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Pressureless ultrafast sintering of near-net-shaped superhard isotropic B_4C/rGO composites with Ti-Al additives

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Abstract

Superhard composites of B_4C reinforced with randomly-oriented reduced graphene oxide (rGO) nanoplatelets are manufactured by a near-net-shape fabrication route based on three successive steps. Firstly, aqueous colloidal processing is used for the environmentally-friendly preparation of a semi-concentrated multi-component slurry (B_4C as main component, Ti-Al as sintering additive, and rGO as toughening reinforcement), whose suitability for wet shaping is demonstrated by rheological measurements. Secondly, slip casting is used to produce robust green parts with shapes on demand and microstructures free of macro- and micro-defects. And thirdly, pressureless spark-plasma sintering (PSPS) is used for the ultrafast and energy-efficient densification of the green parts with shape retention. Measurements of shrinkage and hardness, as well as the microstructural observations, are used to identify suitable PSPS temperatures leading to obtaining isotropic B_4C/rGO composites that are superhard and almost twice as tough as the monolithic B_4C ceramics.

Keywords: B_4C ; aqueous colloidal processing; slip casting; pressureless spark-plasma sintering; mechanical properties.

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1. Introduction

There has been growing interest lately in reinforcing the microstructure of the otherwise brittle polycrystalline ceramics with graphene-like nanoplatelets (GNPs) to thus improve their low fracture toughness by crack-bridging mechanisms [1-8]. (The term GNPs is imprecise, and includes nanoplatelets of graphene oxide (GO), of partially reduced graphene oxide (prGO), and of reduced graphene oxide (rGO), but not of graphite. Also, they are multi-layer, not single-layer, two-dimensional materials.) Rather than carbon nanotubes (CNTs), GNPs are currently preferable as reinforcements because their two-dimensional nature makes them in principle more effective in bridging cracks [9], and they are also more easily dispersible in ceramic matrices [8,10]. This interest includes monolithic B₄C ceramics which are very brittle, and have, regardless of the grain size, a low fracture toughness of only ~2 MPa· m^{1/2} [11] that can compromise their mechanical integrity in service thus limiting in practice their great potential as superhard materials. Unsurprisingly, to make them less susceptible to failure, B₄C/GNP composites, often B₄C/rGO composites, are being fabricated by spark-plasma sintering (SPS) or hot pressing (HP) [12-21]. The former is preferable over the latter because ultrafast sintering avoids the more than likely graphitization of the GNPs under prolonged exposure to high temperatures.

Interestingly, B₄C/GNP composites can have either orthotropic or isotropic microstructures [12-21] depending on whether during sintering the GNP reinforcements align perpendicularly to the pressing direction or remain randomly oriented. The microstructural design, fortuitous or not, nonetheless conditions the mechanical performance because the orthotropic composites exhibit a pronouncedly rising *R*-curve [22], indicative of marked toughening, in the direction perpendicular to the GNP reinforcements but with no toughening in

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4 the direction parallel to them, whilst the isotropic composites exhibit a relatively shallow *R*-curve
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6 [22], indicative of moderate toughening, in any direction. Therefore, the orthotropic B₄C/GNP
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8 composites will perform especially well in those structural applications under uniaxial loading
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10 where the cracks, once nucleated, are forced to propagate perpendicularly to the GNPs, but badly
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12 under multi-axial loading where cracks can propagate in any direction. In this last scenario,
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14 isotropic B₄C/GNP composites are doubtless much more recommendable.
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19 Another handicap of the orthotropic B₄C/GNP composites is that they have little capacity
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21 to meet the demand for parts with ever more complex geometries required by industry because
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23 the preferential alignment of the GNPs is achieved thanks to the application of uniaxial pressure
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25 during sintering. This fabrication procedure limits the geometry of the parts fabricated to just
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27 simple shapes, and the fact is that the extensive post-sintering machining and finishing
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29 operations on B₄C-based materials are prohibitively expensive and time-consuming, not to say
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31 completely inviable in most cases. Unlike the orthotropic B₄C/GNPs composites, the fabrication
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33 of isotropic B₄C/GNPs composites does not require the application of pressure, and therefore, in
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35 principle, they are amenable to near-net-shape manufacturing. In particular, isotropic B₄C/GNP
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37 composites could first be shaped into geometrically-complex parts by wet-forming techniques,
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39 and then these green parts densified by pressureless SPS (PSPS). This last ensures ultrafast
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41 densification, and also the preservation of both the external shape given to the piece during
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43 casting and its isotropic microstructure. However, pressureless densification of B₄C constitutes
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45 another challenge to its poor sinterability [23,24], both intrinsic (strong covalent bonding and
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47 low self-diffusion coefficients imposing serious kinetics restrictions) and extrinsic (oxidic
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49 impurities favouring microstructural coarsening over densification). To promote the pressureless
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51 densification of B₄C, sintering additives are required, and those forming transient liquid phases
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4 are currently gaining in interest [25-29].
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7 The present study was aimed in this direction, and was undertaken to explore the possible
8 processability of superhard isotropic B₄C/rGO composites with shape on demand by combining
9 aqueous slip casting for the environmentally-friendly preparation of green parts with the desired
10 geometry, and PSPS with Ti-Al transient liquid-phase additives [25-27] for their ultrafast and
11 energy-efficient densification. The study is thus aimed at contributing towards the near-net-shape
12 manufacture of advanced B₄C composites for engineering applications.
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23 **2. Experimental Procedure**

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27 Ceramic slurries were prepared by aqueous colloidal processing, using de-ionized water
28 as dispersant, commercial powders of B₄C ($d_{50} \sim 0.7 \mu\text{m}$; Grade HD 20, H.C. Starck, Germany),
29 Ti-Al ($d_{50} \sim 38 \mu\text{m}$; 22895, Alfa Aesar, Germany), and prGO (5 μm diameter and 2 nm thickness;
30 2.1, Abalonyx AS, Norway) as solids, and a commercial polyethylenimine (PEI; MW $\sim 25\ 000$;
31 Sigma-Aldrich, USA) as deflocculant. The B₄C, Ti-Al, and prGO powders were used as-
32 received, while PEI was used diluted to 20 vol.% in de-ionized water. Also note that prGO will
33 further reduce to rGO in situ during ultrafast sintering [21]. The slurry was formulated to a total
34 solids loading of 20 vol.%, and was designed to yield B₄C composites with 4.9 vol.% Ti-Al and
35 2 vol.% rGO (implying a composition in wt.% of 89.82B₄C+7.08Ti-Al+3.10prGO).
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49 The slurries were prepared under continuous mechanical agitation with helices at 310
50 rpm, according to the following recipe for 100 ml optimized in an earlier study [21]. First, 0.49
51 ml of diluted PEI were added to 74.44 ml of de-ionized water to deflocculate the prGO powder,
52 and 1 min later 1.63 g of prGO powder was gradually incorporated. (This amount of prGO takes
53 into account that the present prGO loses ~ 42.49 wt.% when reducing to rGO in situ during SPS
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4 [21].) After 5 min, 5.07 ml of diluted PEI was added to deflocculate both the Ti-Al and the B₄C
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6 powders; 1 min later 3.71 g of Ti-Al was introduced; and 15 min later 46.95 g of B₄C was
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8 gradually added. The slurry's pH was then adjusted to 7 (i.e., to neutral pH). Finally, after a
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10 further 30 min, the slurry was sonicated (UP-400S, Hielscher Ultrasonics GmbH, Germany) with
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12 pulses of 240 W (0.5 s of power discharge and 0.5 s of pause) for 2 min. The resulting slurry was
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14 then characterized rheologically to measure its viscosity, using a rheometer (MARS, Haake,
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16 Thermo, Germany) configured in the double cone-plate geometry and operated in controlled
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18 shear rate mode.
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24 Next, the slurry was slip cast in bottomless plastic moulds (greased with wax) of
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26 cylindrical shape placed on top of a permeable, flat, plaster-of-Paris plate to obtain compact
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28 discs, which were allowed to dry in air at room temperature for 48 h within the moulds. Their
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30 green microstructure was then examined by scanning electron microscopy (SEM; Quanta 3D,
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32 FEI, The Netherlands) on fracture surfaces. The green discs were cold isostatically pressed at
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34 150 MPa, and measured carefully to evaluate their dimensions. Note that isostatic pressing does
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36 not cause shape distortion, and promotes a greater green compaction that is essential for B₄C
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38 pieces to densify satisfactorily, as has been demonstrated elsewhere [30]. Lastly, as shown in Fig.
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43 **1**, the isostatically-pressed green discs were individually loaded into a special graphite die
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45 designed to avoid load application, which is lined with graphite foil and covered by a graphite
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47 **felt**, and were PSPS-ed (HP-D-10, FCT Systeme GmbH, Germany) in a dynamic-vacuum
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49 atmosphere at 1900°C, 1950°C, 2000°C, 2050°C, and 2100°C (as measured using an axial
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51 optical pyrometer) for 5 min, under 100°C/min heating. Higher sintering temperatures were not
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53 used to prevent damage of the SPS furnace. The sintered discs were re-measured to evaluate the
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55 degree of shrinkage occurring during sintering, and were characterized microstructurally by SEM
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4 on fracture surfaces and mechanically by Vickers indentation (MV-1, Matsuzawa, Japan) under
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7 9.8 N load on polished surfaces.
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10 11 **3. Results and Discussion** 12 13

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15 **Figure 2** shows the viscosity curve (i.e., viscosity vs shear rate) of the optimal slurry of
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17 B₄C+Ti-Al+prGO prepared by aqueous colloidal processing as explained above, demonstrating
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19 that it has the fluidity required for slip casting. Clearly, it can be seen that this slurry has the
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21 desired shear-thinning rheological behaviour with little thixotropy, exhibiting a high
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23 (exponentially-increasing) viscosity under rest conditions that avoids particle settling during both
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25 its storage and its casting, but a much lower viscosity under flow conditions that facilitates its
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27 pumping and the mould filling [31-33]. Indeed, it is widely agreed that for a slurry to be well-
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29 suited for slip casting operations it has to have a viscosity lower than ~1 Pa·s at a shear rate of
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31 100 s⁻¹ because otherwise it cannot be poured appropriately [34]. As can be seen in **Fig. 2**, the
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33 slurry of B₄C+Ti-Al+prGO prepared in this study amply meets that requirement, with its
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35 viscosity at 100 s⁻¹ of ~0.04 Pa·s being two orders of magnitude lower than the recommended
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37 upper limit [34]. The visual observation also shown in **Fig. 2** confirmed that this slurry is indeed
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39 very fluid, which is also indicative that it has the sought-for good dispersion of the B₄C, Ti-Al,
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41 and prGO.
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49 **Figure 3** shows optical photographs of the green parts obtained by pouring the slurry into
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51 cylindrical moulds without external suction, followed by drying in air at room temperature for 48
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53 h. Most were disc-shaped because this morphology facilitates the subsequent measurement of the
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55 shrinkages occurring during sintering. Clearly, these images confirm the expectation that the
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57 slurry prepared here to a total solids loading of 20 vol.% is very suitable for the slip casting of
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4 green parts with the desired geometry as dictated simply by the mould design. Note that, for slip
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6 casting, concentrated slurries with high total solids loadings are not required, but that, what are
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8 needed are only semi-concentrated slurries with moderate total solids loadings. This is because in
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10 slip casting, unlike other direct forming techniques, the stages of shaping, consolidation, and
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12 drying take place concurrently since draining occurs by filtration in the permeable mould, and
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14 the lower viscosity of the moderately concentrated slurries is very beneficial for making complex
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16 parts. Also importantly, the inspection and control of the green discs indicated that (i) they had
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18 no external macro-defects (cracks, surface voids, colour changes, swelling, etc.), (ii) they were
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20 robust, (iii) they had good handling and storage characteristics, and (iv) they were trimmable in
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22 dry conditions.
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28 **Figure 4** shows an SEM image representative of the fracture surface of the as-cast
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30 compacts (prior to isostatic pressing) in which it can be seen that they have a uniform green
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32 microstructure with both a homogeneous distribution and good packing of particles as well as no
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34 internal macro-defects (large cracks, voids, etc.) or micro-defects (large pores, particle size
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36 segregation, small cracks, laminations, packing gradients, etc.). Interestingly, the green
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38 microstructures show fine Ti-Al particles here and there (brighter particles), whose maximum
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40 size of only a few microns is much less than the ~38 μm of the starting Ti-Al particles, indicative
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42 that the 2 min of sonication applied during the aqueous colloidal processing of the slurry broke
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44 up the large starting Ti-Al agglomerates. Sonication also seems to have re-exfoliated the prGO
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46 platelets, making them, in general, thinner and shorter than the flaky starting prGO platelets.
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48 Thus, the green microstructures have the desired better dispersion of the Ti-Al sintering additive
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50 and prGO reinforcements between the B_4C particles, which should doubtless be beneficial for the
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52 pressureless sinterability of $\text{B}_4\text{C}/\text{rGO}$ composites with uniform isotropic microstructures.
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4 **Figure 5** shows the linear and volume shrinkages that occurred during sintering relative to
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6 the isostatically-pressed green discs (which have a relative density of ~61%). As expected, it was
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8 observed that the discs shrank isotropically thus retaining their shape given during slip casting,
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10 undergoing increasing linear shrinkages from ~9.5% when sintered at 1900°C up to ~13.2%
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12 when sintered at 2100°C. Accordingly, the volume shrinkage gradually increased from ~27% up
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14 to ~35% as the sintering temperature increased from 1900°C to 2100°C.
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19 **Figure 6** shows SEM images representative of the fracture surface of the discs sintered at
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21 temperatures between 1900°C and 2100°C. As can be observed, the disc sintered at 1900°C (**Fig.**
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23 **6A**) is poorly densified, and has an inhomogeneous fine-grained microstructure dominated by
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25 large, very porous regions together with small, dense regions formed by only a few
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27 submicrometre grains. **Grain sizes are thus essentially the same as the particle sizes in the**
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29 **starting B₄C powder (~ 0.7 μm).** There are also rGO platelets all over the microstructure. This
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31 disc is thus in a very incipient state of densification, having reached, if at all, just the early stage
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33 of the intermediate sintering regime. The microstructure of the disc sintered at 1950°C (**Fig. 6B**)
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35 is similar in qualitative terms, **overall with the same submicrometre grain size (~ 0.7 μm),** but
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37 quantitatively it has much less porosity and somewhat larger well-densified regions. It therefore
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39 had reached the middle stage of the intermediate sintering regime. The disc sintered at 2000°C
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41 (**Fig. 6C**) is only moderately porous, and its microstructure exhibits partially-densified regions
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43 with fine grains (**< 1 μm**) and irregular pores plus well-densified regions (**~ 10 μm**) with coarser
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45 grains and relatively spherical pores. It therefore seems that these dense regions were formed
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47 because the formerly fine grains within the small dense regions grew, and then coalesced leaving
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49 some pores entrapped. Hence, the disc sintered at 2000°C had already reached the later stage of
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51 the intermediate sintering regime. The microstructure of the disc sintered at 2050°C (**Fig. 6D**) is
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4 different, without the partially-dense regions observed before and with coarser grains (apparently
5 one ten of microns in size) and rGO platelets here and there. The occurrence of notable
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9 microstructural coarsening above certain PSPS temperature is not however a surprise because it
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11 has been already observed for B₄C monolithics fabricated by SPS [11,35]. Some pores are very
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13 spherical (internal pores), while others have irregular (corner pores) or lenticular (edge/face
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15 pores) shapes. This disc had thus reached the early stage of the final sintering regime. Lastly, the
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17 disc sintered at 2100°C (Fig. 6E) is near-fully dense (with only a few spherical pores), and its
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19 microstructure has even coarser grains (apparently several tens of microns in size) and randomly-
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21 oriented rGO platelets. This last is more evident in the higher-magnification SEM image of Fig.
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24 7 in which some rGO platelets are more easily distinguishable (some other second phases are
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26 intuited as well). The disc sintered at 2100°C had thus reached the desired later stage of the final
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29 sintering regime.
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34 It is also important to mention that while the green parts contain prGO platelets and Ti-Al
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36 intermetallic particles, the PSPS-ed composites contain however rGO platelets and TiB₂ and
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38 Al₄C₃ particles. The former is because prGO further reduces thermally in situ during SPS to
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40 rGO, as demonstrated by Raman spectroscopy [21]. Also note that the rGO reinforcements, like
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42 other flaky [36] and non-flaky [37-39] reinforcements, retard grain growth and hinder
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44 densification because they are obstacles to the diffusion [22]. The latter is because Ti-Al is a
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46 transient liquid phase sintering additive that during SPS first melts helping in densification, and
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48 then this liquid reacts with part of the B₄C ($6B_4C+4Ti_3Al\rightarrow 12TiB_2+Al_4C_3+3C$ and
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50 $B_4C+4TiAl+C\rightarrow 4TiB_2+Al_4C_3$) [25-27], disappearing. Therefore, strictly speaking, these are not
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52 only, but essentially, B₄C/rGO composites. The importance of using the Ti-Al additives becomes
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58 comparatively evident considering that the green parts prepared from the B₄C powders by cold-
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4 uniaxial pressing at 50 MPa plus cold-isostatic pressing at 200 MPa and then PSPS-ed at 2100°C
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6 are quite porous, having reached only the later stage of the intermediate sintering regime [30].
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9 **Figure 8** shows the hardness of the resulting isotropic B₄C/rGO composites as a function
10 of the sintering temperature. It can be seen that hardness increases exponentially from ~8 GPa up
11 to ~30.5 GPa with increasing sintering temperature from 1900°C up to 2100°C. Thus, as
12 expected, hardness correlates inversely with the residual porosity [11], rising with the increase of
13 densification. The discs sintered at or below 2000°C are very soft (to be B₄C composites),
14 attributable to their not even having reached the final sintering regime. The disc sintered at
15 2050°C has the hardness typical of the B₄C ceramics fabricated by conventional pressureless
16 sintering (~18-24 GPa) [23], but with the advantage that its sintering time is less than 30 min
17 instead of several hours. To put this hardness value in perspective, it must be noted that this
18 porous B₄C/rGO composite is harder, or much harder, than the typical well-densified structural
19 oxide ceramics – ZrO₂ (~14 GPa), Al₂O₃ (~18 GPa), etc. Lastly, the disc sintered at 2100°C has
20 the super-hardness above 30 GPa desired for the B₄C-based materials, being indeed **much harder**
21 **than the monolithic B₄C ceramics fabricated by PSPS (~14.9±1.3 GPa) [30] and** only slightly
22 softer than the monolithic B₄C ceramics with coarse-grained microstructures (~17 μm grain size)
23 fabricated by SPS under pressure of 75 MPa, these last with a hardness of ~33 GPa [11]. This
24 slight hardness difference (~2.5 GPa) is due simply to the low residual porosity, the Ti-Al
25 sintering additives, and the rGO platelets that together reduce the hardness of the B₄C/rGO
26 composite relative to the monolithic B₄C ceramic. However, with both materials having coarse-
27 grained microstructures, the present super-hard B₄C/rGO composite is, as intended, tougher than
28 the monolithic B₄C ceramics since the former reaches a fracture toughness as high as ~3.9
29 MPa· m^{1/2} which is essentially twice as high as that of the latter (~2 MPa· m^{1/2} [11]). This
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4 excellent combination of super-hardness and enhanced fracture toughness, together with the
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6 feasibility of successfully fabricating geometrically-complex parts with near-net shape, make
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8 these isotropic B₄C/rGO composites especially appealing for a myriad of engineering
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10 applications.
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14 Nonetheless, it would be ideal if these near-net-shaped B₄C/rGO composites were to have
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16 finer-grained microstructures, which perhaps could be achievable in future studies making some
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18 adjustments to the fabrication route followed here. For example, implementing more complex
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20 PSPS cycles could minimize the exposure times within the intermediate temperature range
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22 responsible for grain coarsening without densification. Also, preparing non-aqueous slurries in
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24 methanol, albeit not environmentally-friendly, would cleanse the B₄C particles of the detrimental
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26 surface oxides that promote grain coarsening [40,41]. And finally, imposing electrical contact
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28 between the punches and the green parts during PSPS would result in a pulsed electrical current
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30 circulating through the compact, thus favouring densification with less grain coarsening.
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38 **4. Concluding Remarks**

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41 We have demonstrated that it is possible to fabricate superhard, toughened B₄C/rGO
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43 composites with isotropic microstructures by combining aqueous slip casting and pressureless
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45 spark-plasma sintering. In particular, we have shown that the former enables the
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47 environmentally-friendly preparation of slurries with shear-thinning rheological behaviour, low
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49 viscosity, and little thixotropy to obtain robust green parts with shape on demand and
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51 microstructures free of macro- and micro-defects, and that the latter enables the ultrafast
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53 densification of these green parts while retaining their shape. Also, thanks to the measurement of
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55 shrinkages and hardnesses, as well as to the microstructural observations, we have identified
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4 sintering temperatures suitable for obtaining superhard isotropic B₄C/rGO composites with
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6 enhanced fracture toughness relative to monolithic B₄C ceramics.
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4 **Figure Captions**
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8 **Figure 1.** Schematic illustration of the experimental assembly of the graphite tools used for
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10 PSPS. The different elements are indicated.
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14 **Figure 2.** Dependence of the viscosity on the shear rate for the semi-concentrated slurry of
15 89.82B₄C+7.08Ti-Al+3.10prGO prepared to a total solids loading of 20 vol.% and sonicated for
16 2 min, and optical photograph showing its visual appearance (inset). The arrows indicate the
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uploading and downloading stretches of the viscosity curve.

Figure 3. Optical photographs of some compacts prepared by slip casting, taken (A) during their
drying within the moulds and (B) once dried.

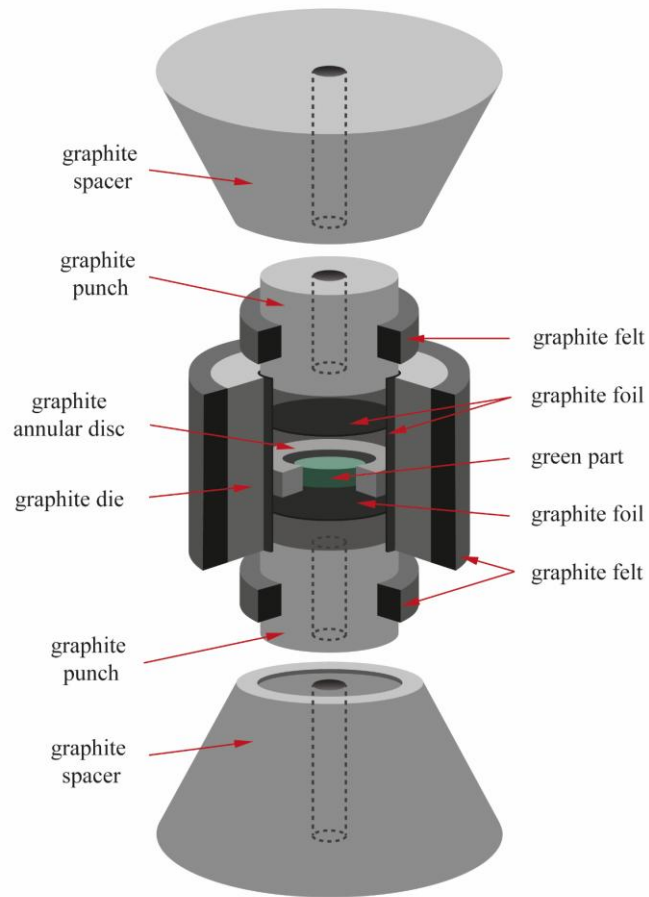
Figure 4. SEM image (23 500×) of the fracture surface of the green compacts showing their
microstructure in the as-cast and dried conditions (prior to isostatic pressing).

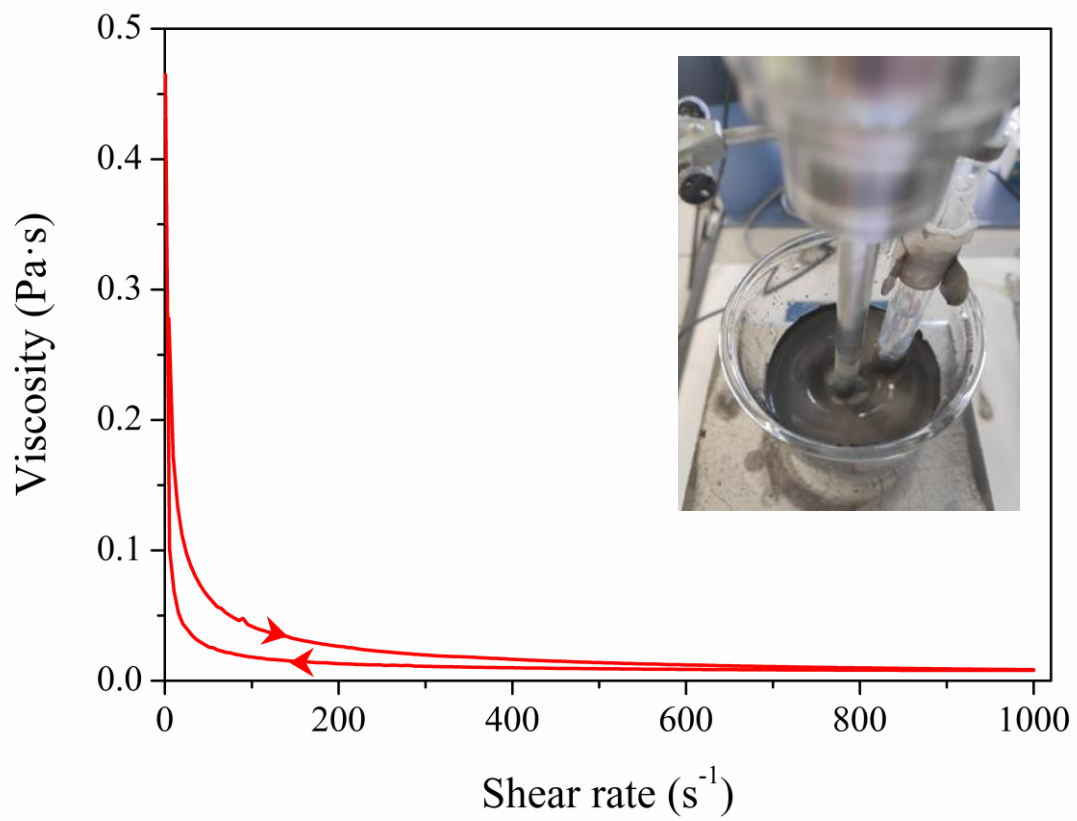
Figure 5. Degrees of linear and volume shrinkages undergone by the green compacts as a
function of the sintering temperature. The solid lines are guides for the eye.

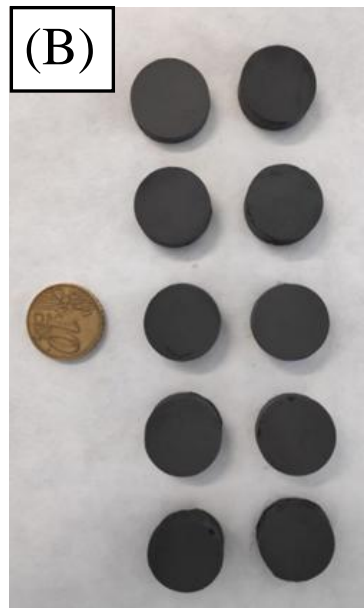
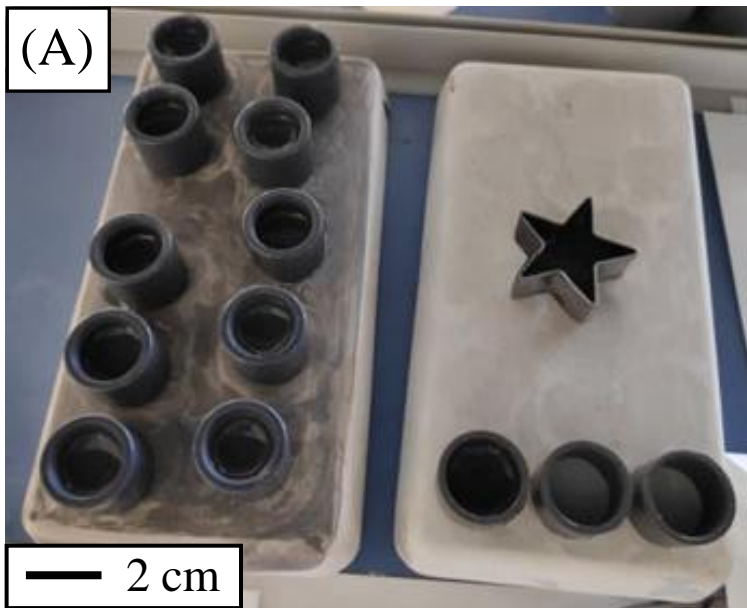
Figure 6. SEM micrographs of the fracture surface of the B₄C/rGO composites sintered at (A)
1900°C (10 000×), (B) 1950°C (10 000×), (C) 2000°C (5000×), (D) 2050°C (5000×), and (E)
2100°C (2000×) for 5 min.

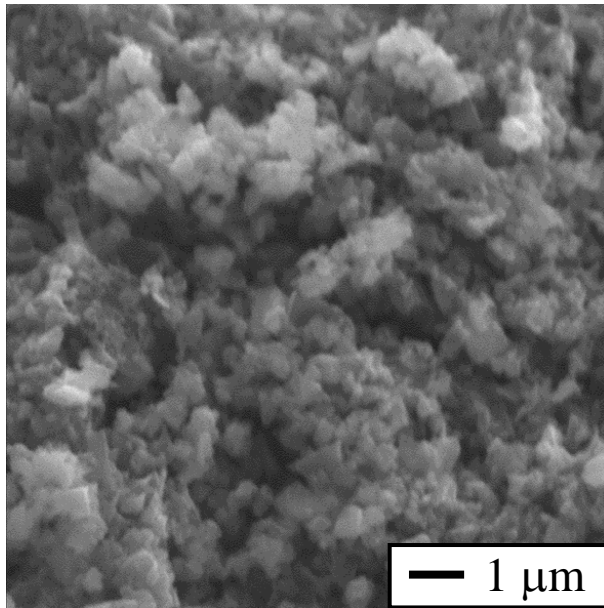
Figure 7. SEM micrograph of B₄C/rGO composite sintered at 2100°C for 5 min, taken at higher
magnification (20 000×). rGO reinforcements are marked with arrows.

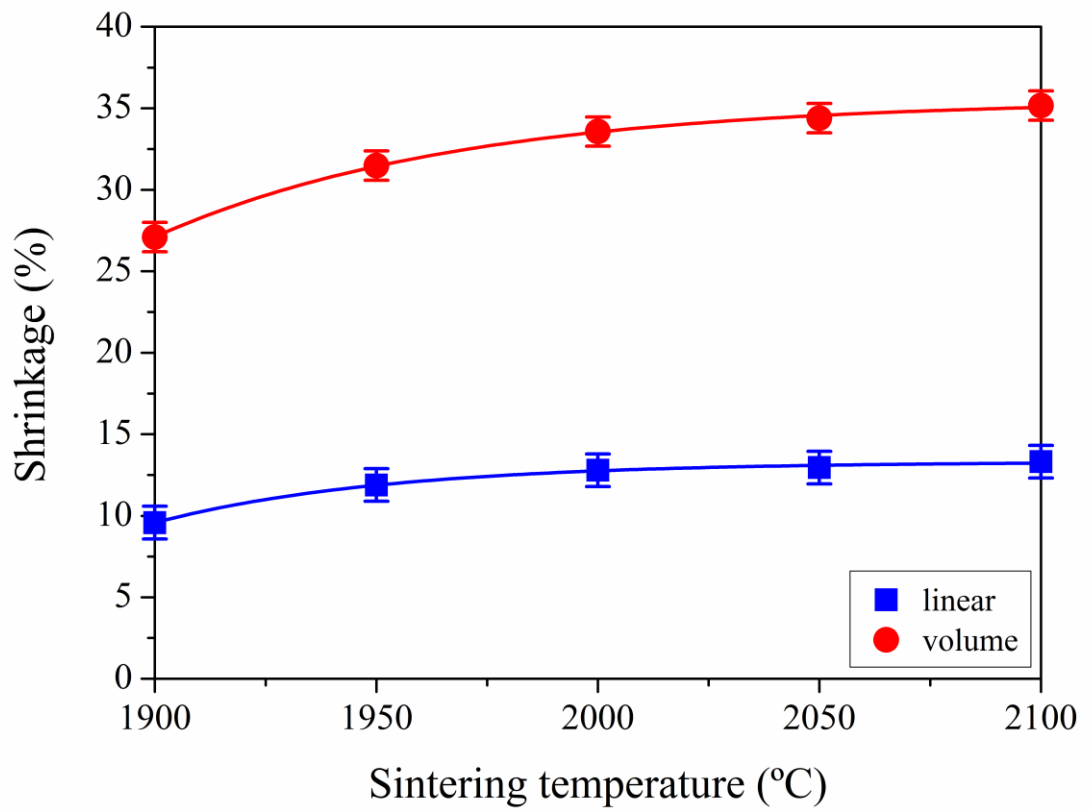
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4 **Figure 8.** Hardness of the B₄C/rGO composites as a function of the sintering temperature. The
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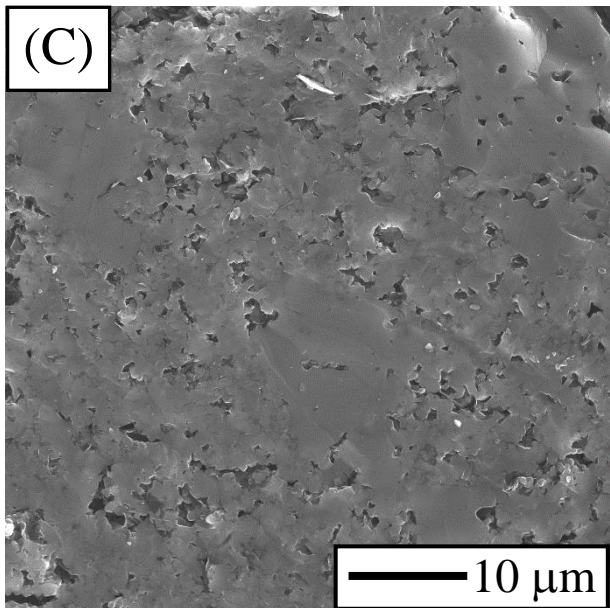
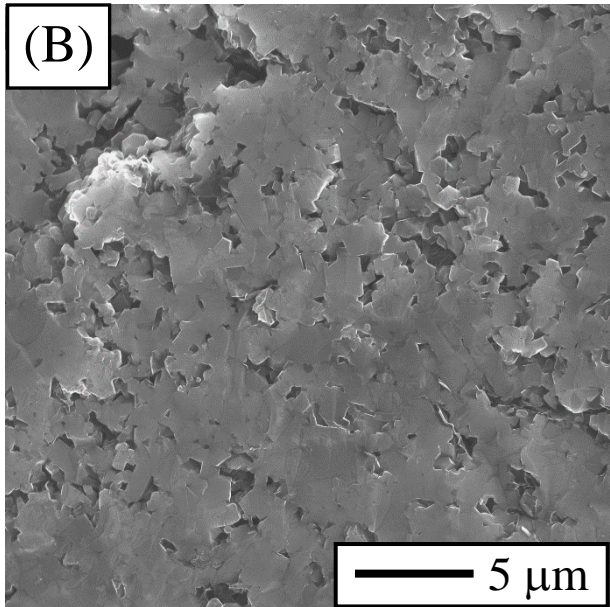
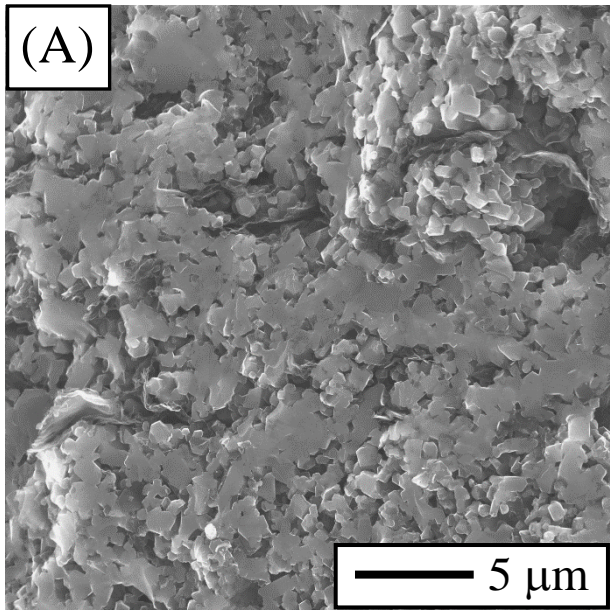


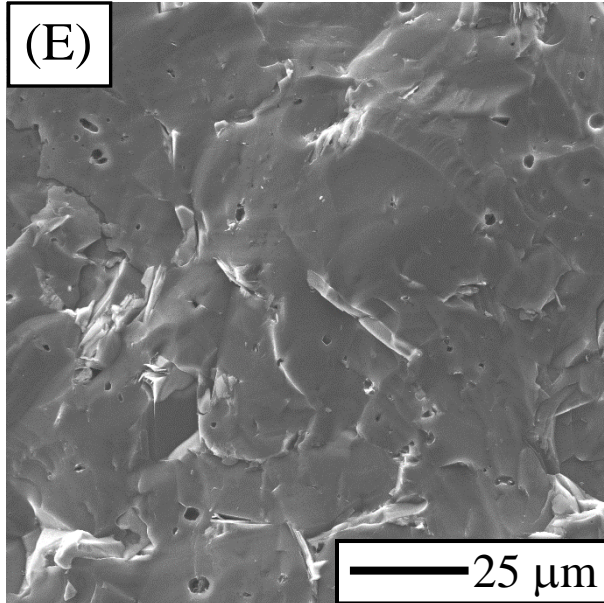
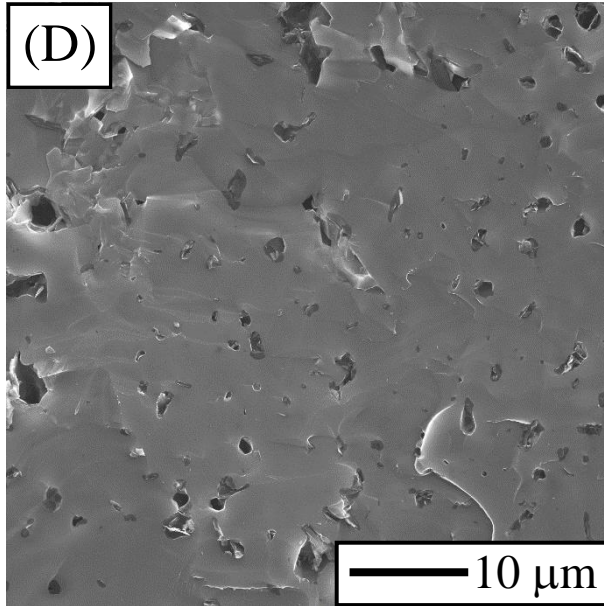


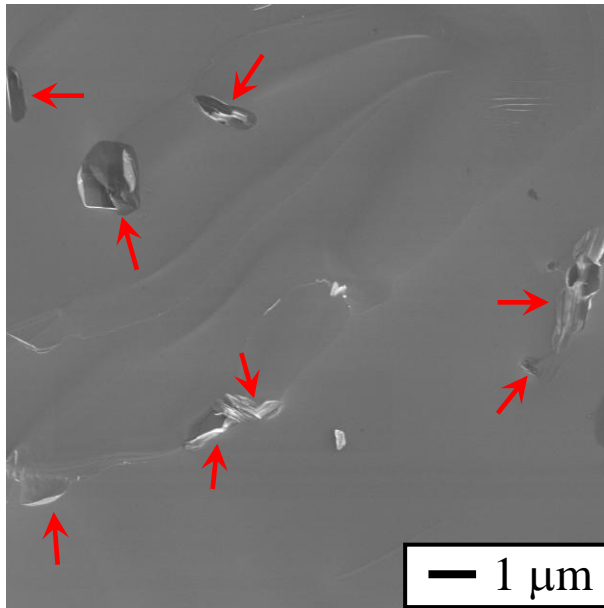


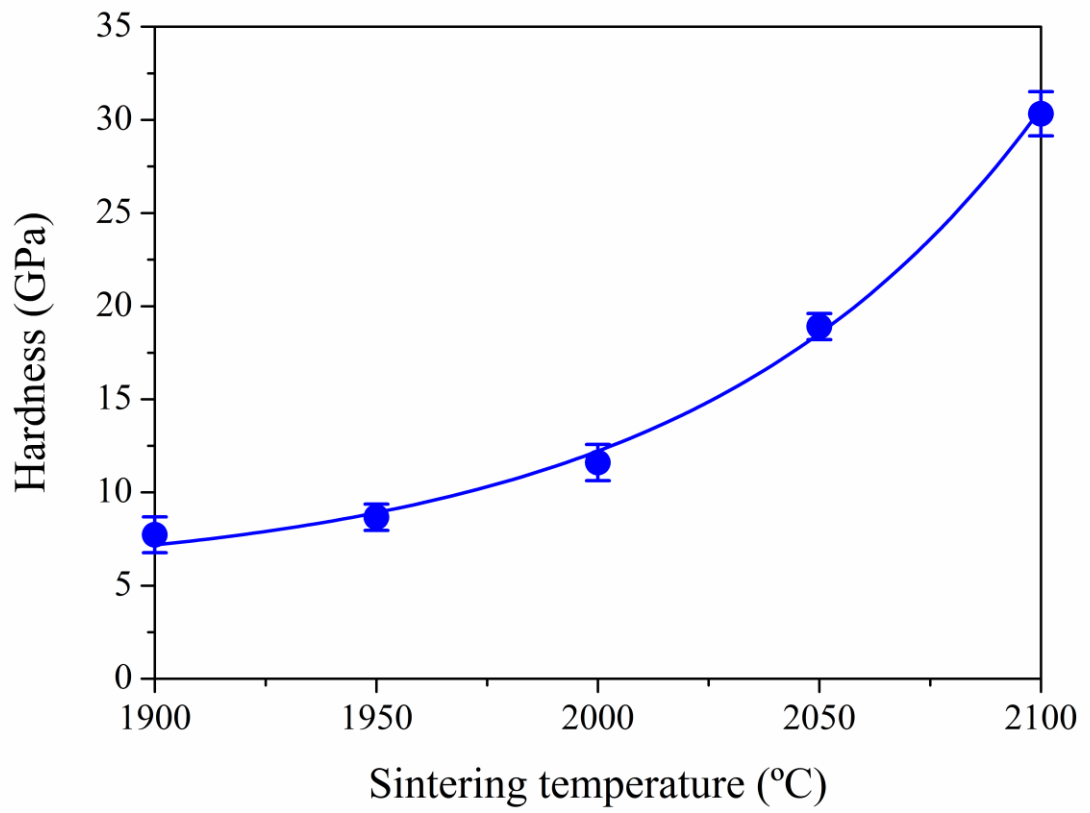












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Figure Captions

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*Summary of Novel Conclusions

- Superhard composites of B_4C reinforced with randomly-oriented reduced graphene oxide (rGO) nanoplatelets are manufactured with near-net shape.
- The fabrication route is simple and environmentally friendly, and uses aqueous slip casting to obtain robust green parts with shape on demand and pressureless spark plasma sintering for their ultrafast densification with shape retention.
- The isotropic B_4C /rGO composites sintered at $2100^\circ C$ are superhard and almost twice as tough as the monolithic B_4C ceramics.