Unique chemical activity in porous YbB$_2$C$_2$ ceramics with high porosity and high compressive strength

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High purity layered YbB$_2$C$_2$ powder is synthesized by a boro/carbothermic reduction method using YbBO$_3$, B$_4$C and graphite powders as raw materials. Its X-ray diffraction data are presented, and the space group $P4/mmbm$ (No. 127) is confirmed. The lattice parameters are $a=b=5.3389$ Å and $c=3.5683$ Å, and the atom positions are Yb (0.0000, 0.0000, 0.0000), B (0.3621, 0.8621, 0.5000), and C (0.1606, 0.6606, 0.5000). Porous YbB$_2$C$_2$ ceramics have a high porosity in the range of 69.89–58.11% and a high compressive strength in the range of 19.49–63.44 MPa. Furthermore, the as-produced porous YbB$_2$C$_2$ ceramics show unique chemical activity. Porous YbB$_2$C$_2$ ceramic with a porosity of 69.89% emits so much heat that it can burn a piece of paper when this ceramic is wetted by water. The rate of reaction between the porous YbB$_2$C$_2$ ceramic and water can be simply controlled by adjusting the porosity. The solid reaction products are YbB$_6$, C and an unknown amorphous phase.

REB$_2$C$_2$ (RE = Y and lanthanides) compounds have a layered crystal structure, which can be described as a stacking of layers, \( \text{–RE–B}_2\text{C}_2\text{–RE–B}_2\text{C}_2\text{–RE–} \), along the $z$-direction, with the covalently bonded B–C network consisting of non-regular squares and octagons$^{1–4}$. The structure of REB$_2$C$_2$ is similar to that of $M_{n+1}AX_n$ phases (“MAX phases”, where M is an early transition metal, A is an A-group element, X is C or N, and $n=1–3$)$^{5–7}$. Two different bonds, namely, the strong metallic-covalent bond of M–X and the weak M–A bond, occur in the MAX phases.

The fabrication methods of REB$_2$C$_2$ include arc melting$^{8–12}$, the two-step method$^{13–15}$, in situ hot pressing$^{16,17}$ and the boro/carbothermic reduction method derived from the synthesis of transition metal borides$^{16,18–20}$, as summarized in Table 1. In all REB$_2$C$_2$ ceramics, YbB$_2$C$_2$ is rather difficult to synthesize$^{14}$. Sakai et al.$^{14}$ thought the reason was the high vapor pressure of Yb carbide under high temperature. However, a closer study of Yb shows that there are two other possible reasons. First, the number of 4f valence electrons in Yb is different from those in other rare earth metals$^{21}$. Second, the divalent state of 2+ is also reflected in the normalized cell volume $V_n = V/Z$ of the compound, which does not follow the usual lanthanide contraction trend$^{22}$. In this work, YbBO$_3$ instead of Yb$_2$O$_3$ was employed to fabricate YbB$_2$C$_2$ by the boro/carbothermic reduction method. During the process, the possible reaction is shown in Table 1.

To date, most researchers have focused on the magnetic$^{14,23,24}$ or electrical properties$^{11,15}$ of REB$_2$C$_2$. To our knowledge, only a few researchers have recently used first-principles calculations to study the mechanical properties of REB$_2$C$_2$ compounds$^{25,26}$. Regarding experimental work, Zhao et al.$^{16,17}$ successfully synthesized high purity bulk YbB$_2$C$_2$ and studied its physical and mechanical properties, which showed excellent damage tolerance, easy machinability, high melting point (2500 °C < $T_m$ < 2600 °C) and excellent high temperature rigidity (the value of Young's modulus at 1500 °C is still similar to that at room temperature). These features of bulk YbB$_2$C$_2$ ceramic might endow it with great untapped potential for future ultrahigh temperature applications$^{16,17}$. Chen et al.$^{27}$ reported that porous YbB$_2$C$_2$ ceramics fabricated by a high-temperature reaction/partial sintering process possess high porosity (75.26–57.17%), high compressive strength (9.32–34.78 MPa), and anisotropy in the microstructure and mechanical behavior. These features of porous YbB$_2$C$_2$ ceramic render it promising as a thermally insulating lightweight component for transpiration cooling systems$^{27}$.

As the number of 4f valence electrons in Yb is different from those in other rare earth metals, the YbB$_2$C$_2$ ceramic may possess unique properties. In this work, high purity YbB$_2$C$_2$ powder was successfully synthesized. The crystal structure and lattice parameters were studied. Then, porous YbB$_2$C$_2$ ceramics with high porosity and high compressive strength were prepared. In addition, the as-prepared porous YbB$_2$C$_2$ ceramics were found to possess individual chemical activity in wet environments.

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Table 1. Comparison of different methods for synthesizing REB₂C₂.

| Methods               | Starting materials | Routes or reactions                                                                 |
|-----------------------|--------------------|-----------------------------------------------------------------------------------|
| Arc-melting technique | RE, B and C        | (1) \((\text{RE} + B + C)_{\text{powder}} \rightarrow (\text{RE} + B + C)_{\text{pellet}}\)   |
|                       |                    | (2) \((\text{RE} + B + C)_{\text{pellet}} \rightarrow (\text{REB}_2\text{C}_2)_{\text{single crystal}}\) |
| Two-step              | RE, B, O, C        | (1) \((\text{RE}_2\text{O}_3 + B + \text{C}) \rightarrow \text{REB}_2\text{C}_2\) (or \(\text{REB}_4\text{C}_2\))   |
|                       | Y, C and B         | (1) \(2\text{Y} + 2\text{C} \rightarrow \text{Y}_2\text{C}_2\)   |
|                       |                    | (2) \(\text{Y}_2\text{C}_2 + 2\text{B} \rightarrow \text{YB}_2\text{C}_2\)   |
| In situ hot pressing  | \(\text{YH}_2\), B, C and C | 2\(\text{YH}_2\) + B + 3C \(\rightarrow\) YB₂C₂ + 2H₂   |
| Boro/carbothermic reduction | RE, B, O, C and C | \((\text{RE}_2\text{O}_3 + \text{B} + \text{C})_{\text{pellet}} \rightarrow \text{REB}_2\text{C}_2 + 3\text{CO}\) (This work) |
|                       |                    | \(\text{RE}_2\text{O}_3 + \text{B} + \text{C} \rightarrow \text{REB}_2\text{C}_2 + 3\text{CO}\)   |

Experimental

YbB₂C₂ powder and porous YbB₂C₂ ceramics were synthesized by the boro/carbothermic reduction method with a mixture of YbBO₃, B₄C (99%, 200 mesh, Jingangzhuan, China), and graphite (99%, 200 mesh, Tianyuan, China) powders. The routes for fabricating YbB₂C₂ powder can be described as follows. First, raw powders with a 4:0:1:28:18:16 molar ratio were milled in a polypropylene jar for 6 h in alcohol to obtain a homogeneous mixture. The powder mixture was then dried in an oven at 60 °C for 24 h. After that, the powder mixture was placed in a graphite crucible heated at a rate of 10 °C/min to 1950 °C and held for 1.0 h under flowing Ar. The route for synthesizing porous YbB₂C₂ ceramics can be generalized as follows: at first, the homogeneous mixture powders of YbBO₃, B₄C, and graphite (as above) were uniaxially pressed into columnar compacts by applying different pre-pressures (10, 20, 30, 50, 100, 200 and 300 MPa) with a dwell time of 5 min. Then, these green bodies were placed in a graphite crucible and heated at a rate of 8 °C/min to 1980 °C and held for 1.5 h under flowing Ar.

The phase composition was identified using an X-ray diffractometer with Cu Kα radiation (Rigaku D/max-2400, Tokyo, Japan). Rietveld refinement was performed on the XRD results using the GSAS suite with EXPGUI. The morphology was investigated by a SUPRA 35 scanning electron microscope (SEM) (LEO, Oberkochen, Germany) equipped with an energy dispersive spectroscopy (EDS) system. Selected area electron diffraction (SAED) was performed using a Tecnai G2 F20 (FEI, Eindhoven, the Netherlands) instrument equipped with a field emission gun. During the process, a perforated carbon/copper net served as a support for the as-prepared powder.

The powder mixture was then dried in an oven at 60 °C for 24 h. After that, the powder mixture was placed in a graphite crucible and heated at a rate of 8 °C/min to 1980 °C and held for 1.5 h under flowing Ar.

The density of the porous YbB₂C₂ ceramics was calculated geometrically, by measuring the volume and weight of five identical samples and averaging the data to ensure accuracy. The porosity (\(\eta\)) of porous YbB₂C₂ ceramics was determined by Eq. (1), where \(\rho\) and \(\rho_0\) refer to the sintered density and the theoretical density of YbB₂C₂ ceramics, respectively. The compressive strength was measured using a microcomputer control electron universal testing machine (CMT4204, Shenzhen SANS testing machine Co., Ltd, Shenzhen, China). The tested samples were rectangular bars with dimensions of 5 mm × 5 mm × 10 mm. The compressive strengths of the as-prepared porous YbB₂C₂ ceramics were tested in the directions parallel (\(\sigma_\parallel\)) and perpendicular (\(\sigma_\perp\)) to the forming direction. For each group, five samples with the same density were used to obtain the average value. The crosshead speed was 0.5 mm/min.

\[
\eta = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\%
\]  

Results and discussion

XRD analysis and Rietveld refinement of YbB₂C₂. To date, the crystal structure of REB₂C₂ is still controversial. Bauer and Sakai et al. believed that its space group is \(P\overline{4}\text{2}1\text{bm}\) (No. 127). In this work, the \(P\overline{4}\text{2}1\text{bm}\) space group is used as a starting model for refining the YbB₂C₂ sample, and the initial values of the cell parameters and atom coordinates come from the isostructural compound YB₂C₂. The experimental XRD spectrum (red) and the calculated pattern obtained by Rietveld analysis (black) from 20 = 20° to 80° are shown in Fig. 1a. Only the YbB₂C₂ phase is detected, which confirms that high purity YbB₂C₂ powder has been successfully synthesized. Considering the difficulty of synthesizing the YbB₂C₂ compound, the as-fabricated YbB₂C₂ powder is remarkable, and the boro/carbothermic reduction method shows more advantages than other methods.
The lattice parameters of YbB₂C₂ calculated from the refinement are $a = b = 5.3389 \text{ Å}$ and $c = 3.5683 \text{ Å}$, respectively, and the atom positions are Yb (0.0000, 0.0000, 0.0000), B (0.3621, 0.8621, 0.5000), and C (0.1606, 0.6606, 0.5000). The crystal structure of YbB₂C₂ can be seen in Fig. 1b,c. The results are in accordance with the cell parameters and (or) atom positions of the known REB₂C₂ compound4,11,26,32. The detailed XRD results of the structural refinements are grouped in Table 2. In addition, the theoretical density of the YbB₂C₂ ceramic calculated from the refinement is 7.05 g/cm³.

Microstructure of the YbB₂C₂ powder. The morphology of the YbB₂C₂ powder observed by SEM is shown in Fig. 2a,b. The YbB₂C₂ powder consists of typical laminated plates with a size of approximately several microns in thickness and tens of microns in length and width. The laminated plates of YbB₂C₂ reflect the alternate arrangement of the B–C networks and Yb sheets, as shown in Fig. 1c. To clearly observe the morphology of the YbB₂C₂ powder, TEM was used as well. Figure 2c shows the bright field image (BFI) of YbB₂C₂. The as-prepared YbB₂C₂ possesses a typical laminar microstructure. Figure 2d,e show the diffraction results along the [001] and [010] zone axes. All maxima can be indexed on the basis of a tetragonal cell, with parameters $a = 5.2835 \text{ Å}$ and $c = 3.4920 \text{ Å}$; both values are in good agreement with those measured results from the XRD spectra. In addition, Fig. 2d,e and Table 2 show that the reciprocal space spots were not extinct as long as they met “0kl: k = 2n, h00: h = 2n or hkk: h + k = 2n”. According to the International Tables of Crystallography35, the reflection conditions are compatible with the space group P4/mmbm (No. 127), which confirms the previous choice for Rietveld refinement.

Porous YbB₂C₂ ceramics. Advanced porous ceramics (also called ceramic foams) usually have low density, high porosity, large specific surface area, thermal shock resistance, corrosion and wear resistance, and high chemical stability36–38. SEM images of the as-prepared porous YbB₂C₂ samples with porosities of 69.88%, 61.58% and 58.11% are shown in Fig. 3. The microstructure can be described as an incompact stacking of uniform lamellae with a size of approximately one or two microns in thickness and tens of microns in length and width. It should be noted that the microstructure of porous YbB₂C₂ is slightly different from that of porous Yb₂C₂.
Table 2. Reflections, 2θ positions, d (interplanar spacing) and intensity data of YbB₂C₂ powder from observation (Obs.) and calculation (Calc.).

| Reflection (hkl) | 2θ_Obs (°) | 2θ_Cal (°) | d_Obs (Å) | d_Cal (Å) | I/I₀_Obs (%) | I/I₀_Cal (%) |
|-----------------|------------|------------|-----------|-----------|--------------|--------------|
| 110             | 23.60      | 23.55      | 3.775     | 3.785     | 65.74        | 63.50        |
| 001             | 24.96      | 24.93      | 3.568     | 3.593     | 30.46        | 28.28        |
| 200             | 33.60      | 33.54      | 2.669     | 2.677     | 29.22        | 26.48        |
| 111             | 34.60      | 34.56      | 2.593     | 2.606     | 100.00       | 100.00       |
| 201             | 42.29      | 42.24      | 2.138     | 2.146     | 52.63        | 48.91        |
| 220             | 48.22      | 48.17      | 1.888     | 1.893     | 14.57        | 11.78        |
| 002             | 51.21      | 51.16      | 1.784     | 1.797     | 15.76        | 12.44        |
| 310             | 54.32      | 54.29      | 1.688     | 1.693     | 23.38        | 21.03        |
| 221             | 55.04      | 54.99      | 1.669     | 1.674     | 19.20        | 16.17        |
| 112             | 57.07      | 57.05      | 1.613     | 1.623     | 21.36        | 19.26        |
| 311             | 60.65      | 60.63      | 1.526     | 1.531     | 21.91        | 20.55        |
| 202             | 62.61      | 62.57      | 1.483     | 1.492     | 14.48        | 13.63        |
| 400             | 70.53      | 70.49      | 1.335     | 1.338     | 3.59         | 3.20         |
| 222             | 72.92      | 72.89      | 1.297     | 1.303     | 9.62         | 9.31         |
| 330             | 75.51      | 75.48      | 1.258     | 1.262     | 2.93         | 2.78         |
| 401             | 76.11      | 76.07      | 1.254     | 1.254     | 8.41         | 7.86         |
| 312             | 77.86      | 77.83      | 1.226     | 1.232     | 15.78        | 15.64        |
| 411             | 78.50      | 78.52      | 1.217     | 1.221     | 0.85         | 0.80         |

Figure 2. SEM images of the YbB₂C₂ powder: low magnification (a) and high magnification (b). TEM image of the YbB₂C₂ powder (c). SAED patterns corresponding to the YbB₂C₂: [001] (d) and [010] (e) zone axes.
This difference in microstructure comes from the different kinds of raw materials employed. For porous YbB\(_2\)C\(_2\) ceramics, Y\(_2\)O\(_3\), BN and C were used as raw materials, and small grains and large lamellar grains were obtained due to the in situ reaction process and inheritance from graphite, respectively\(^\text{27}\). In the porous YbB\(_2\)C\(_2\) ceramics, the lamellas are oriented to a certain degree, more or less, in the plane perpendicular to the forming direction; this may be due to the raw material of graphite, which has a typical lamellar structure. The anisotropic microstructure of the porous YbB\(_2\)C\(_2\) becomes more obvious with decreasing porosity.

For porous ceramics, the compressive strength is an important parameter. To confirm the anisotropic mechanical properties of porous YbB\(_2\)C\(_2\) samples, a compression test was carried out in two directions: \(\sigma//\) (the loading direction parallel to the forming direction) and \(\sigma\perp\) (the loading direction perpendicular to the forming direction), as shown in Fig. 4a and Table 3. The \(\sigma//\) strengths of the as-prepared porous YbB\(_2\)C\(_2\) samples with porosities of 69.89–58.11% are in the range of 19.49–63.44 MPa. It is obvious that the \(\sigma//\) strength decreases with increasing porosity. Different from the trend of the \(\sigma//\) strength, the maximum \(\sigma\perp\) strength occurs at a porosity of 61.58% (62.40 MPa). The \(\sigma\perp\) strengths are higher than the corresponding \(\sigma//\) strengths for samples with porosities of 69.89–61.58%, while the former are lower than the latter for samples with porosities of 58.98–58.11%. Two factors determine the \(\sigma\perp\) strengths, namely, the porosity and anisotropic microstructure. With increasing porosity, the \(\sigma\perp\) strength decreases as well, which is similar to the trend of the \(\sigma//\) strength. The anisotropic microstructure, i.e., the YbB\(_2\)C\(_2\) lamellas are oriented in the plane perpendicular to the forming direction has an adverse effect on the \(\sigma\perp\) strength. This may be due to the weak adhesion between the YbB\(_2\)C\(_2\) laminates. The influence of the anisotropic microstructure of the porous YbB\(_2\)C\(_2\) samples on their compressive strengths can be understood by a model, as shown in Fig. 4b,c. On one hand, when lamellas of porous YbB\(_2\)C\(_2\) samples are oriented to a small

Figure 3. SEM images of the as-prepared porous YbB\(_2\)C\(_2\) samples with different porosities. Top surface perpendicular to the forming direction (a) and cross section parallel to the forming direction (b) of the as-prepared sample (\(\eta = 69.89\%\)). Top surface (c) and cross section (d) of the sample (\(\eta = 61.58\%\)). Top surface (e) and cross section (f) of the sample (\(\eta = 58.11\%\)).
degree in the plane perpendicular to the forming direction (Fig. 4b), some lamellas act as diagonal bracings that enhance the $\sigma_\perp$ strength (samples with porosity of 69.89–61.58%, $\sigma_\parallel < \sigma_\perp$). On the other hand, when the lamellas of the porous YbB$_2$C$_2$ samples are oriented ideally in the plane perpendicular to the forming direction (Fig. 4c), the oriented lamellas easily disintegrate because of the weak adhesion between them, which weakens the $\sigma_\perp$ strength (samples with porosities of 58.98–58.11%, $\sigma_\parallel > \sigma_\perp$). For the porous YbB$_2$C$_2$ sample with a porosity of 61.58%, the porosity is not high enough and the lamellas are oriented to an appropriate degree. These two factors work together and ultimately enhance the $\sigma_\perp$ strength (a maximum of 62.40 MPa). According to Chen et al.\textsuperscript{27}, porous YbB$_2$C$_2$ ceramics also exhibit anisotropy in their mechanical properties: samples with porosities of 75.26–57.17% possess $\sigma_\parallel$ strengths of 9.32–34.78 MPa, samples with porosities of 72.40–54.02% possess $\sigma_\perp$ strengths of 17.47–98.57 MPa. However, the mechanism of the anisotropic properties in porous YbB$_2$C$_2$ ceramics
is different from that in porous YB$_2$C$_2$ ceramics. For the latter, the mechanism can be described as follows: the failure of $\sigma_{//}$ is caused by accumulated damage$^{27,39}$, and the failure of $\sigma_{\perp}$ is caused by permanent damage$^{27,40}$.

In addition, the as-prepared porous YbB$_2$C$_2$ ceramics were found to produce a large amount of heat when they were wetted by water. One typical example is the reaction between a porous YbB$_2$C$_2$ sample (Φ10 × 3 mm) with a porosity of 69.89% and water, as shown in Fig. 5a–d. The sample was first immersed in deionized water for 1 min (Fig. 5a), then the soaked sample was wrapped by a piece of A4 paper (Fig. 5b), and the paper was completely burned up after about approximately 3 h (Fig. 5c,d). It is clear that a large amount of heat was emitted during the reaction process. This result implies that porous YbB$_2$C$_2$ ceramics possess individual chemical activity in wet environments, which is different from the chemical inertness of other porous ceramics$^{37,38}$. It was also found that the reaction between porous YbB$_2$C$_2$ ceramic and water became slow and non-obvious with decreasing porosity. For example, when the porous YbB$_2$C$_2$ ceramic's porosity was reduced to 58.11%, the paper could not be burned up by reaction heat. Obviously, the chemical activity of the porous YbB$_2$C$_2$ ceramics can be controlled by adjusting their porosity, which can be understood by a sponge model (Fig. 6). During the reaction process, the porous YbB$_2$C$_2$ ceramic acts as a sponge that can easily soak up water at the beginning. The soaked water can keep the reaction going, while a large amount of heat begins to accumulate. Finally, the wrapped paper was burned up by the accumulated heat.

Figure 5e,f show the microstructures of the as-prepared porous YbB$_2$C$_2$ sample and its solid reaction products with water for 3 h. The laminated plates of the porous YbB$_2$C$_2$ sample are smooth (Fig. 5e), while the plates of its products with water are rough and look like floccules (Fig. 5f). The XRD spectrum of the solid reaction products of the as-prepared porous YbB$_2$C$_2$ sample with water for 3 h is shown in Fig. 7a. Obviously, apart from the residual YbB$_2$C$_2$, the solid products consist of YbB$_6$, C and an unknown amorphous phase. The amorphous phase

![Figure 5.](image-url)
Figure 6. Sponge-like structure of the porous YbB$_2$C$_2$ sample (a). The structure of the water-absorbed YbB$_2$C$_2$ sample (b).

Figure 7. XRD spectrum (a) and SEM images (b) of solid reaction products of the as-prepared porous YbB$_2$C$_2$ sample ($\eta=69.89\%$) with water for 3 h.
can be converted into YbBO₃ by annealing (800 °C for 1 h under argon flow). Figure 7b shows the morphologies of the solid products. According to the EDS analysis, the lamellas are residual YbB₂C₂, the small particles are amorphous phases, the white plates are YbBO₃, and the black plates are graphite.

Conclusions
High purity YbB₂C₂ powder was successfully synthesized by the boro/carbothermic reduction method. The space group P4/mmm (No. 127) of YbB₂C₂ was confirmed. Its X-ray diffraction data, lattice parameters and atomic positions were obtained as well. The as-prepared YbB₂C₂ powder possesses the typical feature of a layered microstructure. The porous YbB₂C₂ ceramics possess a high porosity of 69.89–58.11% and a high compressive strength of 19.49–63.44 MPa, and show unique chemical activity in wet environments. The reaction between the porous YbB₂C₂ ceramic and water can be controlled by changing the porosity. The solid reaction products of the as-prepared porous YbB₂C₂ sample with water consist of YbBO₃ and an unknown amorphous phase. The amorphous phase can be converted into YbBO₃ by annealing.

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Author contributions
Z.L. and J.C. wrote the main manuscript. Z.L., J.C., H.Z. and Y.Z. synthesized the YbB2C2 sample and performed the SEM analysis. Z.L., L.S. and M.L. carried out the Rietveld refinement. J.Y., M.H. and Z.Z. performed the TEM analysis. All authors discussed the results and contributed to the preparation and critical revision of the manuscript.

Competing interests
The authors declare no competing interests.

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