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RAPID COMMUNICATION

Gas encapsulation technology for large volume press

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For samples in the gaseous state at room temperature and ambient pressure, mature technology has been developed to encapsulate them in a diamond anvil cell (DAC). However, the large volume press (LVP) can only treat samples with starting materials in solid or liquid form. We have achieved stable encapsulation and reaction treatment of carbon dioxide in a centimeter sized sample chamber for a long time (over 10 min) under conditions of temperature higher than 1200 °C and pressure over 5 GPa through the use of integrated low-temperature freezing and rapid compression sealing method for LVP cell assemblies. This technology can also be applied to the packaging of other gaseous or liquid samples, such as ammonia, sulfur dioxide, water, etc. in LVP devices.

Keywords: large volume press, gas encapsulation, low-temperature

PACS: 07.35.+k, 82.40.Fp **DOI:** 10.1088/1674-1056/ad7af8

1. Introduction

The large volume press has the advantage of a large sample volume and is popular with high pressure synthesis in laboratories and industry.[1–8] At present, various large volume presses are used in different scenarios in the world, such as Walker type multi-anvil press, Kawai type multi-anvil press, large volume cubic press, and so on.[9–11] Through these devices, researchers have successfully synthesized superhard materials such as cubic boron nitride and synthetic diamond. What's more, according to subsequent in-depth research people are still working on continuously improving the physical and chemical properties of artificial superhard materials. Along with these studies, the pressure transmitting medium, pressure-generation efficiency, sealing performance, pressure calibration, and so on have been investigated. Nowadays, to satisfy different requirements of high pressure researches, people choose various powders and lumps as experimental samples. However, due to the physical properties of gas and liquid, high pressure studies related to gas and liquid can only be performed in diamond anvil cell (DAC).[12,13] Benefiting from the small size of DAC the gas-loading devices can create the desired starting pressure for gas and liquid loading. This method does not work for the large volume press. At the same time, devices and technologies for loading gas and liquid in DAC are becoming increasingly sophisticated.[14–17] Correspondingly, the small space inside DAC makes it almost impossible for DAC-related research to be applied to industrial production. In many reactions, the amount of substance determines whether the reaction can take place. For example, nuclear reactions require the mass of matter greater than the critical mass to sustain the nuclear chain reaction, the products formed by carbon combustion also vary with the oxygen content. Therefore, it is necessary to increase the amounts of substances in high pressure studies. Meanwhile, from the classical thermodynamic and chemical theory, the gas molecule contains the highest energy and is the most chemically active state among solid, liquid and gas states. If it is possible to heavily load gas into a large volume press, it will surely help the application of DAC-related research to industrial production and some unexpected results may also be obtained. From another point of view of pressure transfer performance, previous studies have demonstrated that soft substances can better maintain the quasi-hydrostatic pressure in ultra-high pressure environments. Guided by this conclusion many researchers choose liquid as the pressure transmitting medium when the pressure range exceeds 10 GPa, and when the pressure exceeds 100 GPa, they tend to use solid gas for their experiments.[18–21] Unfortunately, accompanied by high maintenance costs due to sealing failure and other issues, there is still no study devoted to loading gas or liquid into the large volume press so far. This greatly limits the possibilities of the large volume press in high pressure research. For these reasons, this work fills in a previous research blind spot and develops a new gas encapsulation technology by using liquid nitrogen-assisted cooling based on the high temperature high pressure (HTHP) large-volume cubic press technology. We successfully loaded carbon dioxide into the large-volume cubic press with a nearly centimeter-sized sample chamber and then pressurized it to 5.0 GPa without sealing failure.

2. Experiment and methods

Dry ice (A Chinese gas company, $>99\%$ purity) was chosen as the starting material and sealed in a molybdenum cup.

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An analytical balance with a precision of 10^{-3} g was used to weigh appropriate dry ice into the molybdenum cup. The HTHP experiments were conducted in a DS6×14 MN cubic press (a multiple-anvil apparatus developed at Sichuan University, including 6 anvils of tungsten carbide with a top square edge length of 23.5 mm). The press chamber pressure was calibrated by the pressure-induced phase transitions of Bi, Tl, and Ba and semiconductor metals (ZnTe and ZnS). Manganin was also used to calculate the calibration results under high pressure.[22–26] The pressure error was ±0.1 GPa. The temperature of the press chamber was directly measured by using the *in situ* high pressure temperature measurement method. The temperature error measured using the thermocouple was approximately ±2 °C. The *in situ* high pressure temperature signal was recorded with a multi-channel data recorder, which was designed for continuous monitoring. Details of the assemblies and high pressure measurements designed for the furnace chamber are shown in Figs. 1(a) and 1(b). XRD (model DX-2700, Dandong, China) with a Cu K_α radiation source ($\lambda = 0.15406$ nm) was used to characterize the composition of the initial materials and HTHP-treated samples (canned from 10° to 90°).

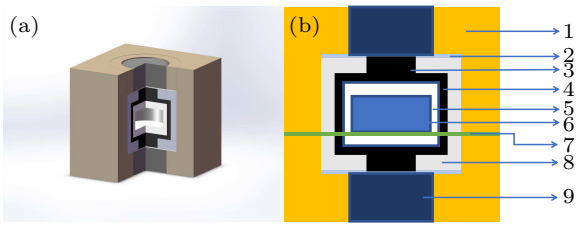


Fig. 1. (a) Details of the assemblies. (b) Schematic diagram of the cell assembly: (1) pyrophyllite, (2) molybdenum, (3) graphite conductor, (4) graphite furnace, (5) hexagonal boron nitride (h-BN), (6) furnace chamber (sample in molybdenum capsule), (7) thermocouple, (8) dolomite, and (9) steel ring.

3. Results and discussion

Dry ice has a boiling point of −78.5 °C and is readily sublimated during pressurization. In the heating and pressurization process, the nature of the gas is active, which easily leads to seal failure. Therefore, the entire cell assembly was frozen for 30 min with liquid nitrogen to approximately −150 °C before pressure loading. Tables 1 and 2 record the temperature changes inside the assembly during the pressurization process and under atmospheric environment after freezing in liquid nitrogen. To increase the success rate of encapsulation, we used a rapid pressurization method to increase the pressure to 1.5 GPa in 75 s, followed by a gentle approach to the load pressure. In order to prevent seal failure due to moisture in the assembly, the assembly was dried at 150 °C for 10 min prior to the heating experiments. The schematic of the HTHP experimental procedure and temperature, pressure rise curves are shown in Fig. 2.

Table 1. Temperature (T_A) changes inside the assembly under atmospheric environment after freezing in liquid nitrogen.

Time (min)	1	2	3	4	5	6	7	8
T_A (°C)	−14	−130	−90	−78	−70	−59	−48	−39

Table 2. Temperature (T_P) changes inside the assembly during the pressurization process after freezing in liquid nitrogen.

Time (s)	5	10	15	20	30	40	50	60
T_P (°C)	−133	−110	−97	80	66	49	33	20

By comparing T_A and T_P, we found that the temperature inside the assembly rose dramatically due to the pressure input and the heat transfer with the large volume press. At the same time, we noted that after about 20 s of pressure loading, the temperature of the assembly chamber rose to the sublimation point of dry ice. Currently, the pressure of the chamber rose to about 500 MPa, right around the yield strength of molybdenum.[27] (Generally speaking, the boiling point of dry ice will increase with increasing pressure. So this may also be an important factor that the dry ice could be encapsulated inside the molybdenum cup under rapid compression.)

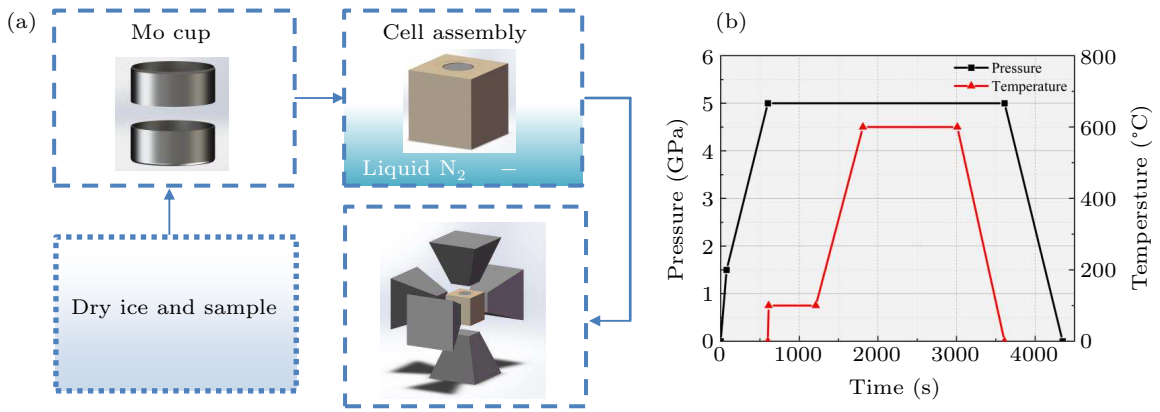


Fig. 2. (a) Schematic of the HTHP experimental procedure. CO_2 and sample were sealed in the molybdenum cup, and frozen with liquid nitrogen after putting into the HTHP cell assembly. The HTHP experiments were carried out after the temperature of the entire cell assembly dropped to −150 °C. (b) Temperature (black), pressure (red) rise curves.

In 2006, Valentina M. Giordano measured the melting curve of carbon dioxide under high pressure in detail.[28] He pointed out that carbon dioxide melts close to room temperature at a pressure of 500 MPa. As Table 2 shows, when the pressure of the chamber rose to about 500 MPa, the temperature inside the chamber was about −80 °C. Because we froze the sample with liquid nitrogen in advance, the melting point of carbon dioxide rose much faster than the temperature inside the chamber in the range of 0–2 GPa during the experiment. We analyze that at this moment the molybdenum started to shape and deform then filled the gaps between the molybdenum cup. When the pressure was greater than 2 GPa, the gas could be successfully encapsulated inside the molybdenum cup. We set up three sets of experiments to observe the encapsulation of carbon dioxide. Group A: place about 0.4 g of dry ice in the molybdenum cup then freeze to −150 °C with liquid nitrogen. Group B: no dry ice and freeze to −150 °C with liquid nitrogen. Group C: place about 0.4 g of dry ice in the molybdenum cup but without freezing. We pressurized these three groups to 5.0 GPa and held pressure for 2 min using the above pressurization method and then relieved the pressure. We found that the morphologies of the three groups of molybdenum cups were very different after the experiment under the same condition, and we measured the volume and density of the three groups of molybdenum cups after the experiment, the results are shown in Table 3. We hypothesize that the deformation of the molybdenum cup is reduced due to the presence of dry ice. At the beginning of pressurizing, dry ice is sealed as solid inside the molybdenum cup until the temperature reaches its sublimation temperature, meanwhile, the molybdenum cups begin to deform plastically to fill their internal void, allowing the carbon dioxide to be continually encapsulated inside the cups.

Table 3. Volume and density of the three groups of molybdenum cups after the experiment.

	Group A	Group B	Group C
Volume (cm^3)	0.1785	0.0692	0.0701
Density (g/cm^3)	2.1229	5.4042	5.3241

To further test the encapsulation of carbon dioxide, a simple chemical reaction was used to set up the following experiments:

$$CaO + CO_2 \xrightarrow{\text{high temperature}} CaCO_3.$$

We placed about 0.15 g of calcium oxide in a molybdenum cup. The controlled tests with and without dry ice were then conducted, after the same HTHP experiments shown in Fig. 2(b), we tested the experimental products respectively, the XRD results are shown in Fig. 3.

From the XRD results in Fig. 3, we can first find that the initial calcium oxide powder was pure and contained no other impurity and the experimental product without adding carbon dioxide was basically consistent with the initial calcium oxide powder, which indicates that the calcium oxide powder did not react in this set of experiment. However, after the addition of carbon dioxide, the peaks of calcium oxide in the experimental products were significantly reduced, while the peaks of calcium carbonate were detected. At the same time, the characteristic peak of boron nitride at $2\theta = 26.7°$ was also detected. This is because we used h-BN to wrap the molybdenum cups, which inevitably contaminated some h-BN powder when we went for XRD experiments and it is also illustrated by the XRD results of the initial calcium oxide powder.

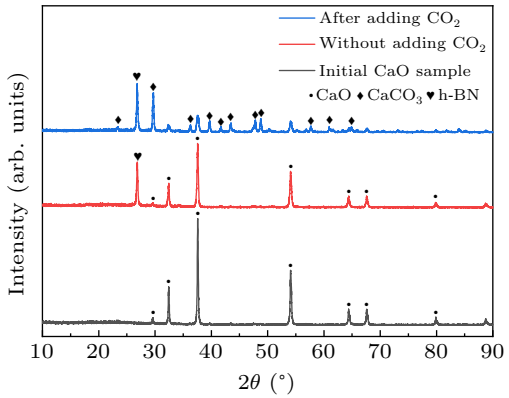


Fig. 3. XRD patterns of the initial powder and samples treated at 5 GPa and 600 °C for 20 min with and without dry ice, respectively.

At last, we conducted an insulation experiment at 5 GPa, 2.2 kW and kept warm for 5 min. We saved the thermoelectric signal data of type K thermocouple inside the cell assembly during the warming process, the thermoelectric signal data is shown in Fig. 4. From this data, we found that the peak temperature of the experiment reached nearly 1300 °C. With the maintenance of the power, the gradual heat absorption temperature of the internal sample decreased, but the temperature was still higher than 1200 °C during the whole insulation process, and no sealing failure occurred during the experiment.

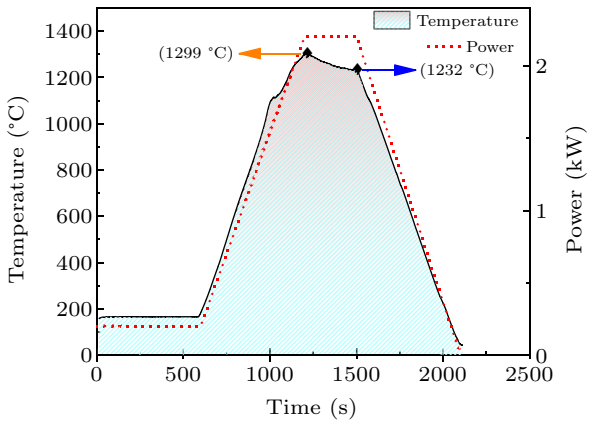


Fig. 4. Thermoelectric signal data of type K thermocouple inside the cell assembly during the warming process.

Through the above experiments, it can be confirmed that we successfully loaded carbon dioxide in the cubic large volume press by the method of liquid nitrogen-assisted freezing and ensured that there would be no sealing failure under the experimental conditions of 5.0 GPa.

4. Conclusion

For the first time, this work successfully loads gas in the large volume press, which provides a new research direction for the HTHP study in the large volume press. Especially in many organic chemistry studies, gaseous organics are involved. In this way, we can experiment with various gases as research objects. At the same time, as carbon dioxide is the most involved in the carbon cycle, we also hope to study the new possibilities of carbon dioxide in high-pressure chemistry through this way in the future. From a thermodynamic point of view, we can even use the same method to encapsulate various liquids into the large volume press experiment. This encapsulation method enables more research in DAC to have industrial application possibilities, which also means that we can explore more industrial production possibilities. Through more in-depth research, we also hope to detect the performance of various gas pressure transmitting medium in the large volume press and look forward to finding a substance with better pressure transfer performance to improve the current large volume press technology.

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