ISIJ International, Vol. 49 (2009), No. 8, pp. 1259–1264

Effect of Microwave Irradiation on Hydrothermal Treatment of Blast Furnace Slag

Soon-Jae TAE,[1] Toshihiro TANAKA[2] and Kazuki MORITA[3]

1) Formerly Graduate Student at Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505 Japan. Now at R&D Center of Hyundai Steel Corporation, Dangjin-Gun, Chungnam, Korea.
E-mail: sj_steel@hyundai-steel.com 2) Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871 Japan. 3) Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan.

(*Received on October 16, 2008; accepted on April 4, 2009*)

The effect of microwave irradiation on the hydrothermal treatment of blast furnace (BF) slag was investigated using a 2.45 GHz microwave irradiation system. The comparison of the features of a microwave-hydrothermal (M-H) reaction with those of a conventional hydrothermal (C-H) reaction showed that in both these reactions, tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) was formed as the major phase in the treated samples. When the BF slag was hydrothermally treated by the C-H reaction, tobermorite was formed in the vapor state as the major phase at 200°C after a holding time of 48 h; in the M-H reaction, tobermorite was rapidly formed within 3 h at the same temperature. It was elucidated that microwave irradiation promoted the hydrothermal reaction to a significant extent.

Furthermore, effects of microwave irradiation on BF slag subjected to hydrothermal hot-pressing were investigated. After microwave irradiation, the compressive strength of the slag compact and rate of porosity in the compact after treatment increased and decreased, respectively, in comparison with those before treatment. Moreover, microwave irradiation was advantageous over conventional heating at the same temperature in that it enhanced the compressive strength of the BF slag.

KEY WORDS: blast furnace slag; hydrothermal treatment; hydrothermal hot-pressing; microwave irradiation; microwave-hydrothermal treatment; recycling.

1. Introduction

Most of the blast furnace (BF) slag has been well recycled mainly in construction industry, such as cement and concrete, and so on. However, in the past few years, other recycled materials have prominently been used as BF slag, and new applications of BF slags are being considered.[1]

Recently, hydrothermal reactions have been carried out for recycling waste materials. Materials in the hydrothermal reaction are exposed to highly reactive water including high-pressure water vapor and/or a high-temperature aqueous solution.[2] The reaction is carried out at low temperatures (below 300°C) that can be controlled using waste heat exhausted from the iron and steelmaking process.[3] Therefore, in a previous study, we investigated the hydrothermal reaction of BF slag and reported that calcium silicate hydrate (C-S-H) and tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) were formed as the main phases.[4] In addition, we found that the optimum conditions for the formation of tobermorite (the vapor state) in the hydrothermal treatment of BF slag were a temperature of 200°C and duration of 48 h.

Microwave processing has several advantages over conventional heat processing methods,[5] and it has been widely used in the processing of materials. In previous studies, we focused on the application of microwave irradiation to the treatment of waste slags and refractories.[6–9]

Hydrothermal reactions involve water as a catalyst at elevated temperatures. In addition, microwaves are absorbed directly by water, and the use of microwaves yields a higher heating rate than that achieved by using a conventional heating system. Hence, when microwave irradiation is carried out along with the hydrothermal reaction, some synergy effects may be produced. However, the effects of microwaves on hydrothermal reactions have not been investigated satisfactorily.

Hydrothermal hot-pressing (HHP) is a method by which a hard compact can be produced from powders in a short time and at relatively low temperature under saturated vapor pressure.[10] It was recently reported that BF slag could be hydrothermally solidified by HHP.[11–13] The HHP treatment of BF slag showed that crystal water and a large amount of water were present in the compact. If microwaves influence water in the compact, we can not only irradiate BF slag compact effectively using microwaves but also improve the properties of this compact.

The objective of this study is to investigate the effect of microwave irradiation on the hydrothermal reaction of BF slag and compare the features of a microwave-hydrothermal (M-H) reaction with those of a conventional hydrothermal

(C-H) reaction. Furthermore, the effect of microwave irradiation on HHP-treated BF slag compact is investigated.

2. Experimental

2.1. Materials

Actual water-quenched BF slag was used in the experiments; its chemical composition in shown in **Table 1**. Before the treatment of samples used in the experiments, X-ray diffraction (XRD) was used to confirm their glass structure.

Table 1. Chemical composition (mass%) of blast furnace slag.

SiO_2	CaO	Al_2O_3	MgO	Others
34.5	43.2	14.0	4.5	3.8

2.2. M-H Reaction

The M-H reaction was carried out in a MARS-5 microwave system (CEM, USA), as shown in **Fig. 1**. The system operates at a frequency of 2.45 GHz, and it can operate at 0 to 100% of its maximum power (1 600 W). Distilled water and BF slag powder (≦125 μm) were placed in lined vessels (10 mL/g); each lined vessel is double-walled, having a Teflon inner lining and enclosed in an Ultem polyetherimide shell. The pressure and/or temperature of the entire assembly could be controlled, with the maximum pressure being 40 atm. The temperature inside the vessels was measured using a optical fiber probe. The C-H reaction experiments were carried out in an autoclave in an electric furnace. Details of the apparatus and experimental method are provided in our previous paper.[4] In most M-H and C-H experiments performed in this study, the samples were hydrothermally treated in vapor state, on the basis of previously obtained results.[4]

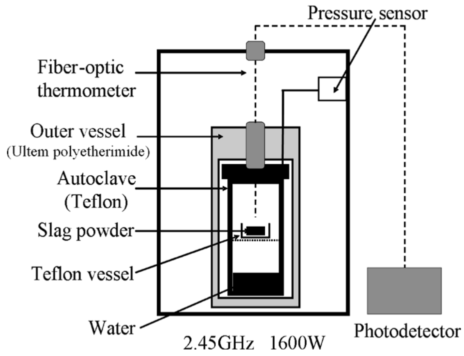

Fig. 1. Schematic diagram of experimental apparatus.

After the experiments, the samples were characterized by powder XRD. Scanning electron microscopy/energy-dispersive X-ray (SEM-EDX) analysis was carried out for characterizing and observing the morphologies of products of C-H and M-H treatments. The degree of crystallization was then estimated by the internal standard method using TiO_2 as the internal standard and a glassy synthesized slag and synthesized tobermorite as the matrix.

2.3. HHP Treatment of BF Slag Powder

The BF slag was subjected to the HHP process developed by Yamasaki *et al.*[10] Detailed descriptions of the experimental apparatus and procedure are available elsewhere.[12,13] The BF slag was ground and sieved such that its particle diameter was less than 125 μm. BF slag powder (2 g) was mixed with distilled water (0.4 g) and charged in an HHP autoclave with an internal diameter of 20 mm. After this mixture was pressed at 40 MPa, the autoclave was heated to 300°C and maintained at this temperature for 60 min. After the HHP treatment, the autoclave was cooled down to room temperature, and the morphologies of the obtained compacts were examined by XRD and SEM-EDX analyses.

2.4. Microwave Irradiation of HHP-treated BF Slag Compact

HHP-treated BF slag compacts were subjected to 2.45 GHz microwave irradiation. The experimental apparatus used in the microwave irradiation is shown in **Fig. 2**. A commercial microwave furnace (Model XJ-03MK100, Panasonic Semiconductor Discrete Devices Co., Ltd., Japan) was used in the 2.45 GHz irradiation experiment. The samples were charged in the furnace, and the temperature inside the furnace was measured using a sheathed thermocouple placed in the furnace as shown in Fig. 2. In addition, SiC granules were used as an auxiliary heat source (so-called hybrid microwave heating) in the furnace to ensure the heating of the samples to high temperature.[9] In contrast, conventional heat treatment experiments were carried out in a SiC electric resistance furnace.

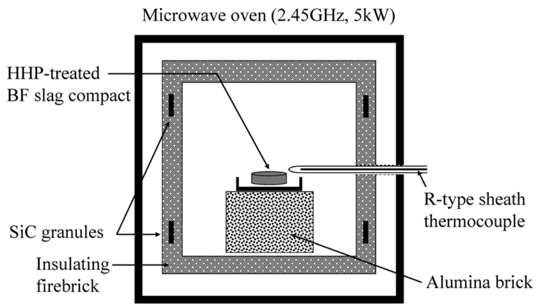

Fig. 2. Experimental apparatus for 2.45 GHz irradiation (hybrid heating).

After heat treatment, the compacts were characterized by XRD and SEM-EDX analyses. In addition, they were subjected to a compressive strength test. The test was performed by following the Japanese Industrial Standard JIS-A 1108 for testing the compressive strength of concrete.

3. Results and Discussion

3.1. Behavior of BF Slag after M-H Treatment

The M-H treatment of BF slag in the vapor state was carried out at 200–230°C for 1–10 h in distilled water. XRD patterns of BF slag and treatment products are shown in **Fig. 3**. These results show that the treatment of the BF slag resulted in the formation of the tobermorite phase after a holding period of 8 h at 200°C. Further, tobermorite was completely formed after a holding period of 5 h at 230°C. Clearly, the formation of tobermorite in the BF slag proceeded significantly by increasing the temperature of the M-H reaction.

It was also observed that the ratio of the amount of tober-

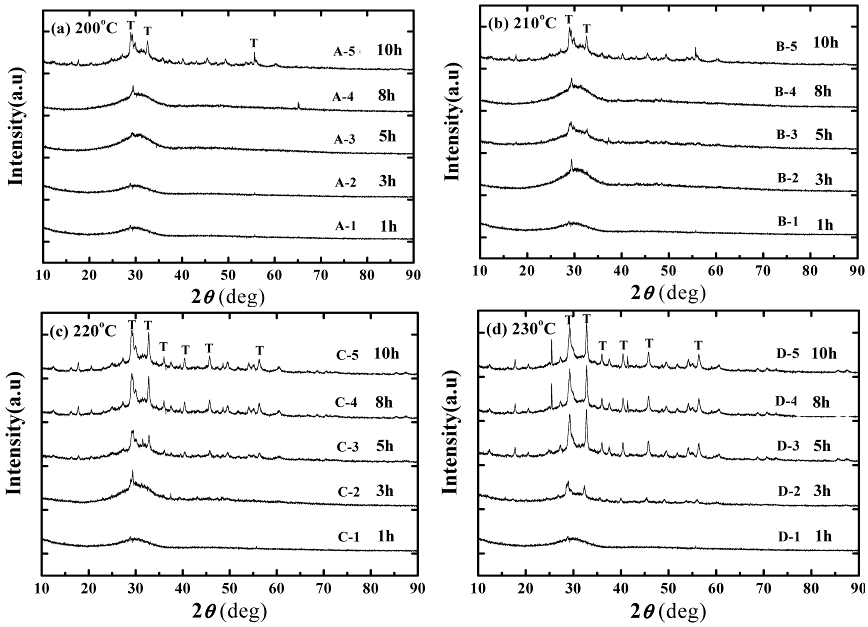

Fig. 3. XRD patterns of hydrothermally treated BF slag under microwave irradiation (T: tobermorite).

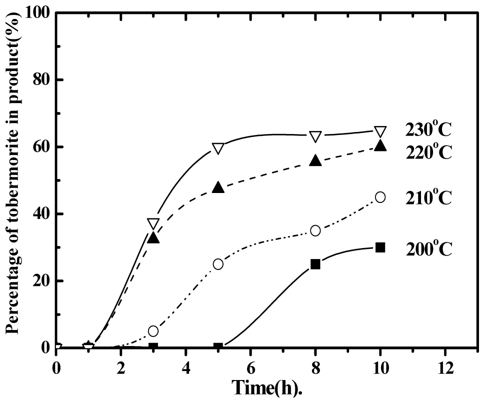

Fig. 4. Percentage of tobermorite in products of M-H treatment of BF slag.

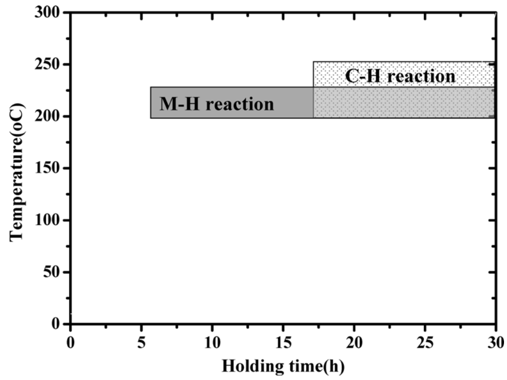

Fig. 5. Formation region of tobermorite in BF slag by hydrothermal reaction.

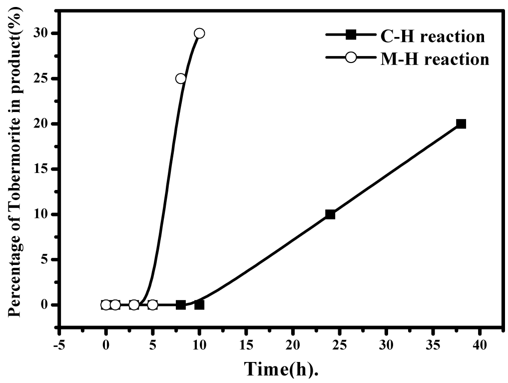

Fig. 6. Percentage of tobermorite in products of C-H and M-H reactions (200°C).

morite to the total amount of products tended to increase with increasing holding time and temperature. **Figure 4** shows the amount of tobermorite formed by the M-H reaction, determined by the quantitative XRD analysis. Powdered raw materials of the BF slag still remained as an amorphous phase after the treatment, but 30% of the tobermorite was formed after 10 h at 200°C. Furthermore, with increasing temperature (230°C), the percentage of tobermorite increased to 65% for the same holding time.

In previous studies,[4] it was reported that the C-H treatment had no effect on the phase transformation of the BF slag when samples in the liquid state were placed in distilled water at 300°C for more than 60 h; however, when samples were placed in distilled water at 200°C for 48 h, C-S-H and tobermorite were formed in the vapor state. In contrast, in the M-H reaction, tobermorite was rapidly formed within 8 h at the same temperature. **Figure 5** shows the dependence of the regions in which tobermorite is formed in the BF slag in the M-H and C-H reactions on holding time and temperature.

The results of the C-H reaction were similar to those of our previous study.[4] Further, **Fig. 6** shows XRD results of the percentage of tobermorite obtained by the C-H and M-H reactions at 200°C.

Although hydrothermal reactions are very versatile, one of their main drawbacks is their slow kinetics at any given temperature. When the BF slag was hydrothermally treated by the C-H reaction, tobermorite was formed at 200°C for a holding time of 48 h in vapor state with distilled water, as shown in Fig. 5. However, from Figs. 3 and 5, it can be ob-

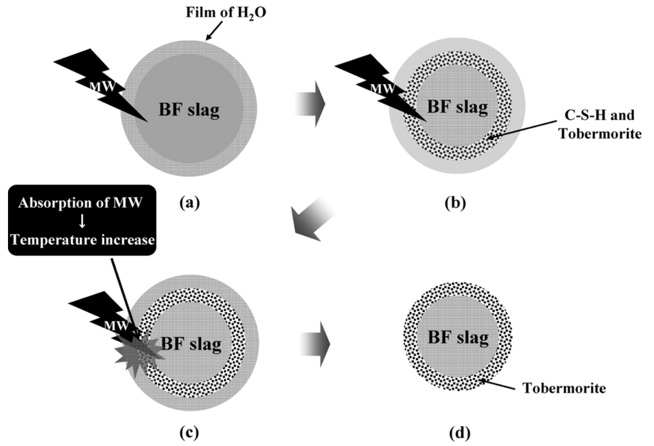

Fig. 7. Schematic diagram of hydrothermal reaction of BF slag under microwave irradiation.

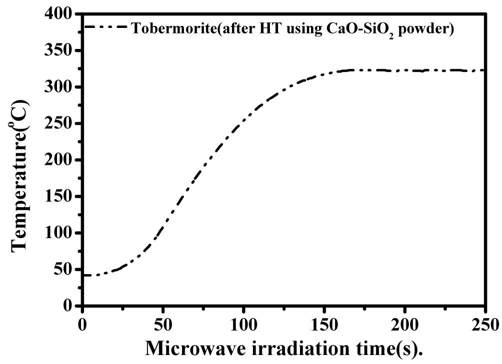

Fig. 8. Heating curves of tobermorite synthesized by microwave irradiation.

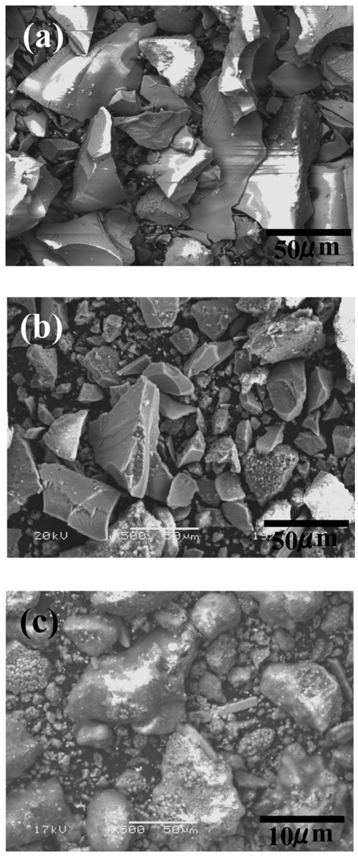

Fig. 9. Morphology of BF slag (a) before C-H reaction, (b) after C–H reaction, and (c) after M–H reaction (200°C).

served that microwave irradiation during the hydrothermal treatment of the BF slag enhanced the formation of tobermorite, thereby increasing the reaction rate and kinetics of the reaction. In addition, from Fig. 6, it is apparent that the percentage of the major phase in the M-H reaction was better than that in the C-H reaction even though both the reactions were carried out at the same temperature.

On the basis of the obtained results, we explain the effect of microwave irradiation on the formation of tobermorite in the BF slag as follows. **Figure 7** shows the schematic diagram of the hydrothermal treatment of BF slag subjected to microwave irradiation. First, it was predicted that the temperature in the autoclave increases rapidly due to the property of water that it efficiently absorbs microwaves. The setup temperature was attained within 10 min. Then, a water film was formed over each slag powder and the hydrothermal reaction occurred between the slag and the water film as shown in Figs. 7(a) and 7(b). Accordingly, supersaturated water films were formed on C-S-H and tobermorite as shown in Fig. 7(b). The abovementioned prediction is supported by the results of our previous study.

On the basis of the fact that C-S-H and tobermorite contain an H_2O phase, it was predicted that this phase could efficiently absorb microwaves. To confirm that the H_2O phase could absorb microwaves effectively, synthesized tobermorite was heated in the 2.45 GHz microwave irradiation system and the temperature of tobermorite was measured. The corresponding heating curve is shown in **Fig. 8**. The temperature increased above 300°C within 3 min. This rapid increase in the temperature of synthesized tobermorite without any addition is cleared that synthesized tobermorite can be heating itself and tobermorite can be absorb the microwave. Therefore, when the C-S-H phase and tobermorite are formed over the slag particles as shown in Fig. 7(b), tobermorite absorbs the microwaves and its temperature is higher than those of other reaction products, as shown in Fig. 7(c). It can be observed that the absorption of microwaves by tobermorite enhances the kinetics of the hydrothermal reaction.

Figure 9 shows the SEM images of the sample particles. Original slag particles have a rough surface because of pulverization. After the C-H treatment, the slag surface was found to be covered by a layer of reaction products; however, only a part of the slag underwent the hydrothermal reaction. In contrast, after the M-H treatment, most of the slag surface was covered by a layer of hydrothermal reaction products and a spherical form was observed. It was also relative to the percentage of tobermorite in the reaction products, as shown in Fig. 6.

3.2. Microwave Irradiation on HHP-treated BF Slag Compact

The BF slag powder was solidified after being subjected to HHP treatment at 300°C for 1 h. **Figure 10**(a) shows the XRD patterns of the HHP-treated BF slag compact. Although the major phase is regarded to be of the glass structure of the BF slag, tobermorite is identified as the only hydrothermal phase. Further, SEM results of the microstructure of the slag are shown in Fig. 10(b). The hydrothermally

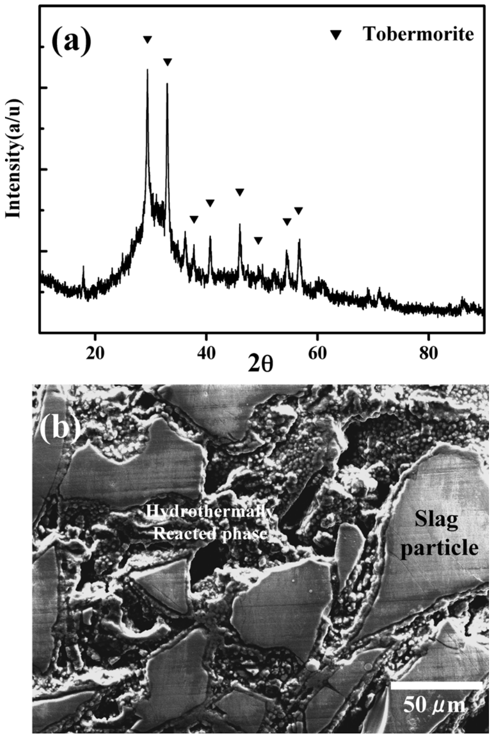

Fig. 10. (a) XRD patterns of BF slag and (b) microstructure of slag compact after HHP treatment at 300°C for 1 h.

Table 2. Treatment conditions, temperatures, and corresponding products.

	300°C	600°C	900°C
Conventional heating	T	T	T
Microwave irradiation	T	T	CAS

T: Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) CAS: $2CaO \cdot Al_2O_3 \cdot SiO_2$

reactive tobermorite phase fills up the intragrain space in slag particles.

To gain a better understanding of the microwave irradiation on the HHP-treated BF slag compact, samples were subjected to microwave irradiation and conventional heating. The XRD patterns of samples maintained at a controlled temperature for 30 min are shown in **Table 2** and **Fig. 11**. In both the heat treatments (300 to 900°C) without microwave irradiation (which was carried out at 900°C), the crystalline phase did not appear within 30 min of treatment. Crystalline phases such as $2CaO \cdot Al_2O_3 \cdot SiO_2$ (CAS) were formed by microwave irradiation at temperatures above 900°C, as shown in Fig. 11. Kuroki *et al.*[9] reported that the crystalline $CaO–SiO_2–Al_2O_3$ phase of the slag could not be irradiated by the 2.45 GHz microwaves. However, the H_2O phase formed in the slag by HHP treatment caused the acceleration of heating by microwave irradiation.

Figure 12 shows the relation between the temperature and the shrinkage of the BF slag compact. In the case of heating by both electric furnaces and microwave irradiation, an increase in the shrinkage was observed with an increase in temperature. In the case of microwave heating, shrinkage of approximately 90% was observed at 300°C

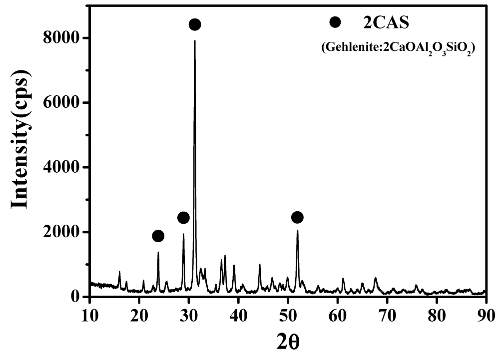

Fig. 11. XRD pattern of slag compact after 2.45 GHz irradiation at 900°C.

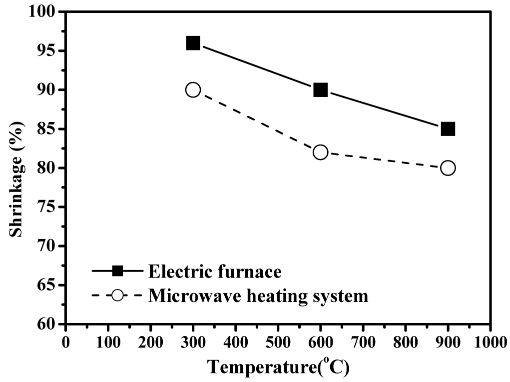

Fig. 12. Shrinkage ratio of compact after treatments.

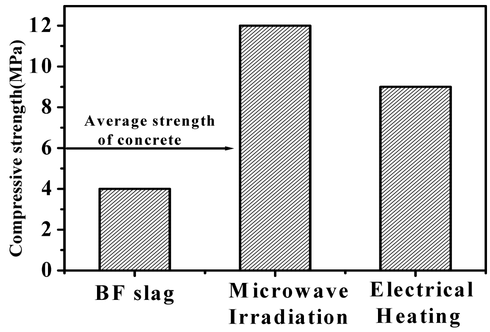

Fig. 13. Measured compressive strength of HHP-treated BF slag compact before and after treatments.

and shrinkage of approximately 21% was observed at 900°C. From these results, it can be concluded that both conventional heating and microwave heating cause the densification of the compact.

However, the BF slag compact that is more density than an electric furnace is obtained though it is a low temperature in case of the microwave (600°C in an electric furnace and the microwave 300°C in case of the shrinkage rate 90%). It can be predict that the escape revolt respondent of H_2O is promoted from the water heat aspect of the solidification inside of the body part by internal heating of the microwave, and the low temperature, short time is thought to be an occurrence of making more density of compact from an electric furnace.

The compressive strength of the BF slag compact was measured, and samples were heated to 900°C by both conventional heating and microwave heating. The measured compressive strengths are shown in **Fig. 13**. The average compressive strength of the compact before treatment was 4 MPa, which was smaller than that of concrete (6 MPa). However, the average compressive strength of the compact after conventional heating was 8 MPa, which was larger than those of concrete and green BF compact. In addition, the microwave irradiation on the BF slag increased its compressive strength to 12 MPa. Therefore, it can be concluded that microwave irradiation increased the compressive strength of the BF slag by approximately 25%, as shown in Fig. 13. Hence, BF slag compact subjected to microwave irradiation can possibly be used as a construction material, particularly in applications where materials with high compressive strengths are required.

In conclusion, microwave irradiation was advantageous over conventional heating in that it promoted the densification of BF slag compact.

4. Conclusions

The effects of microwave irradiation on the hydrothermal reaction of BF slag and HHP-treated BF slag compact were investigated. The results of the investigation are as follows.

(1) Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) was the major phase formed in BF slag subjected to hydrothermal treatment, and microwave irradiation increased the hydrothermal reaction rate by one to two orders of magnitude. In addition, the ability of tobermorite to absorb microwaves could play an important role in increasing the kinetics of hydrothermal reactions.

(2) In the cases of both microwave heating and conventional heating treatments, the compressive strength of BF slag compact and the rate of porosity in the compact after treatment increased and decreased, respectively, compared to those before treatment. However, microwave irradiation was advantageous over conventional heating in that it promoted the densification of the compact.

Acknowledgement

The authors would like to thank Dr. Masashi Nakamoto and Dr. Takeshi Yoshikawa, Division of Materials and Manufacturing Science, Osaka University, for their help with the experimental setup of hydrothermal hot-pressing experiments.

REFERENCES

1) M. Fujiwara: *Bull. Iron Steel Inst. Jpn.*, **8** (2003), 883.
2) T. Yoshikawa, M. Hosokawa and T. Tanaka: *ISIJ Int.*, **48** (2008), 557.
3) T. Akiyama and J. Yagi: *Tetsu-to-Hagané*, **82** (1996), 177.
4) S.-J. Tae and K. Morita: *ISIJ Int.*, **47** (2007), 1813.
5) K. Morita: *Bull. Iron Steel Inst. Jpn.*, **10** (2005), 485.
6) K. Morita, M. Guo, Y. Miyazaki and N. Sano: *ISIJ Int.*, **41** (2001), 716.
7) K. Morita, M. Guo, N. Oka and N. Sano: *J. Mater. Cycles Waste Manage.*, **4** (2002), 93.
8) T. Yoshikawa and K. Morita: *Mater. Trans.*, **44** (2003), 772.
9) T. Kuroki, Y. Uchida, H. Takizawa and K. Morita: *ISIJ Int.*, **47** (2007), 592.
10) N. Yamazaki, K. Yanagisawa, M. Nishioka and S. Kanahara: *J. Mater. Sci. Lett.*, **5** (1986), 335.
11) M. Nakamoto, J. Lee, T. Tanaka, J. Ikeda and S. Inagaki: *ISIJ Int.*, **45** (2005), 1567.
12) S. Sato, T. Yoshikawa and T. Tanaka: *ISIJ Int.*, **47** (2007), 245.
13) S.-J. Tae and K. Morita: *CAMP-ISIJ*, **19** (2006), 224.