consider K or φ_b, equation 1. The ΔE_b plot shows that in order to have complete reaction the transferred energy per hit has to be higher than 2.656×10^{-14} kJ (BPR above 115:1). Below that energy, the reaction is scarce. This tendency is clearly observed on Figures 1 and 2.

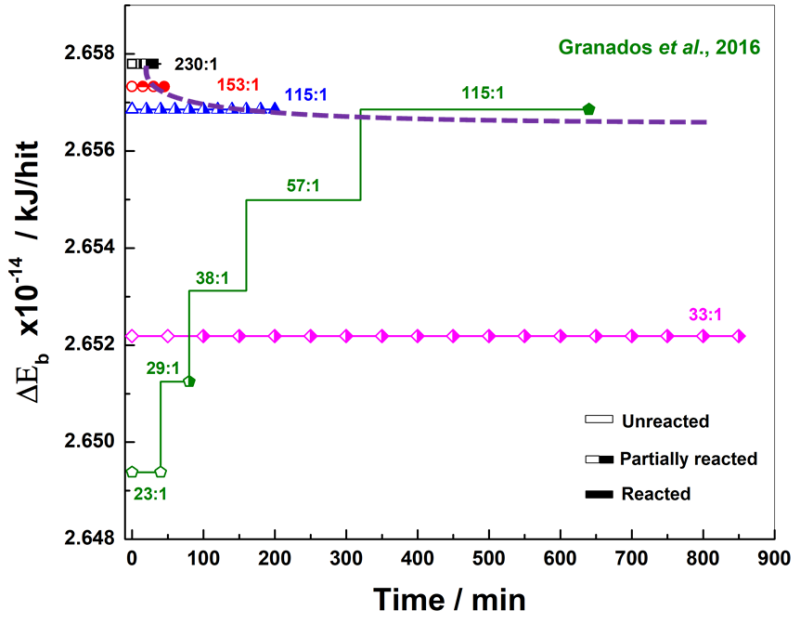


Fig. 4. Transferred energy for one ball in one impact (ΔE_b) as a function of the balls to powder ratio (BPR) during the mechanosynthesis of Re_2C. The ΔE_b was calculated using equation 1. The dot line is a guide to the eye.

The calculation of ΔE_b has shown that the determination of K needs to be modified in order to improve the calculation of accumulated energy when a change of sample mass is involved. Nevertheless, if the accumulated energy is plotted in the region where the BPR is above 115:1 then a clear tendency regarding the formation of Re_2C is observed, Figure 5. The critical or minimum energy to trigger the mechanosynthesis of Re_2C is ΔE_{accum} ~150 $\frac{kJ}{g}$. The coexistence of Re and Re_2C is observed between ΔE_{accum} ~ 150 - 500 $\frac{kJ}{g}$. The reaction of Re and C is complete if ΔE_{accum} > 500 $\frac{kJ}{g}$ (and if ΔE_b > 2.656×10^{-14} kJ).

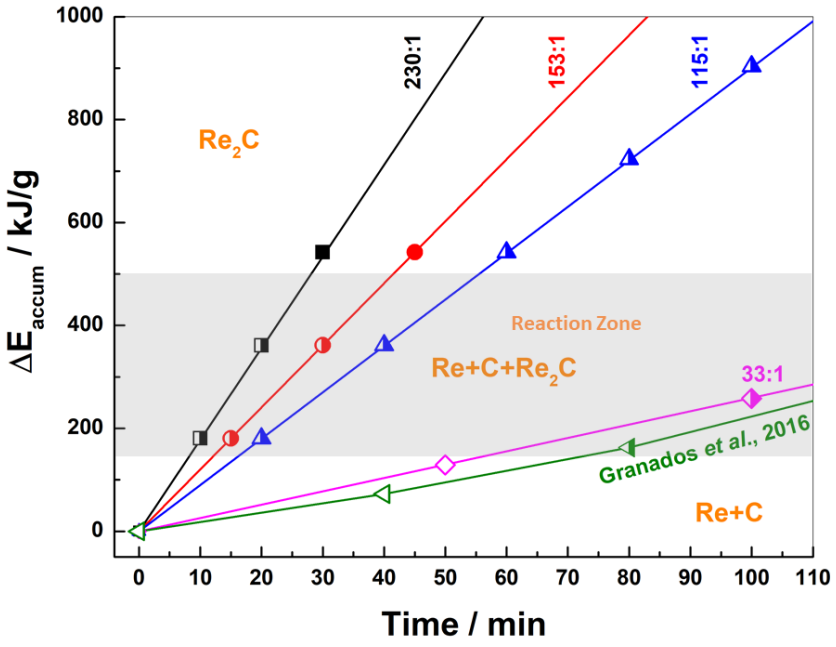


Fig. 5. Accumulated energy map (ΔE_{accum}) showing the mechanochemical synthesis conditions of Re_2C as a function of the balls to the powder ratio (BPR). The ΔE_{accum} was calculated using the model reported by Burgio et al. (1990).

The accumulated energy needed to complete the formation of Re_2C is very high if compare it with the energy needed to form MgO (ΔE_b~1.59 $\frac{kJ}{g}$, (Martinez-Garcia et al. 2015)). The transferred energy per hit is a very important parameter since it empirically defines whether the energy is enough to complete the reaction (Figure 2) or if it is mainly used to increase the strain-stress concentration through the cold welding and fracturing (Figure 1).

3.1 Re_2C: bulk and linear compressibility

There are two experimental reports on the compressibility of Re_2C performed with data from the synthesis at in-situ at high-(p,T) conditions (Juarez-Arellano et al. 2008; 2009) and one from a quenched sample (Yasui et al. 2015). The significant scatter in the in-situ data resulted in large uncertainties in the derived bulk modulus, while in the quenched sample the lack of hydrostatic conditions limited the derivation of the bulk modulus up to 10 GPa. Additionally, it is interesting to investigate the influence of ball-milling on the compressibility behavior of Re_2C. Since it is known that the cold working during high-energy ball-milling produce cold welding and fracturing, introducing defects as dislocations, vacancies and grain boundaries (Suryanarayana 2004). Those defects may produce strain hardening which may also affect the bulk modulus. Thus, in order to derive the bulk modulus from the mechanosynthesized Re_2C the BPR 115:1 sample was chosen due to the apparent higher strain-stress concentration (from the X-ray diffraction patterns, Figure 1) and to use WC (milling media) as internal standard.

Representative synchrotron X-ray powder diffraction patterns of Re_2C, obtained from mechanosynthesis, collected at different pressures are shown in

Figure 6.

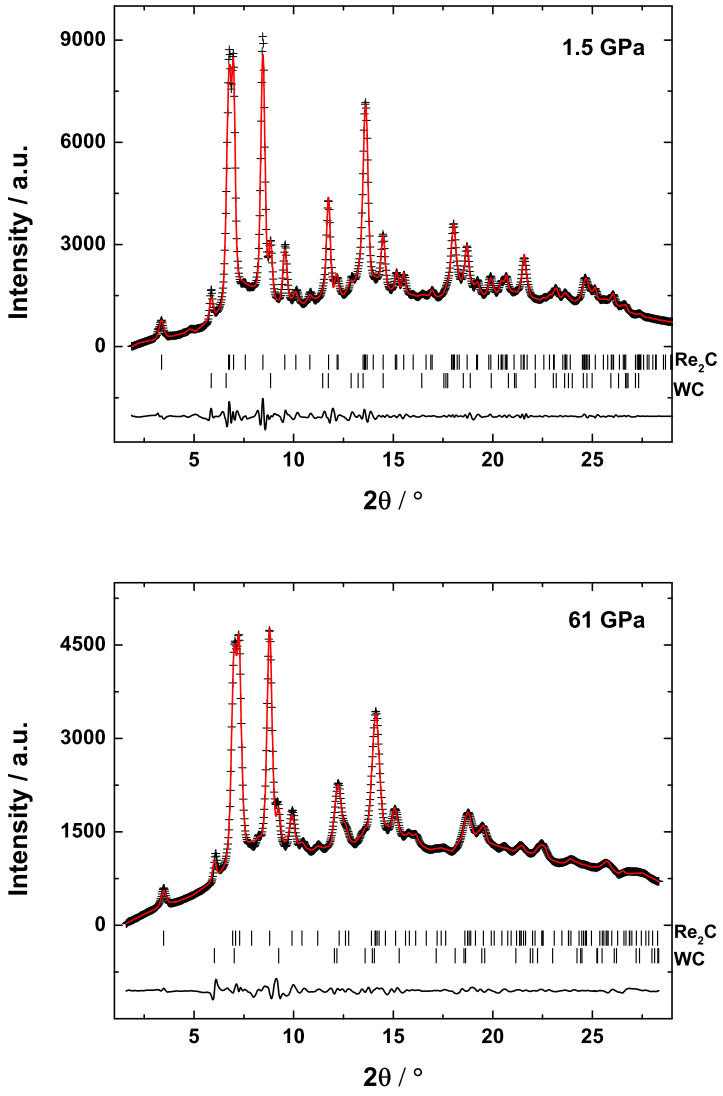


Fig. 6. Synchrotron X-ray powder diffraction patterns at different pressures, 1.5(1) and 61(2) GPa, of Re_2C obtained from mechanosynthesis.

The Re_2C equation of state has been obtained up to a pressure of 61(2) GPa. The bulk modulus and linear compressibility have been obtained from fits of 2^{nd}-order Birch-Murnaghan equations of state to the experimental data. The results are given in Figure 7 and Table 1. This experiment confirms that the

peculiar compression behavior above 10 GPa reported by Yasui et al. (2015) is because the lost of hydrostatic conditions due to the use of 4:1 methanol-ethanol mixture as a pressure transmitting medium. Thus, no structural phase transition or peculiar compression behavior has been observed upon pressure increase up to 61(2) GPa.

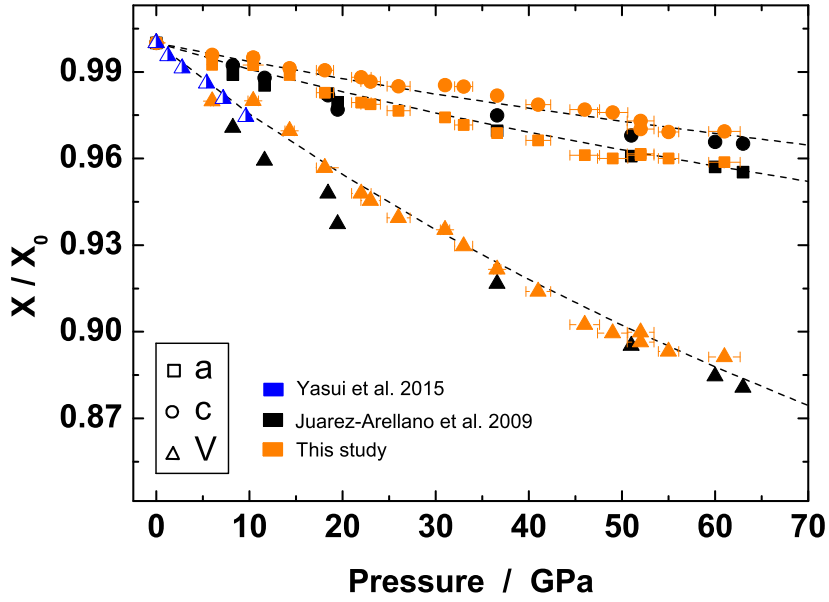


Fig. 7. Experimental pressure dependence of mechanosynthesized (115:1) Re_2C lattice parameters up to 61(2) GPa, as well as fittings of 2nd-order Birch-Murnaghan equations of state. Black solid symbols represent experimental data from Juarez-Arellano et al. (2009). Blue symbols represent experimental data from Yasui et al. (2015).

The bulk modulus of WC obtained in this study (B_0 = 357(14)), and which is used as internal standard, agrees to what is reported (329-435 GPa Friedrich et al. (2011)). The bulk modulus obtained in this study for Re_2C (B_0 = 374(3) GPa) agrees with the values obtained from the quenched sample and from previous DFT results (Juarez-Arellano et al. 2009, Zhao et al. 2010, Yasui

et al. 2015) (Table 1). This result shows that the cold working and defects generated during high-energy ball-milling do not have a significant effect in the compression behavior of the mechanosynthesized compound.

The compression behavior of the lattice parameters of Re_2C is also shown in Figure 7 and Table 1. The a-axis is more compressible than in previous reports (Table 1). However, what is confirmed is that Re_2C along the c-axis is significantly less compressible than the a-axis. This behavior is associated to the AABB stacking sequence of Re_2C crystal structure, Figure 8.

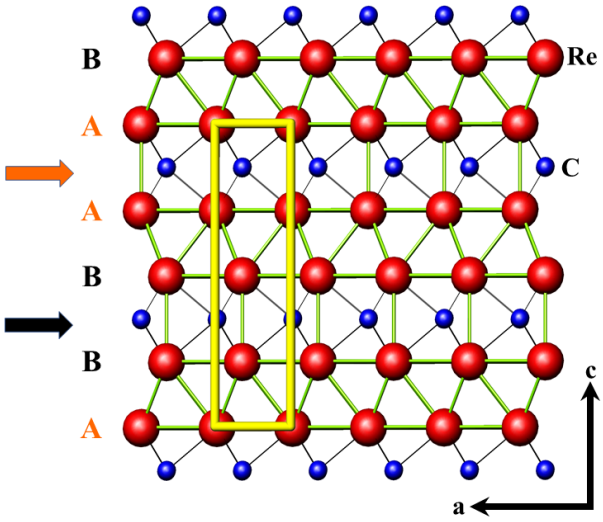


Fig. 8. AABB stacking sequence of Re_2C crystal structure.

Table 1
Bulk modulus and linear compressibilities obtained from fits of 2nd-order Birch-Murnaghan equations of state to the experimental data of Re_2C obtained by mechanosynthesis.

	V_0 / Å^3	B_0 / GPa	χ^2
Exp - Mechanosynthesis [a]	69.250(3)	374(3)	1.7
Exp - High-(p,T) synthesis [b]	68.4(4)	423(30)	26.4
Exp - Quenched Sample [c]	68.9	386(10)	-
Theory - DFT [d]	70.75(9)	385(3)	1.1
Theory - DFT [e]	70.84	378(1)	-
Theory - DFT [f]	-	388.9	-
	a_0 / Å	B_{a0} / GPa	χ^2
Exp - Mechanosynthesis [a]	2.8433(8)	331(6)	3.2
Exp - High-(p,T) synthesis [b]	2.835(4)	372(18)	9.3
Theo - DFT [e]	2.8478(1)	349(3)	1.2
	c_0 / Å	B_{c0} / GPa	χ^2
Exp - Mechanosynthesis [a]	9.875(1)	540(9)	2.8
Exp - High-(p,T) synthesis [b]	9.85(4)	521(90)	17.7
Theo - DFT [e]	10.0731(1)	484(3)	1.2

[a] From sample obtained by mechanosynthesis at ambient pressure using a BPR of 115:1 (this study).

[b] From in-situ high(p,T) synthesis experiments (Juarez-Arellano et al. 2009).

[c] From quenched sample from multi-anvil press experiment (Yasui et al. 2015).

[d] From a 3rd-order BM-EOS fit to DFT results reported in (Juarez-Arellano et al. 2009), $B' = 4.6(7)$, $B'_{a0} = 4.26(8)$, $B'_{c0} = 5.50(9)$.

[e] Derived from the elastic stiffness coefficients reported in Juarez-Arellano et al. (2008).

[f] Derived from the elastic stiffness coefficients reported in Zhao et al. (2010).

Based on the results obtained in this study, in Figure 9 is shown a schematic

representation of the mechanosynthesis of Re_2C in terms of milling time, ball to powder ratio, accumulative energy and phase stability.

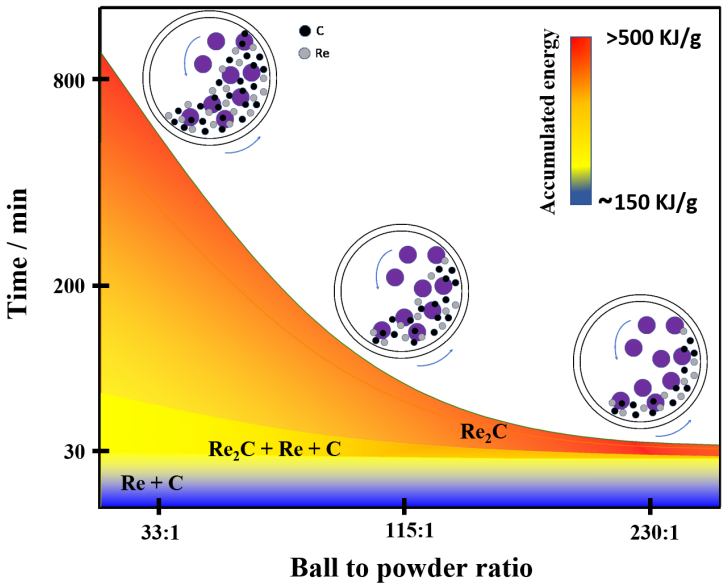


Fig. 9. Schematic representation of the mechanosynthesis conditions of Re_2C.

4 Conclusions

Based on the accumulated energy, the mechanosynthesis conditions to obtain Re_2C can be set experimentally. The balls to powder ratio (BPR) has a significant effect on the time required to achieve the formation of Re_2C. At higher BPR less wear of the grinding medium is observed and therefore less contamination in the products. The bulk modulus of Re_2C obtained by mechanosynthesis is similar to the bulk modulus of Re_2C obtained in-situ at high-(p,T) conditions or in quenched samples. Our results shows that Re_2C can be synthesized at ambient pressure, at large quantities, at short times and having the same compression behavior than quenched samples from high-(p,T) conditions.

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Effect of ball to powder ratio on the mechanosynthesis of Re_2C and its compressibility

Highlights

Increment on the ball to powder ratio (BPR) reduces the mechanosynthesis time of Re_2C.

Mechanosynthesis of Re_2C was obtained at BFR of 230:1, 30 min of milling, accumulated energy $> 500\ \frac{kJ}{g}$ and transferred energy $> 2.656\times10^{-14}$ kJ.

Cold working and defects generated during high-energy ball-milling do not have a significant effect in bulk modulus of Re_2C.