

REPORT

Magnesia-Spinel Brick with Good Coating Property for Cement Rotary Kiln

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Abstract

The formation of a stable coating layer on bricks relined at the burning zone in cement rotary kilns is one of the important factors for enhancing the durability of refractories. By investigating samples of magnesia-spinel brick obtained from a cement rotary kiln as well as carrying out simulative experiments on liquid slag penetration into brick, it was clarified that stability of the coating layer is influenced by the anchor effect realized by penetration of cement clinker liquid phase into brick with a tendency for the cement clinker liquid phase to penetrate mainly into the micropores of magnesia-spinel brick. Based on the simulative experiment result in which liquid phase penetration into magnesia coarse grain was influenced by the type of magnesia raw material, a new magnesia-spinel brick, ELK-8X-1, was developed by implementing an improved coating property.

1. Introduction

Cement, a base material used for construction of buildings, dams, bridges or tunnels, is indispensable for our life at present. Large amounts of waste products and by-products generated in a variety of industries are utilized as alternative raw materials or fuel in the cement rotary kiln, which is an important facility for cement production. In this regard, it can also be said that the cement rotary kiln plays an important role in the reduction of environmental pollution¹⁾. Since temporary cessation of rotary kiln operation caused by virus troubles influences not only cement production but also reduces reduction of waste treatment, stable operation of the rotary kiln is highly desirable.

Since the maximum temperature at the burning zone in cement rotary kilns is roughly 1450 °C, the thermal load to relined refractories is severe²⁾, and

refractories relined at the burning zone tend to be corroded under severe circumstances. Build-up of an adherent material layer, so called as the coating layer, which is formed on relined bricks, protects the working surface of the bricks and prevents corrosive damage. In addition, since temperature distribution in relined bricks is eased by the thermal insulation effect of the coating layer, mechanical equipment of cement rotary kiln, such as the steel shell or kiln supporting rollers, are guarded from high temperature. In short, the coating layer plays an important role in stable cement rotary kiln operation and a good coating property is thought to be one of the essential characteristics of refractory brick used in the cement rotary kiln.

ELK-8X-1, a new magnesia-spinel brick for the cement rotary kiln, was developed by implementing knowledge attained by examining the coating layer formation mechanism.

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2. Mechanism of Coating Layer Formation

2.1 Investigation of bricks used in cement rotary kiln

Improvement of the coating property of cement rotary kiln bricks by examination of the coating layer formation mechanism have been conducted³⁻⁵⁾ because it is so important to kiln stability during the operation. Much information on the reaction between relined bricks and cement clinker in the early stage of coating layer formation was attained by this investigation. However, other aspects in coating layer formation have not been examined at full length. The authors investigate bricks obtained from the burning zone in a cement rotary kiln once again⁶⁾, the time, focusing on the brick surface on which the coating layer is formed.

A densified layer can be observed directly under the working surface along with unchanged original brick structure in the deeper region in Fig. 1, which is an image of the microstructure at the working surface area of a chrome-free magnesia-spinel brick obtained from the burning zone in cement rotary kiln is shown. Fig. 2 shows an SEM image of part of the densified layer circumscribed with red dotted line in Fig. 1. The many tiny white colored regions with high brightness are micropores into which liquid phase derived from cement clinker has penetrated while reacting with the original brick components.

Penetration of cement clinker liquid phase into the relatively large size pores cannot be observed here. The mechanism of coating layer formation has been surmised as is illustrated in Fig. 3, based on observation results on the obtained brick.

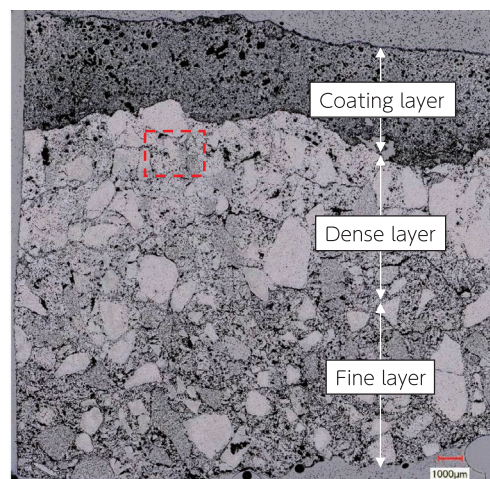


Fig. 1 Microstructure of chrome-free magnesia-spinel brick retrieved from burning zone⁶⁾.

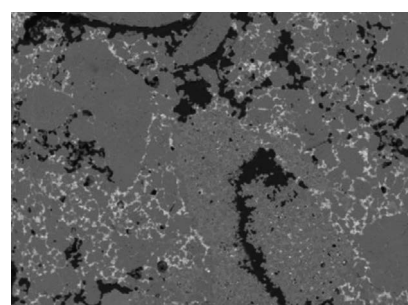


Fig. 2 SEM image of densified layer⁶⁾.

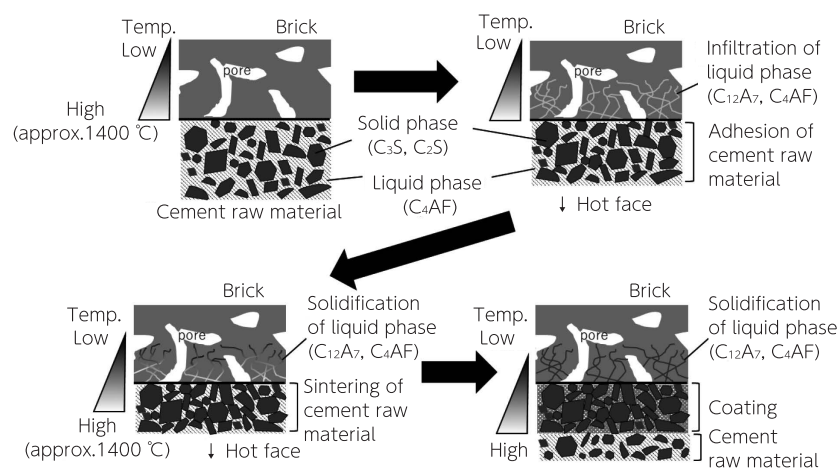


Fig. 3 Schematic diagram of coating layer formation on working surface of brick.

The mechanism is described in four steps as follows:

- (1) Semi-melted cement clinker contacts brick surface.
 - (2) Liquid phase contained in cement clinker penetrates in brick through micropores, and the cement clinker of which the liquid phase has been absorbed into the brick adheres to the brick surface.
 - (3) Because of the temperature distribution in the relined brick, the penetrated liquid phase gradually solidifies in accordance with the penetration depth into the brick. In association with further depletion of liquid phase, cement clinker adhering to the brick surface becomes bulky by sintering.
 - (4) When the brick surface is covered with sintered bulky cement clinker, namely, the newly formed coating layer, the temperature in the brick is lowered by the thermal insulation effect of the coating layer, which promotes completion of liquid phase solidification. Since the solidified liquid phase is entrenched in the micropores or grain boundaries as if spreading roots, the coating layer is stabilized by the anchor effect^{3,4)}.
- In above surmised coating layer formation mechanism, it is inferred that penetration of the liquid phase in the cement clinker into the relined brick plays an important role. The liquid phase has the unique tendency of penetrating so as to fill micropores preferentially.

2. 2 Brick dipping test in cement clinker liquid phase

In order to examine the penetration behavior of cement clinker liquid phase into bricks which were observed in investigation work on bricks retrieved from the burning zone in a cement rotary kiln, reproduction of liquid phase penetration into brick was carried out with a laboratory experiment⁷⁾. That is, a sample specimen of new magnesia-spinel brick which was similar to a retrieved brick was dipped into melted synthetic slag in a platinum crucible in a vertical type electric furnace. As shown in Table 1, the chemical composition of the synthetic slag

Table 1 Chemical composition of synthetic slag used in dipping test

	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃
mass%	2	17	4	51	26

Table 2 Dipping test conditions

Ambient temperature during dipping process / °C	1400
Dipping time / s	30
Dipping depth / mm	10
Preheating temperature before dipping / °C	1230
Preheating time before dipping / s	1200



Fig. 4 Cross section of dipping test sample⁷⁾.

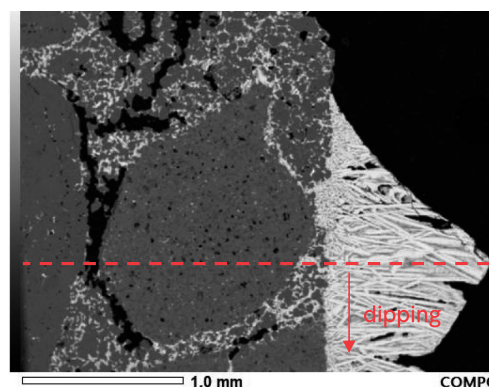


Fig. 5 SEM image of dipping test sample near melted slag surface⁷⁾.

imitated that of cement clinker liquid phase, namely, ferrite phase (C₄AF). 10 mm of a brick sample tip, which was preheated to 1230 °C was dipped into melted synthetic slag, of which the temperature was kept at 1400 °C, for 30 seconds. The experimental conditions are summarized in Table 2.

Fig. 4 shows a cross section of dipping test sample. The penetrating liquid phase is observable

not only in the dipped area of the brick sample but also in the undipped area of the brick sample, which was above the melted slag surface. SEM image of a dipping test sample near the melted slag surface is shown in Fig.5. The white colored regions with high brightness correspond to the areas into which liquid slag has penetrated. Penetration of liquid slag into micropores is clarified in SEM image, but liquid slag penetration into the black colored large pores is not observable in the image. Since the dipping test results are quite similar to observation results on the obtained brick, it is inferred that liquid slag penetrated with a similar mechanism described in the previous sub-section. The fact that liquid slag penetration is observed in the undipped area of the brick above the liquid slag surface indicates that slag penetration is driven by capillary force.

2. 3 Influence of type of magnesia raw material on liquid phase penetration

Penetration of cement clinker liquid phase into magnesia-spinel brick, which plays an important role in coating layer formation, was reproduced in the dipping test. The influence of type of magnesia raw material on liquid phase penetration was investigated by preparing test brick samples made of solely magnesia, the major raw material of magnesia-spinel brick. The major specifications of the two types of magnesia raw materials used for test brick samples are compared in Table 3. Magnesia raw material A is a typical high purity magnesia which is commonly blended in chrome-free magnesia-spinel brick. Magnesia raw material B, of which the starting material and fabrication process differ from those of magnesia raw material A, exhibits slightly inferior

Table 3 Major specifications of two types of magnesia raw material

		Magnesia Raw Material A	Magnesia Raw Material B
Apparent porosity / %		0.9	4.3
Bulk density / -		3.43	3.29
Chemical composition / mass%	MgO	98.6	97.2

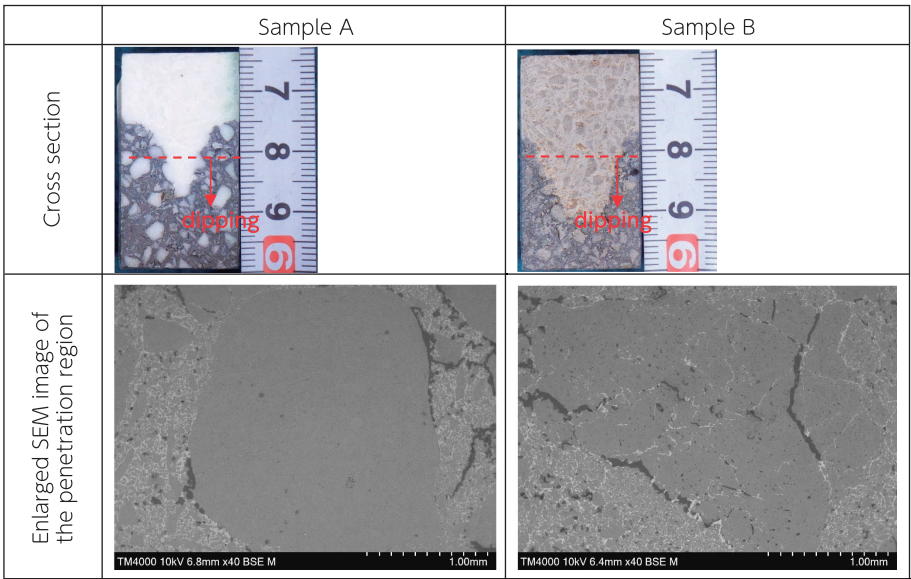


Fig. 6 Cross section near slag surface and SEM images of liquid slag infiltration area of test brick samples A and B.

purity and physical properties. The magnesia brick test samples were named sample A and sample B. Particle size distribution of the blended material, as well as fabrication conditions, were adjusted so as to duplicate those of chrome-free magnesia-spinel brick commonly used for cement rotary kiln. Dipping test of these two test brick samples was conducted with similar experiment conditions to those summarized in Table 2. After the dipping test, the magnesia brick test samples were halved for visual and SEM observation of the cross sections.

Fig.6 compares the cross sections near the synthetic slag surface and SEM images of the liquid slag penetration area of test brick samples A and B. No significant differences are observed between the cross section photographs of samples A and B. That is, a similar manner of liquid slag penetration can be observed in dipping test of in both magnesia-spinel brick samples A and B. There was liquid slag penetration at the undipped area of both test brick samples above melted slag surface. Liquid slag penetration into micropores can be observed in SEM image of both samples A and B. However, a clear difference between samples A and B can be observed in the manner of liquid slag penetration into the coarse grains. That is, no liquid slag penetration into the coarse grains can be observed in sample A. While, liquid slag penetrates and fills pores in the coarse grains in sample B. In summary, despite no difference in liquid slag penetration into micropores existing in the brick matrix between samples A and B, slag penetration into the coarse grains in sample B was more marked than that in sample A.

3. New Magnesia-Spinel Brick with Good Coating Property, ELK-8X-1

Based on knowledge attained by a series of investigations on the penetration of cement clinker liquid phase into brick, a new chrome-free magnesia-spinel brick, ELK-8X-1, in which conventionally blended magnesia raw material A was replaced with magnesia raw material B, was developed. The aim of the investigation was to improve the coating property. The major specifications of ELK-8X-1 are

shown in Table 4, and an exterior cross section of ELK-8X-1 is shown in Fig. 7.

Penetration of cement clinker liquid phase into brick plays an important role in coating layer formation with its anchor effect^{3,4)}. It is inferred that cement clinker liquid phase penetrates only into the micropores in matrix but not into magnesia A in conventional magnesia-spinel brick, resulting in insufficient anchor effect for coating layer formation. A reinforced anchor effect which is combinedly materialized by liquid phase penetration into micropores in the matrix and liquid phase penetration into magnesia B coarse grains is expected to improve coating formation in newly developed magnesia-spinel brick, ELK-8X-1.

Fig. 8 shows the exterior appearance of ELK-8X-1 which was relined in the burning zone so as to cover 1.0–1.5 of L/D (L: distance from clinker outlet point, D: diameter of cement rotary kiln) in the cement

Table 4 Major specifications of ELK-8X-1

		ELK-8X-1
Apparent porosity / %		14.8
Bulk density / -		3.02
Cold crushing strength / MPa		42
Chemical composition / mass%	MgO	90.1
	Al ₂ O ₃	7.5



Fig. 7 Cross section of ELK-8X-1.

rotary kiln and has experienced high thermal load for half-year. After half-year operation, relined ELK-8X-1 exhibited a healthy appearance with no severe damage.

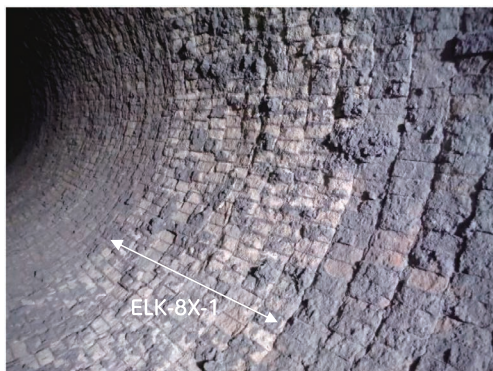


Fig. 8 Exterior appearance of ELK-8X-1 used at 1.0–1.5 of L/D in cement rotary kiln for half-year.

4. Conclusion

It was clarified by this investigation work on the mechanism of coating layer formation on relined bricks in the cement rotary kiln that stable coating layer formation is influenced by the anchor effect created by penetration of cement clinker liquid phase into brick. In conventional magnesia-spinel brick, however, such anchor effect is insufficient because of no liquid phase penetration into magnesia coarse grain occurs. A new chrome-free magnesia-spinel brick, ELK-8X-1, was developed by blending a different type of magnesia raw material into which effect of the liquid phase penetration is highly advantageous. The improved coating property was realized through a reinforced anchor effect which is a result of liquid phase penetration into both micropores in the matrix and into magnesia coarse grain.

References

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