IMPROVEMENTS OF STRENGTH OF REFRACTORY BRICKS BY CNF COMPOSITENESS

Yoshinori Matsuo[1], Li Wei[1], Masato Tanaka[2], Jin Miyawaki[3], Isao Mochida[4], Seong-Ho Yoon[1,3]

[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University
[2]Technical Research Laboratories, KROSAKI HARIMA Co.
[3]Institute for Material Chemistry and Engineering, Kyushu University
[4]Art, Science and Technology Center for Cooperative Research, Kyushu University

Introduction

The interest on MgO–C refractories for steelmaking application has been resumed and the improvement of their properties is of great concerns.[1-3] These refractories have been developed due to their excellent thermal shock and slag corrosion resistance for application in steel industries such as converters, electric arc furnaces and steel treatment ladles.[4,5] However, demands for high productivity increase casting amount of scraps, causing a problem of severe damage on the MgO-C refractory bricks, which are lined at a charging wall of the converter furnace. Therefore, to minimize maintenance and repair periods of the damaged MgO-C refractory bricks, improvement of strength of refractory is highly required.

To improve the strength of refractory, the addition of a small amount of additives to form a second bonding should be an effective approach. Such concept has been experimentally demonstrated in this work, in which MgO/carbon nanofiber (MgO/CNF) composites were used as the second bonding to improve the strength of MgO-C refractory. We found that the specially designed CNF-MgO composite could improve the strength of MgO-C bricks by twice through the only 1.5 wt% additions.

Experimental

Three kinds of MgO/CNF composites were synthesized by chemical vapor decomposition over MgO supported catalysts. The catalyst composition and growth conditions are summarized in Table 1.

Table 1. Preparation conditions of three kinds of MgO/CNF composites

Samples	Catalyst (wt/wt)	Carbon Source	Growth temperature (°C)	Yield (times)
KNF003	Fe/Mo/MgO (2/24/100)	CH_4	900	0.87
FN64MgO	Fe/Ni/MgO (48/32/20)	CO	670	19.5
CoCrMgO	Co/Cr/MgO (6/2/2)	C_2H_4	560	19.5

MgO-C refractory bricks were made by mixing the magnesia material, graphite, antioxidant agent, phenolic resin and MgO/CNF composites, followed by pressing at 250 °C and 120 MPa for 5 h. The bricks were further heated at 1400 °C. The strain of brick was measured at 1400 °C or after cooled down to room temperature.

Results and Discussion

Fig. 1 shows the typical SEM images of MgO/CNF composites. The MgO nanoparitcles were closely wrapped by the fine CNFs to form an aggregated particle with the mean diameter of some micrometers. Such aggregated particle was highly fleecy, and should have reversible elasticity to withdraw the pressure pressing, as illustrated in Fig. 1b.

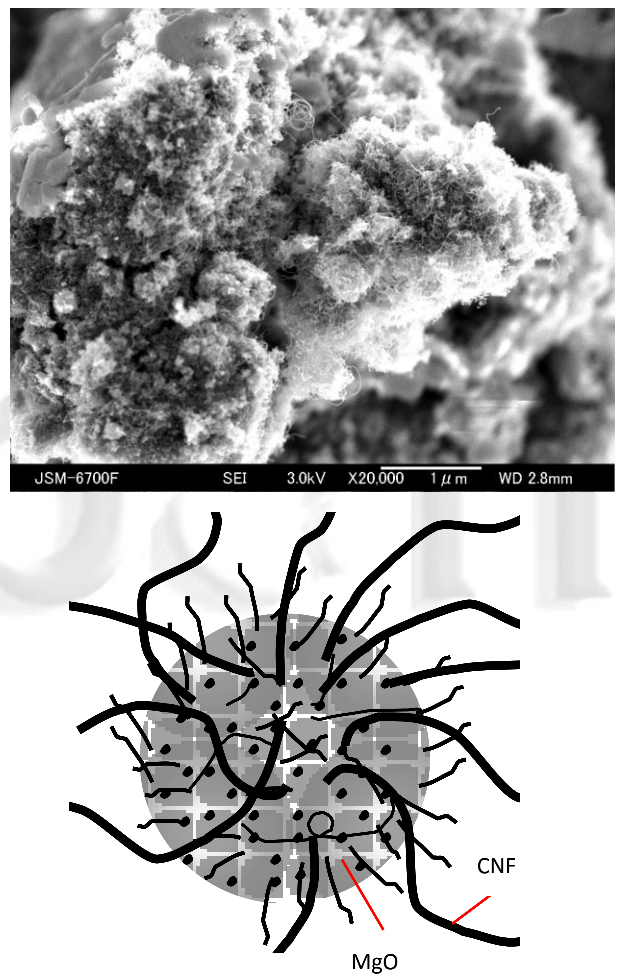

Fig. 1 Typical SEM image and schematic illustration of the MgO/CNF (KNF003) composite

Fig. 2 depicts the stress-strain curves of bricks with different MgO/CNF composites at 1400 °C and room temperature. At 1400 °C, addition of any MgO/CNF composite into bricks caused remarkable increase of strain compared to the blank sample. However, the increase of strain was at the cost of stress decreasing for the samples of

FN64MgO and CoCrMgO. Only the sample with the addition of KNF003 showed a both increase in the strain and stress. After cooling to room temperature, similar stress-strain relations with those at 1400 ^{o}C were obtained. The brick with the addition of 1.5% KNF003 showed two times increase both in its stress and strain, while the strain for samples of FN64MgO and CoCrMgO increased at the cost of significant decrease of stress.

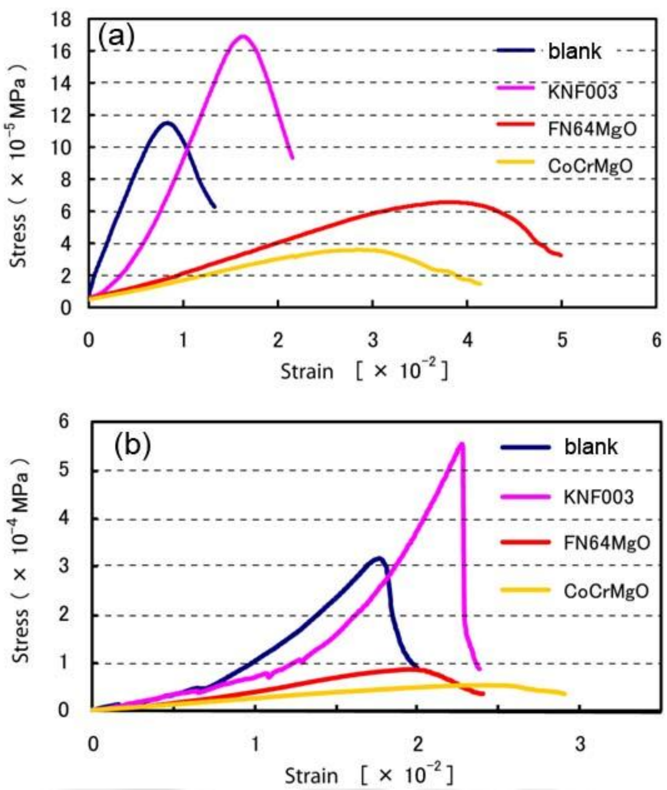

Fig. 2 The stress-strain curves of bricks with and without addition of MgO/CNF composites at the 1400 ^{o}C (a) and room temperature (b). Contents of MgO/CNF in bricks were 1.5 %.

Fig. 3 shows the SEM images of a brick with the addition of KNF003. We found that the MgO/CNF composites were distributed in the matrix, and formed voids of hundreds nanometer size between CNFs intertwined with each other.

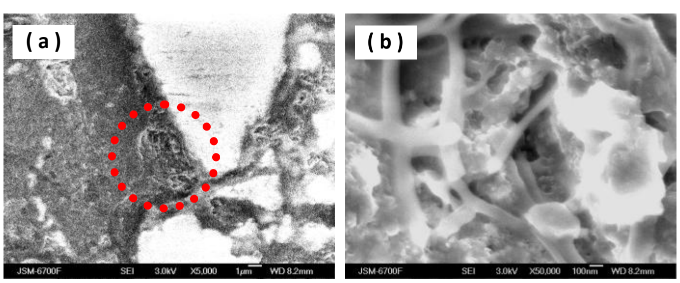

Fig. 3 SEM images of bricks with addition of 1.5% KNF003 at low (a) and high (b) magnifications.

Based on the SEM results, we propose a model to explain an improvement of stress by the addition of KNF003 as follows. Without the MgO/CNF addition, a shock induces crack formations mainly at the matrix instead of hard magnesia aggregate, which progressively advance to deep into the brick, giving rise to eventual break down. On the other hand, in case of with the MgO/CNF addition, there are the voids of hundreds nanometer size in MgO/CNF. When the cracks reach to such voids, elastic CNF networks would act as a shock-absorber to scatter and release the applied stress, and thus the progress of cracks to deep part of the brick would be relieved. The relaxation of crack progress could increase the strength of the overall MgO-C brick.

From TEM and STM observations, we found that CNFs are composed of two kinds of structural units, nano-rod and nano-plate (data not shown). KNF003 was composed of long nano-rod units, but the structural unit of FN64MgO or CoCrMgO was nano-plate or short nano-plate, respectively. The long nano-rod structural unit of KNF003 is considered to give fewer amounts of defects compared with short nano-rod or nano-plate unit, thus should be stronger than others. According to the aforementioned model, the scattering of the applied stress by the CNF networks suppresses the progressive crack developments. Therefore, the CNFs of KNF003 with the high mechanical strength could show the high stress as shown in Fig. 2. For FN64MgO (nano-plate) and CoCrMgO (short nano-rod), however, CNFs would be broken down upon the stress application due to an insufficient strength, and then the progress of cracks would be accelerated. This may result decrease of the brick strength.

Conclusion

MgO/CNF composites were used as an additive to improve the strength of MgO-C refractory brick. Two times increase both in stress and strain were achieved when MgO/CNF having the long nano-rod structural unit was added. A mechanism of the stress improvement by the MgO/CNF addition was proposed based on the microscopic observations of the MgO/CNF mixed brick. The present results would greatly improve the creep or spalling resistance and operation life of refractory brick.

References

[1] Brant PORC, Limm WA, Grocener C A. Development of high erosion and corrosion resistant MgO–C bricks for BOF application. In UNITECR'93 Proceedings, ALAFAR, Sao Paulo, Brazil, 1993, pp. 462–71.

[2] Lubaba NG, Rand B, Brett NH. Microstructure and strength of MgO–carbon composite refractory materials. Trans.Br. Ceram. Soc., 1989, 89, 47–54.

[3] Hanagiri S, Harada T, Fugihara S. Effects of the addition of metal and CaB6 to magnesia carbon bricks for converters. Taikabutsu Overseas, 1993, 13, 20–27.

[4] Naruse Y, Fujimoto S, Kamata Y, Abe M. Results of investigation of mag-carbon bricks used in converter. Taikabutsu, 1983, 3(2), 3–7.

[5] Nagai B, Matsumura T, Hosogawa K, Geji M, Magnesia carbon bricks for hot steel ladles. Taikabutsu, 1986, 38(3), 207–209.