

## Utilization of Carbon Dioxide to Synthesize Large Scorodite Particles under Ultrasound Irradiation

粗大なスコロダイト粒子の合成を目的とした超音波照射過程における二酸化炭素の利用

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### 1. Introduction

Arsenic is toxic for the human body. Therefore, waste materials and factory effluents containing arsenic must be treated and stored using the appropriate methods. In mining field, arsenic is commonly found in the form of enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{10}\text{Fe}_2\text{AsS}_{13}$ ) sulfide minerals that are present in the copper ore deposits.<sup>1)</sup> Recently, the highly-concentrated arsenic is accrued by the repeated processing of flue cinder in copper smelting because of the use of low-grade copper ore. Thus, it is required the disposal of the highly-concentrated arsenic in copper smelting. Scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) has been studied as a promising storage material of arsenic.<sup>2,3)</sup> Scorodite releases little arsenic in the acidic solution. Scorodite is synthesized by oxidation in an acidic solution containing divalent iron [Fe(II)] and pentavalent arsenic [As(V)]. A larger particle size is preferred because a low surface-to-volume ratio makes it difficult to dissolve scorodite in an acidic solution. Large scorodite particles ( $>10 \mu\text{m}$ ) are synthesized using stirrer at high temperature ( $>90^\circ\text{C}$ ) for long reaction time (7 h).<sup>2)</sup> Previous study, large scorodite particles were successfully synthesized at low temperature ( $70^\circ\text{C}$ ) for 3 h with  $\text{O}_2$  gas flow using oxidation effect and agglomeration effect of ultrasound irradiation.<sup>4)</sup> However, fine particles ( $<1 \mu\text{m}$ ) were also generated due to the generation of  $\text{O}_2$  fine bubbles during ultrasound irradiation. Thus, we expect agglomeration effect of ultrasound to synthesize large scorodite particles without fine particles generation by ultrasound irradiation. To prevent the fine bubbles generation, we focused on  $\text{CO}_2$ .  $\text{CO}_2$  gas is low vapor pressure ( $20^\circ\text{C}$ :  $\text{CO}_2$  21.6 MPa,  $\text{O}_2$  54.2 MPa) and high solubility [Mole fraction of gas in the water ( $20^\circ\text{C}$ , 1 atm):  $\text{CO}_2$   $6.18 \times 10^{-4}$ ,  $\text{O}_2$   $2.50 \times 10^{-5}$ ].<sup>5)</sup> In this study, we investigated the effect of  $\text{CO}_2$  gas on size and morphology of scorodite particles synthesized using ultrasound irradiation.

### 2. Experimental

The acidic solutions containing As(V) were prepared using  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , and ion-exchange water. Then, Fe(II) solution was added to the As(V) solution. Finally Fe(II)-As(V) solution (50 mL) was adjusted to a Fe/As molar ratio of 1.5. As(V) concentration of the solution was 20 g/L. pH of the solution was adjusted at pH 2.0. Sonication was performed with ultrasonic generators (TA-4021; KAIJO) and submersible transducers (KAIJO). The output and the frequency of the transducer were set to 200 W and 200 kHz. Fig. 1 shows the experimental apparatus of ultrasound irradiation. A submersible transducer was placed at the bottom of a tank filled with water, and a flat-bottom flask containing the solution was placed directly above the transducer. The temperature of the irradiated solution was controlled at  $70^\circ\text{C}$  using hot water circulation around the flat-bottom flask. Sonication for the solution was conducted at  $70^\circ\text{C}$  for 3 h under  $\text{O}_2$  gas (100 mL/min) flow or mixed gas ( $\text{O}_2:\text{CO}_2=80:20$ ) flow (total 100 mL/min). The precipitates from the above process were filtered using a  $0.45 \mu\text{m}$  pore diameter membrane filter. After drying, the precipitates were analyzed using X-ray diffraction (XRD) measurement, scanning electron microscope (SEM) observation.

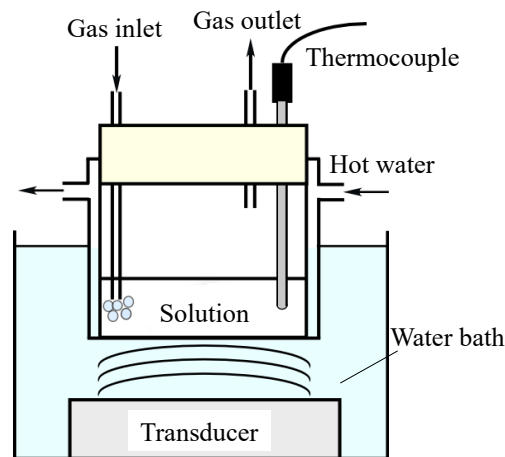


Fig.1 Schematic of the experimental apparatus.

### 3. Results and Discussion

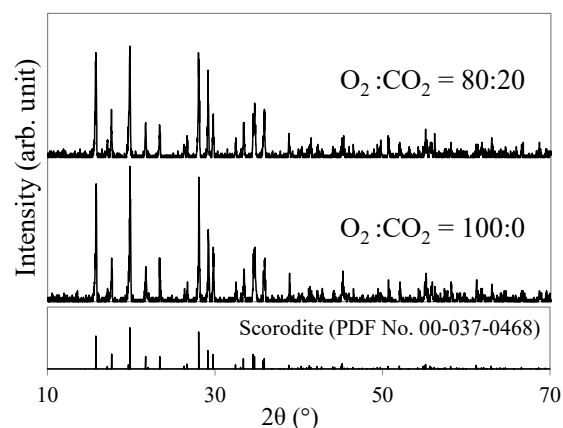
**Fig. 2** shows the XRD patterns of precipitated samples synthesized at 70°C for 3 h using ultrasound irradiation under O<sub>2</sub> gas or mixed gas (O<sub>2</sub>:CO<sub>2</sub>=80:20) flow at 100 mL/min. XRD peaks were identified as scorodite (PDF No. 00-037-0468) at both conditions. Crystallinity values of scorodite synthesized under both conditions were >90%. **Fig. 3** shows the ORP values and yields of scorodite synthesized using each gas. The changes of ORP values ( $\Delta$ ORP) after the reaction using O<sub>2</sub> gas or mixed gas (O<sub>2</sub>:CO<sub>2</sub>=80:20) were 95 mV, 70 mV, respectively and the yields of scorodite synthesized using O<sub>2</sub> gas or mixed gas were 53%, 43%, respectively. The  $\Delta$ ORP and yield were decreased with the increase of content ratio of CO<sub>2</sub> in mixed gas. These low values are unfavorable. **Fig. 4** shows the SEM images of scorodite particles synthesized using each gas. The both sample shapes of particles were polyhedron. Large scorodite particles (>10  $\mu$ m) were observed at both conditions. Under the condition of O<sub>2</sub> gas flow, many amount of fine particles (<1  $\mu$ m) were observed. On the other hand, under the condition of mixed gas flow, the contained ratio of fine particle clearly deceased. Dissolved CO<sub>2</sub> gas in the solution makes the generation of radicals difficult because of the low vapor pressure (20°C: CO<sub>2</sub> 21.6 MPa, O<sub>2</sub> 54.2 MPa) and high solubility [Mole fraction of gas in the water (20°C, 1 atm): CO<sub>2</sub> 6.18 $\times$ 10<sup>-4</sup>, O<sub>2</sub> 2.50 $\times$ 10<sup>-5</sup>].<sup>5)</sup> Therefore, the low contained ratio of the fine particles would come from the prevention of O<sub>2</sub> fine bubbles during ultrasound irradiation.

Thus, we studied on synthesis of large scorodite particles (>10  $\mu$ m) without including fine particles (<1  $\mu$ m) using mixed gas (O<sub>2</sub>:CO<sub>2</sub>=80:20) flow under ultrasound irradiation. However, we found that the CO<sub>2</sub> in the mixed gas causes the significant decrease of yield of scorodite. Therefore, we need to investigate the appropriate condition to synthesize large scorodite particles using CO<sub>2</sub> gas without decrease of yield.

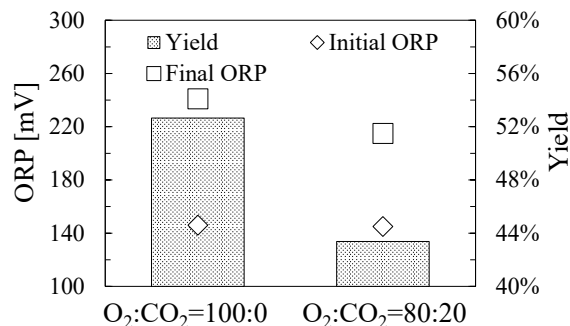
### 4. Conclusion

To investigate the effect of CO<sub>2</sub> on the size and morphology of scorodite synthesized using ultrasound irradiation, we performed the synthesis of scorodite particles at 70°C for 3 h using ultrasound irradiation under O<sub>2</sub> gas or mixed gas (O<sub>2</sub>:CO<sub>2</sub>=80:20) flow at 100 mL/min. We synthesized large scorodite particles (>10  $\mu$ m) without fine particles (<1  $\mu$ m) using mixed gas (O<sub>2</sub>:CO<sub>2</sub>=80:20) flow under ultrasound irradiation. The ratio of fine particles in the synthesized particles is successfully deceased under the

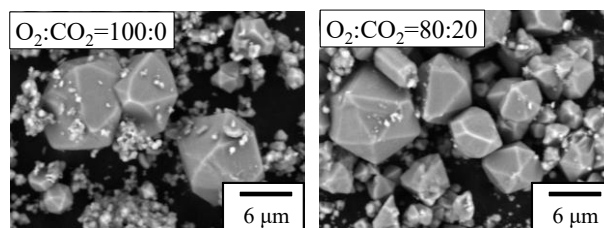
condition of mixed gas flow. However, it caused the decrement of values of the  $\Delta$ ORP and yield with the utilization of mixed gas.



**Fig. 2** XRD patterns of samples synthesized using ultrasound irradiation at 70°C for 3 h under different gas conditions.



**Fig. 3** ORP values of solutions treated by ultrasound and yields of scorodite synthesized under different gas conditions.



**Fig. 4** SEM images of scorodite particles synthesized under different gas conditions.

### Acknowledgment

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