The reactions of CuO at high pressure and high temperature

G Z Ren, T C Zhang, X C Wang, H A Ma, X B Guo, J T Liu and G T Zou

National Laboratory of Superhard Materials, Jilin University, Changchun 130023,
People's Republic of China

Abstract
The decomposition behaviour of CuO is studied at high temperature and high
pressure. Experimental pressure and temperature determine the result. In the
region of higher temperature and pressure ($\geqslant 5.5$ GPa, $\geqslant 1400\,°\text{C}$), the product
is just copper. In the region of lower temperature and pressure (<5.0 GPa,
$<1100\,°\text{C}$), CuO does not decompose. Between the two regions, the product
is a mixture of Cu and Cu_2O or a mixture of Cu_2O and CuO.

1. Introduction

Copper(II) oxide (CuO) is a basic component of many functional materials, such as cuprate
high-temperature superconductors [1]. And the chemical bonding between copper atoms and
oxygen is interesting both as a prototype system by means of which to study the basic chemical
bonding properties of transition metals and oxygen and due to the importance of copper in
bioinorganic chemistry for dioxygen metabolism [2, 3]. The material interatomic distance
changes at high pressure. Pressure tuning is a useful tool for enhancing the rate of discovery of
solid-state materials with improved properties [4]. The T_c of cuprate superconductor increases
with pressure increase [5]. For the cuprate superconductor, the Cu(2)–O(4) distance determines
the performance. Simultaneously, pressure may induce phase transformation of a material and
even chemical reaction. In this condition, the system becomes complex. To investigate this
problem, it is important to investigate the material performance at (high pressure and high
temperature) HPHT. Synthesizing cubic BN with a CuO catalyst, we found particulate Cu in
the samples. And the cBN crystals are transparent. In order to understand the involvement of
CuO in synthesizing cBN crystals, we studied the reaction of CuO at HPHT. We discovered that
CuO decomposes at HPHT. This result will help with understanding the function of pressure
in synthesizing some functional materials with Cu–O chemical bonds.

2. Experimental details

The CuO powder (99%) was pressed into pellets. Around it, high-purity hBN powder
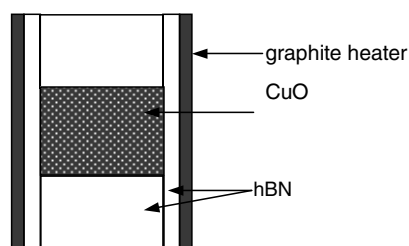(99.8%) was used as an insulator. The sample assembly is shown in figure 1. The high-

Figure 1. The sample assembly.

Table 1. Products at 5.5 GPa and different temperatures.

P (GPa)	T (°C)	t (min)	Results
5.5	$\geqslant 1400$	$\leqslant 2$	Cu
5.5	1200–1400	5–15	Mixture of Cu and Cu_2O
5.5	1100–1200	5–15	Mixture of Cu_2O and CuO
5.5	$\leqslant 1100$	5–15	No decomposition

pressure experiment was carried out using a cubic anvil high-pressure apparatus (DS-029a-type) with a sample chamber of 23 mm. The pressure was given by a calibration curve that was established by determining the applied loads corresponding to the phase transformation pressures of bismuth, thallium and barium. The samples were heated for 2–15 min, then quenched to room temperature.

X-ray diffraction (XRD) data were collected on a D/max-rA diffractometer using Cu Kα radiation.

3. Results and discussion

The XRD patterns of some samples are shown in figure 2. It shows that the product is Cu at 5.5 GPa and 1400 °C and is Cu_2O and Cu under the same pressure but at 1300 °C. And the product is Cu_2O and remanent CuO under 5.2 GPa and at 1400 °C.

Table 1 shows the products at 5.5 GPa and different temperatures. The products over a wider range are shown in figure 3. In figure 3, at a given pressure, the experiment was carried out every 20 °C. The experimental point adopted in figure 3 is the critical point.

From table 1 it is obvious that temperature determines the results at 5.5 GPa. Beyond 1400 °C, CuO decomposes into Cu completely; below 1100 °C, CuO does not decompose; and between these values the products are mixtures. Figure 3 shows that this result holds for a wider range; and pressure has the same action. At 1400 °C, the product is Cu beyond 5.5 GPa, a mixture of Cu_2O and CuO at 5.3 GPa, undecomposed CuO at 5.1 GPa.

Similarly, pressure and temperature affect the reaction velocity. At higher pressure and temperature, the decomposition reaction is very rapid. At 5.5 GPa and 1400 °C, CuO is wholly decomposed into Cu in 2 min. At 5.0 GPa and 1400 °C, there are several red Cu_2O particulates in the black CuO powder, though the time is 15 min. Under 5.5 GPa and at 1200 °C, the serial experiments were accomplished in from 5–15 min. In 5 min, the product is a mixture of Cu_2O and CuO. In the interior of the sample, CuO still exists; however, at the edges of the sample, CuO has turned to Cu_2O. This is due to the different temperatures in the different parts of the sample cell. The temperature inside the sample is lower than that outside the sample. CuO has completely decomposed into Cu_2O after 15 min. The results indicate that
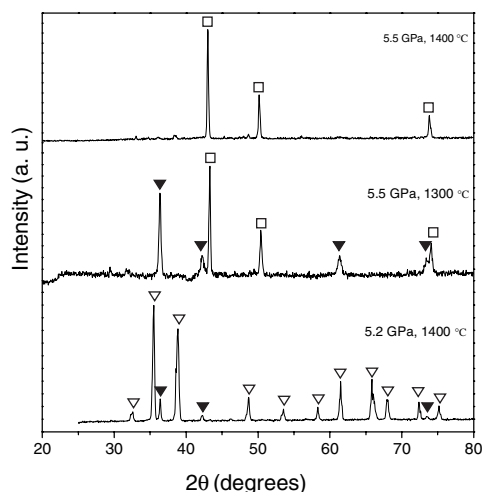
Figure 2. XRD patterns of samples after different pressure and temperature treatments. The peaks of CuO, Cu_2O and Cu are marked by $\triangledown$, $\blacktriangledown$ and $\square$ respectively.
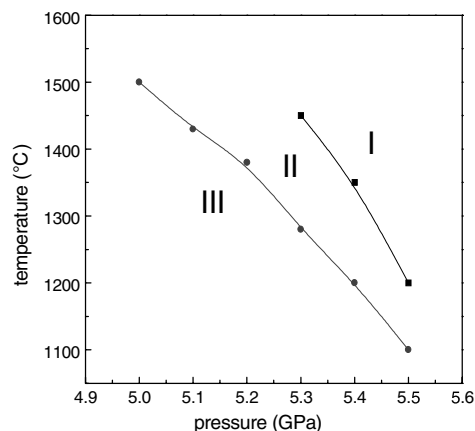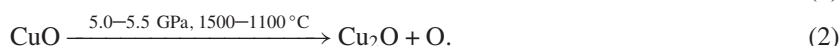
Figure 3. The reaction region of CuO at HPHT. The product in region I is mixture of Cu and Cu_2O. The product in region II is mixture of Cu_2O and CuO. In region III, CuO does not decompose.

the reaction velocity is faster at higher pressure and temperature. At higher pressure, the interatomic distance becomes shorter, so the interatomic action becomes stronger; thus the reaction velocity is faster. At higher temperature, the atom attains a higher excitation energy, which enhances the reaction velocity. The experimental results accord with the basic principle.

Figure 4 shows that there are several millimetre holes in the sample when the main product is Cu_2O. A 'deflating sound' was heard in the experiments producing Cu towards the end of decompression. Although we cannot collect the gas or detect it, the gas must be oxygen from our starting material.

So CuO decomposes at HPHT; the following reaction may take place:

$$CuO \xrightarrow{\text{5.5 GPa, } \geqslant 1400\,°C} Cu + O \tag{1}$$

$$CuO \xrightarrow{\text{5.0--5.5 GPa, } 1500\text{--}1100\,°C} Cu_2O + O. \tag{2}$$

In the chemical reaction, the reaction velocity and product are determined by the change of the Gibbs free energy (ΔG):

$$\Delta G = G_p - G_r \tag{3}$$

$$\Delta G = \Delta U + \Delta V\, P - \Delta S\, T \tag{4}$$

$$d\,\Delta G = \Delta V\, dP - \Delta S\, dT. \tag{5}$$

(Here G_r is the total Gibbs free energy of the reactant and G_p is the total Gibbs free energy of the product. P and T are the reaction pressure and temperature respectively. ΔU, ΔV and ΔS are the change of cohesive energy, the change of volume and the change of entropy respectively.)

The chemical reaction will take place when the value of G_p is smaller than that of G_r ($\Delta G < 0$). At ambient pressure, the pressure effect is negligible; however, it must be considered at high pressure. In the experiment, the reactions (1) and (2) did not take place when the pressure was lower than 5.0 GPa. This suggests that $\Delta G > 0$. It was shown that the action of pressure can make $\Delta G < 0$, so the reaction can take place. The result of the
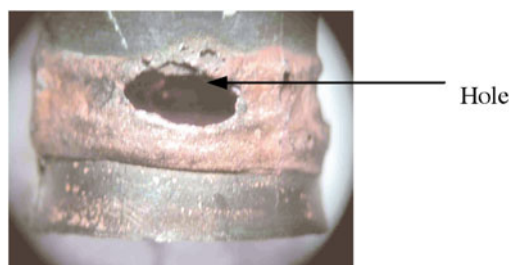
Figure 4. The pattern with several millimetre holes.
(This figure is in colour only in the electronic version)

experiment indicates that CuO decomposes easily with pressure increase. This suggests that the ΔG-value decreases with the rise of pressure, i.e.

$$\partial \Delta G / \partial P|_T < 0; \tag{6}$$

thus,

$$\Delta V = \partial \Delta G / \partial P|_T < 0. \tag{7}$$

Equation (7) suggests that $\Delta V < 0$ in the experiment.

4. Conclusions

CuO decomposes at HPHT. The decomposed reaction of CuO is determined by temperature and pressure. In the region of higher temperature and pressure ($\geqslant 5.5$ GPa, $\geqslant 1400\,°C$), CuO decomposes into Cu. In the region of lower pressure and temperature (< 5.0 GPa, $< 1100\,°C$), CuO does not decompose. Between these two regions, the product is a mixture of Cu and Cu_2O or a mixture of Cu_2O and CuO.

References

[1] Cao Y 1998 *Phys. Rev.* B **58** 11 201
[2] Cox P A 1995 *Transition Metal Oxides* (New York: Oxford University Press)
[3] Tyekar Z 1991 *Chem. Res.* **22** 241
[4] Fernandes A A R 1991 *Phys. Rev.* B **44** 7601
[5] Badding J V 1998 *Chem. Mater.* **10** 2889