

Development of CO₂ Absorbent with Barium Orthotitanate Ceramics

Yoshinori Saito, Yukio Sakabe
Murata Manufacturing Co., Ltd.

1. Introduction

Coinciding with the increased awareness of environmental problems, Murata Manufacturing Co., Ltd. has promoted "Zero Emissions" activities. Murata has also promoted recycling for ceramic containing wastes. Currently, however, ceramics recycling remains limited to low functionality uses, such as cement aggregates and roadbed materials. To cope with increasing emissions in the future, it is necessary to create high value added functional materials that are recycled. To this end, Murata Materials research & development center has conducted research and development of functional materials using various ceramic waste materials.

The Kyoto Protocol formally came into effect on February 16, 2005. Under the protocol, Japan is obliged to reduce emission of greenhouse gases by 6% on average from 2008 to 2012, relative to emissions in 1990.

The Ministry of the Environment estimated CO₂ emission in Japan in 2003 at 1,255 million metric tons. Thus, CO₂ emission equals 9.84 metric tons per capita. This means that total emissions were up 11.9%, and per capita emissions were up 8.3% from 1990.

As indicated above, CO₂ emissions have increased year after year. Therefore, it is suggested that the practi-

cal application of innovative, next-generation energies is necessary. As an immediate task, it is essential to establish CO₂ separation and recovery technologies.

Various separation technologies were considered for the purpose of CO₂ recovery from flue gases. Among them, for practical application, chemical absorption using amine solutions, for which some pilot plants, have been started. Additionally, research on separation technologies further reducing recovery energy has advanced. Specifically, a CO₂ absorbent based on Li₄SiO₄ ceramics can absorb CO₂ at the relatively high temperature of 600°C. This method invites attention as a new approach for CO₂ separation from reformed gases before combustion.

Barium titanate (BaTiO₃) is a principal material of ceramic capacitors. As shown in Fig. 1, barium orthotitanate (Ba₂TiO₄) is synthesized by adding barium carbonate (BaCO₃) to BaTiO₃. Ba₂TiO₄ has a stable phase at high temperatures, and it becomes unstable in the temperature range of 1000°C or lower. Therefore, we investigated the behaviors of CO₂ absorption and emission by using the reaction shown in Fig. 2, and found that Ba₂TiO₄ can be used as a CO₂ absorbent at high temperatures.

The outline is described below:

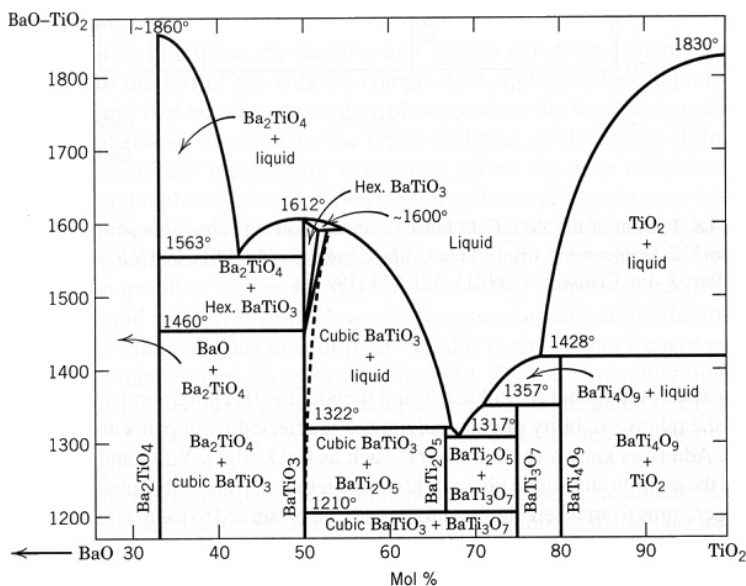


Fig. 1 Barium titanate ceramics phase diagram ⁽²⁾

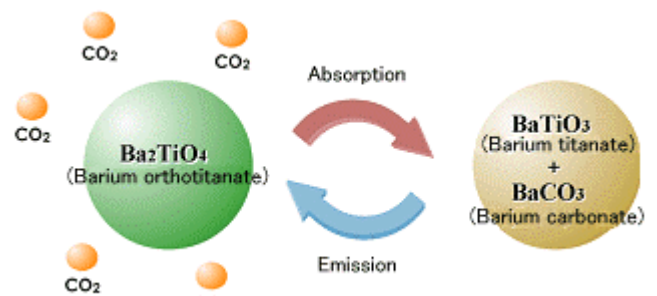


Fig. 2 Absorption and emission of CO₂ from Barium orthotitanate



Fig.3 Appearance of absorbent

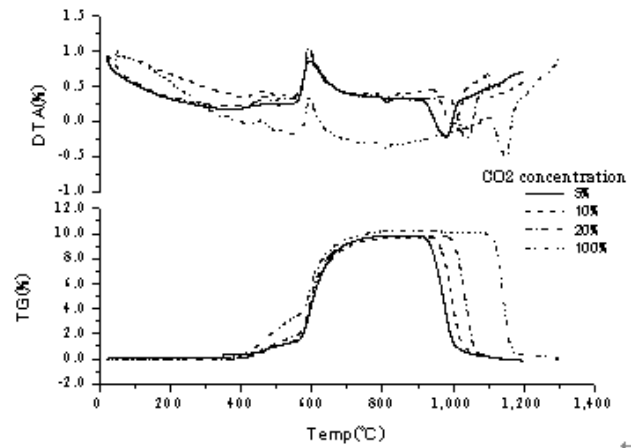


Fig. 4 Absorbing/emitting behavior in various CO₂ concentration atmospheres
Temperature increase rate: 10° C/min

2. Characteristics of Ba₂TiO₄

2.1 CO₂ absorption

Fig. 3 shows appearance of the CO₂ absorbent synthesized from BaTiO₃ dielectric material. Originally, it is white in color, but appears green in color because of influence of the additives in the dielectrics for the ceramic capacitor.

At present, granular samples of 1.5 to 2 mm diameter are used, because evaluation is generally performed with thermal analyzing instruments. However, the absorbent can be formed into the desired shape by granulation or molding.

Fig. 4 shows the CO₂ absorbing behavior of this absorbent in various CO₂ concentration atmospheres, as measured with a Thermogravimetric/Differential Thermal Analyzer

(TG/DTA). The absorbent's weight increased around 400°C due to CO₂ absorption, and the reaction was remarkably accelerated around 600°C. At this stage, almost all of the Ba₂TiO₄ was separated into BaTiO₃ and BaCO₃. As the temperature was further raised, these substances converted to the original Ba₂TiO₄. The emission temperature changed depending on CO₂ concentration, but little influence on the absorbing characteristic was observed.

Further, weight changes were measured at a constant temperature in a 100% CO₂ concentration atmosphere with the same TG/DTA. The result of the reaction speed measurement is shown in Fig. 5. The reaction speed increased rapidly at 600°C, where a reaction speed of 3 to 7%/min was measured. The reaction ratio of this absorbent at a conversion ratio of 1.0 is approximately 10%. Therefore, it is possible to complete the reaction in several minutes at temperatures of 600°C or higher. On the other hand, in a

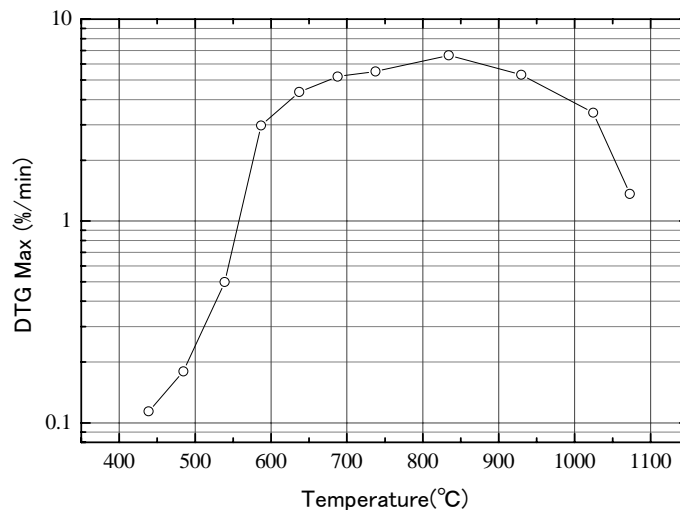


Fig. 5 Relation of temperature to CO₂ absorption speed of barium orthotitanate
Test atmosphere: CO₂ 100%

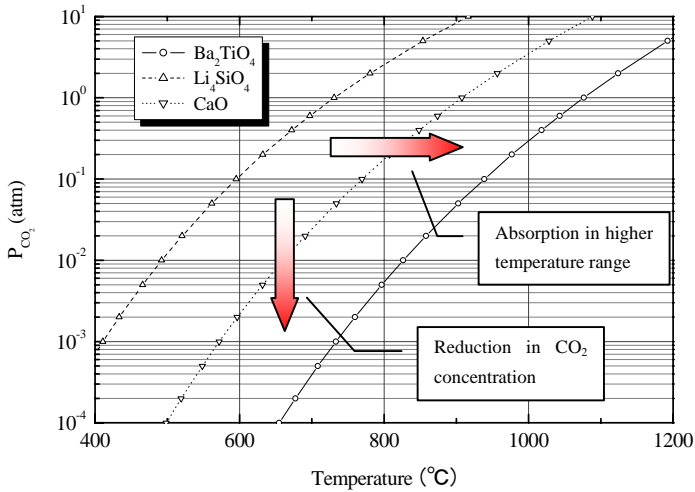


Fig. 6 Comparison of equilibrium CO_2 partial pressures of various absorbents based on thermodynamic calculation

temperature range of 850°C or higher, the reaction speed is decreased because it arrives at the equilibrium rate-determining step due to CO_2 emission.

2.2 Application

For practical use of Ba_2TiO_4 as a CO_2 absorbent, stability over repeated cycles is the most important issue. This absorbent was proved to develop no deterioration after one hundred test cycles. With the above-mentioned Li_4SiO_4 based absorbent, stabilization of the absorbing ratio under repeated use remains a problem to be solved in the future. This aspect, however, is considered to be an advantageous fundamental characteristic of Ba_2TiO_4 . Furthermore, it demonstrates a lesser volume change during absorption than other materials. It is a property of this absorbent that it is subjected to less stress than other materials when absorption and emission are repeated.

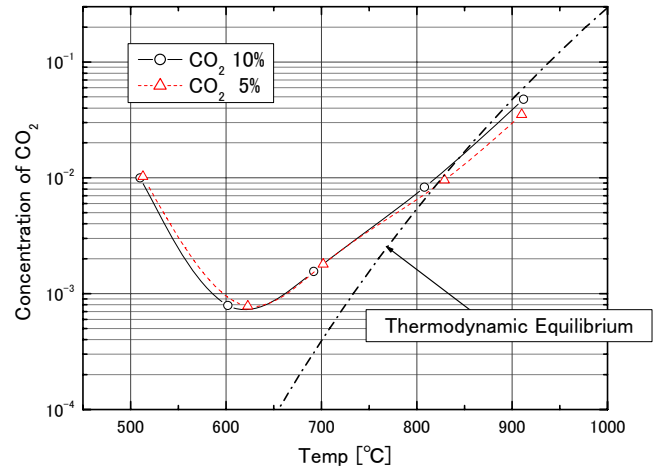


Fig. 7 Relation of process temperature to CO_2 concentration in post-process gas
($\text{SV}2,000\text{h}^{-1}$)

Fig. 6 shows the relationship between various CO_2 absorbent temperatures and equilibrium CO_2 partial pressures based on thermodynamic calculation. CaO and Li_4SiO_4 have been proposed as absorbents that can be used at high temperatures. However, Ba_2TiO_4 enables CO_2 absorption in a completely different range. Since the emission range features high temperatures and low CO_2 partial pressures, the configuration of the entire system is important for reduction of recovery energy. However, when the CO_2 partial pressure is equal, this system enables CO_2 separation from higher temperature gases. In addition, the system can reduce the CO_2 concentration in the post-process gas when it is used at the same temperature. As shown in Fig. 7, when the system is actually charged with CO_2 -containing gas in a temperature range of 500 to 800°C , the CO_2 concentration in the post-process gas can be reduced to 1% or less. Since the CO_2 absorbing rate does not change even in an

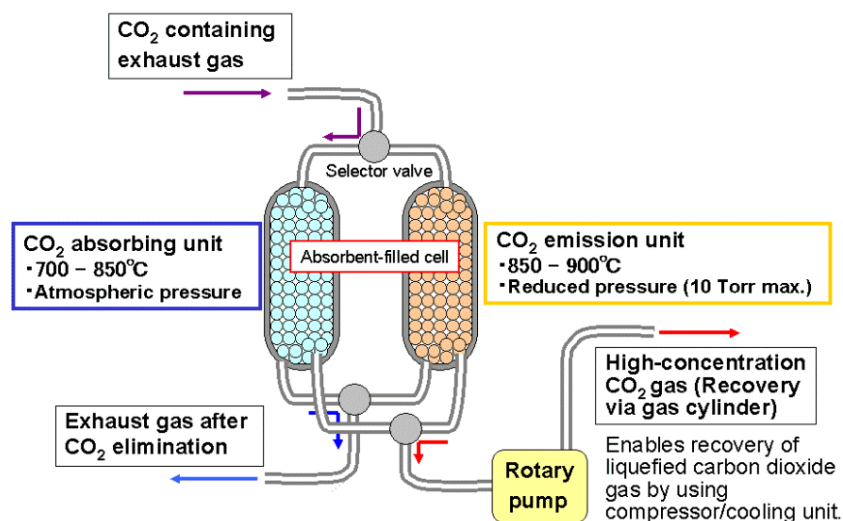


Fig. 8 Outline of CO_2 recovery system

environment containing vapor or hydrogen, this absorbent can effectively eliminate CO₂ from methane steam reformed gas. In this case, as the CO₂ concentration decreases, the shift reaction continues even at high temperatures. It was confirmed that CO concentration is reduced to 1% or less even at a high temperature of 700°C.

Also, low material cost is an advantage of this material because it can be made of industrial grade materials.

3. Future approach for practical use

Fig. 8 shows the outline of the proposed CO₂ recovery system using Ba₂TiO₄. This system can continuously eliminate CO₂ from exhaust gas and enables CO₂ recovery at an extremely high concentration. Since CO₂ is liquefied with a compressor after recovery, various applications can be considered. We are calculating the energy required for CO₂ recovery from flue gas with this system configuration, and expect that the obtained value will be preferable to the performance data on the amine absorption method.

As mentioned above, since CO concentration is considerably reduced by CO₂ separation from reformed gases before combustion, we are now investigating feasibility of a reforming process that needs no CO modifier.

We have confirmed that it offers new characteristics incomparable to other materials as a CO₂ absorbent. We intend to define promising applications of the unique absorbing characteristics of Ba₂TiO₄ in order to promote practical use of this absorbent as a technology that can make contributions to the prevention of global warming.

The above article was re-composed from the contents published in "The Journal of Fuel Cell Technology", a bulletin issued in autumn, 2005.

[Reference]

- (1) Kato, M., et al. "New Series of Lithium-Containing Complex Oxides as a High-Temperature CO₂ Absorbent". Annual Meeting Abstracts of the American Ceramic Society. Indianapolis, USA, 2001, p.69.
- (2) Rase, D.E., Roy, R.: J. Am. Ceram. Soc. 38(1955)102

<Contact us>

Murata Manufacturing Co., Ltd.
Materials Research & Development Center
Functional Materials Research Dept.
Yoshinori Saito
E-mail: saito@murata.co.jp