

Preparation of CaO-Al₂O₃-SiO₂ system glass from molten blast furnace slag

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Abstract: To use the potential heat of molten blast furnace slag completely, a CaO-Al₂O₃-SiO₂ system glass (MSG) was prepared from the molten industrial slag. The corresponding method proposed in this study utilized both slag and its potential heat, improving the production rate and avoiding the environmental pollution. Using appropriate techniques, an MSG with uniform color and superior performances was produced. Based on the experimental results and phase diagram, the chemical composition of MSG by mass is obtained as follows: CaO 27%-33%, SiO₂ 42%-51%, Al₂O₃ 11%-14%, MgO 6%-8%, and Na₂O+K₂O 1%-4%. Thermodynamic processes of MSG preparation were analyzed, and the phases and microstructures of MSG were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that alkali metal oxides serve as the fluxes, calcium oxide serves as the stabilizer, and alumina reinforces the Si-O network. XRD and SEM analyses show that, the prepared MSG displays the glass-feature patterns, the melting process is more complete, and the melt viscosity is lowered with an increase in calcium oxide content; however, a continuous increase in slag content induces the crystallization of glass, leading to the formation of glass subphase. The optimum content of molten slag in MSG is 67.37wt%. With respect to bending strength and acid/alkali resistance, the performance of MSG is better than that of ordinary marble.

Keywords: industrial wastes; slag; glass; thermodynamics; microstructure; waste utilization; heat recovery

1. Introduction

With the rapid development of steel industry in China, the amount of slag discharged from blast furnaces has been increasing, leading to an accumulation of ~150 million tons and covering an area of 1000 km². To deal with the problem of increased slag discharge, a large amount of money has been spent on building the discharging fields and railway lines, wasting huge amounts of resources. In other countries, the utilization of blast furnace slag started from the mid-20th century, whereas it has been introduced to China in the 1980s. At present, all the discharged slag is used up as resources in some developed countries in Europe and America; however, the utilization ratio of slag in our country is about 90% [1]. Although the molten slag is a potential source of heat energy, this energy is lost during the process of water quenching. The temperature of molten slag discharged from blast furnaces is in the range of 1400-1600°C, yielding 1.8 1873 MJ/t energy (equivalent to 64 kg standard coal). Although this energy can be recovered through some industrial

techniques, these may cause water waste and add the pollution, and the recovery rate is relatively low, limiting their application [2-3]. In these heat recovery methods, the potential heat of molten slag is recovered through a cooling medium during the close contact process, which is reserved by heat recovery boiler. Therefore, this process of heat recovery is associated with a great waste, such as water waste, leading to the reduced utilization of molten slag.

Preparation of glass from slag started in the late 1950s. However, slag glass (SG) is prepared from slag and not from molten slag; thus, it is obvious that the potential heat of molten slag is not utilized. For making full use of the potential heat of molten slag, a CaO-Al₂O₃-SiO₂ system glass (MSG) was derived from the liquid industrial slag in this study. Use of appropriate reactions, preheating accessories, and feeding systems resulted in a more complete glass melting process and a transparent and uniform-colored MSG with fewer defects. So far, the fine chemicals were used as raw materials for producing glass. However, producing an MSG from molten blast furnace slag by utilizing both slag

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and its potential heat would bring great economic and social benefits for the country. Besides, the same benefits could apply to the use of copper slag [4].

2. Experimental

The main raw materials used included blast furnace slag, quartz, potassium feldspar, and sodium carbonate. The slag used was derived from a steel plant in Tangshan, Hebei Province, and its chemical composition is given in Table 1.

Since the total content of calcium oxide, alumina, and silica in the blast furnace slag was up to 85wt%, and the content of magnesia was much less than that of calcium ox-

ide, the ternary CaO-Al₂O₃-SiO₂ system was mainly investigated in this study, while the MgO-Al₂O₃-SiO₂ system served as a reference. Owing to a special needle-shaped crystal structure, β -wollastonite shows the excellent mechanical properties, hardness, abrasive resistance, and chemical corrosive resistance [5]. If it serves as the main phase, the glass formed will show the significant improvement in fracture toughness, abrasive resistance, and alkali resistance. Therefore, the main phase should be selected near β -wollastonite, and the temperature of eutectic point should be as low as possible so as to reduce the glass melting temperature.

Table 1. Chemical composition of blast furnace slag

										wt%
SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	Fe ₂ O ₃	FeO	K ₂ O	Na ₂ O	Others	
32.88	15.41	37.98	8.76	0.86	0.79	0.48	0.33	0.32	2.29	

In the ternary phase diagram of CaO-Al₂O₃-SiO₂ system, the eutectic point of tridymite, β -wollastonite, and anorthite is 1170°C, while that of gehlenite, β -wollastonite, and anorthite is 1265°C. Thus, the formulas of MSG are determined near these areas. In this system, the composition of MSG by mass is as follows: 40wt%-55wt% SiO₂, ~10wt% Al₂O₃, 20wt%-30wt% CaO, and 4wt% Na₂O [6-7], as shown in Table 2.

At first, in order to imitate the discharging process taking place in a factory, the blast furnace slag was melted in corundum crucibles at 1500°C for 1.5 h in an air atmosphere. Then, according to the formulas, the molten slag was poured into the preheated accessory, which was held at 1500°C for

2 h in air. Finally, the molten glass, which was produced in bulk, was poured into a preheated iron mold, followed by annealing at 600°C for 1 h. A flow diagram describing the whole process is shown in Fig. 1.

Table 2. Composition of MSG

					wt%
Number	Blast furnace slag	Potassium feldspar	Quartz	Sodium carbonate	
1	52.52	8.04	35.63	3.81	
2	59.91	3.53	32.15	4.41	
3	67.37	3.99	24.38	4.27	
4	74.73	0.53	20.03	4.71	
5	82.15	0	13.13	4.72	

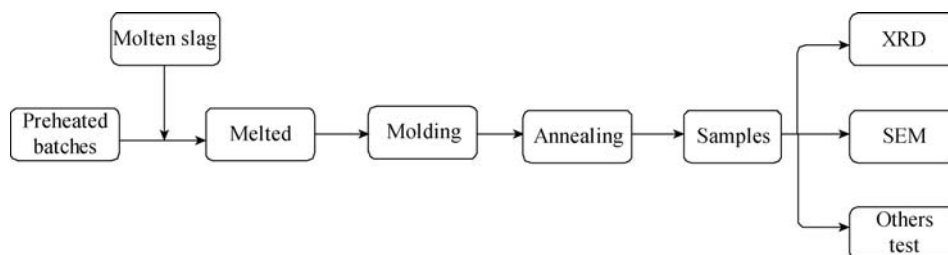
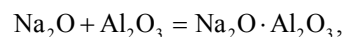


Fig. 1. Flow diagram of the experimental process.

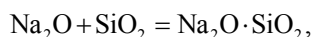
3. Analysis and discussion

3.1. Thermodynamics of glass formation

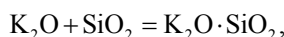
A series of physical-chemical reactions take place in the molten blast furnace slag during the melting process, forming a complicated glass melt. The reactions in this process are endothermic, that is, the reaction rate increases at higher temperatures, which are as the following equations.



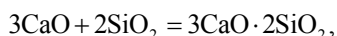
$$\Delta G = -331.18 + 0.05388T \text{ (kJ/mol)} \quad (1)$$



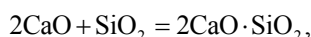
$$\Delta G = -237.7 + 0.00883T \text{ (kJ/mol)} \quad (2)$$



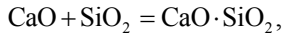
$$\Delta G = -279.9 + 0.00046T \text{ (kJ/mol)} \quad (3)$$



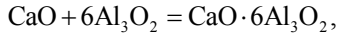
$$\Delta G = -236.8 + 0.0096T \text{ (kJ/mol)} \quad (4)$$



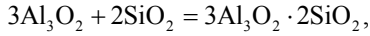
$$\Delta G = -118.8 + 0.01137T \text{ (kJ/mol)} \quad (5)$$



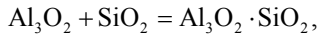
$$\Delta G = -92.5 + 0.00257T \text{ (kJ/mol)} \quad (6)$$



$$\Delta G = -16.38 - 0.037587T \text{ (kJ/mol)} \quad (7)$$



$$\Delta G = -8.6 - 0.017417T \text{ (kJ/mol)} \quad (8)$$



$$\Delta G = -8.8 + 0.003897T \text{ (kJ/mol)} \quad (9)$$

The relationships between Gibbs free energy (ΔG) and temperature (T) of various oxides of MSG are illustrated in Fig. 2.

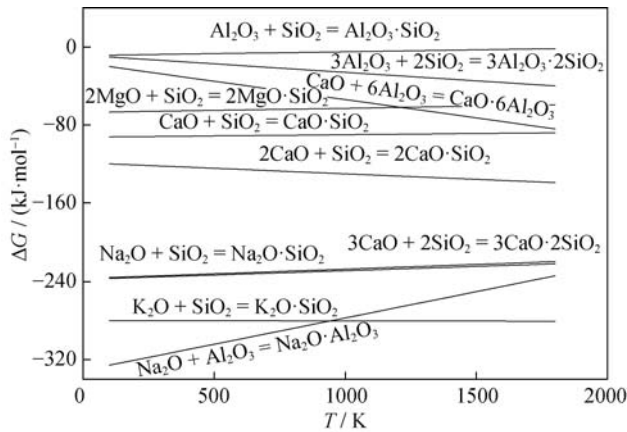


Fig. 2. ΔG - T diagram of glass melting.

(1) Alkali metal oxides

Among all the alkali metal oxides served as fluxes during the melting of glass, silica is more active, as shown in Fig. 2. Ions, such as Na^+ and K^+ , which are derived from the oxides of sodium oxide and kalia, fill the holes of glass network during its melting; on the other hand, the free oxygen atoms, which are released from the broken Si-O bonds, cause low viscosity, leading to the easy melting of glass. The alkali metal oxides are good fluxes; however, the thermal expansion coefficient of MSG increases, the mechanical strength and the thermal and chemical stability decrease with an increase in the contents of alkali metal oxides [8]. Hence, the content of alkali metal oxides in MSG is increased from 1wt% to 4wt%.

(2) Alkali earth metal oxides

Among the alkali earth metal oxides served as stabilizers in glass melting, the reactivity of silica varies greatly, mainly depending on the atom ratio of Ca/Si, as shown in Fig. 2. The migration rate of Ca^{2+} ions in glass melt is relatively high, which decreases the viscosity of melt, acceler-

ating the glass melting and clarification processes. Although the calcium oxide in MSG acts as a good stabilizer, which improves its chemical stability and mechanical properties, the viscosity of glass melt increases rapidly with a decrease in temperature when the calcium oxide content is too high, leading to an increase in the brittleness of glass during annealing [9]. Therefore, it is necessary to design a suitable annealing system.

(3) Alumina

The extent of reaction between silica and alumina, which can reinforce the network of glass melt, is low. Alumina is an intermediate oxide. When the ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ by mass is greater than 1, the aluminum-oxygen tetrahedron and silicon-oxygen tetrahedron will associate with each other, forming a continuous network. Otherwise, the octahedral aluminum will enter the holes of the Si-O network [10]. Alumina not only reduces the crystallization tendency of MSG, but also improves the chemical and thermal stability, mechanical strength, and hardness. However, it also increases the viscosity of MSG. Therefore, the alumina content is increased from 10wt% to 15wt%.

To sum up, the alkali metal oxides served as fluxes, were easy to react with silica, which caused the Si-O network breaking and led to the glass melting easily; the extent of reaction between silica and calcium oxide, which served as a stabilizer, varied greatly; alumina helped to reinforce the Si-O network, depending on the ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$.

3.2. Apparent glass formation analysis

During the reactions presented by Eqs. (1)-(5), the content of molten slag, that is $\text{CaO}+\text{MgO}$, increased. After the first reaction (Eq. (1)), a large amount of scum was formed on the glass melt, making it difficult to pour the melt from the crucibles. All these indicated that the quartz content of glass was too high, leading to a high melting temperature and incomplete melting of ingredients. After the second reaction (Eq. (2)), the glass melt could be poured although a little scum was present on the surface, indicating that the viscosity of the glass melt in this case was lower than that in the previous case. Eqs. (3)-(5) were superior to the former reactions because the prepared MSG was of a uniform color with little scum on the surface, indicating that potassium oxide and calcium oxide were more suitable for glass melting. The yields of reactions in Eqs. (4) and (5) were the same as that of Eq. (3), except for their darker color caused by the presence of ferric oxide. Ferric oxide, which was introduced from slag, was an effective colorant and changed the color of MSG from light yellow to dark brown as the slag content increased.

To sum up, an MSG could not be prepared by the reaction shown in Eq. (1), but could be prepared by those shown in Eqs. (2)-(5); however, for the reaction in Eq. (2), the glass melt was of higher viscosity and some scum was present on its surface. Thus, the appropriate chemical composition of MSG derived based on these results was as follows: CaO, 27wt%-33wt%; SiO₂, 42wt%-51wt%; Al₂O₃, 11wt%-14wt%; MgO, 6wt%-8wt%; and Na₂O+K₂O, 1wt%-4wt%. The optimum amount of molten slag in the MSG was 67.37wt%. Then reactions shown in Eqs. (2)-(5) were discussed subsequently.

3.3. XRD analysis

For the further analysis, MSGs were investigated with XRD, as shown in Fig. 3. As evident from the figure, the XRD patterns of MSG 2 were similar to those of glass, although a quartz peak was present. No apparent quartz peak was observed in MSG 3, but a peak resembling glass features was present. MSG 4 also showed a peak resembling glass features, but the peak location was ahead and the shape was wider, relative to those of MSG 3; MSG 5 was similar to MSG 4, except that the intensity of peak was higher.

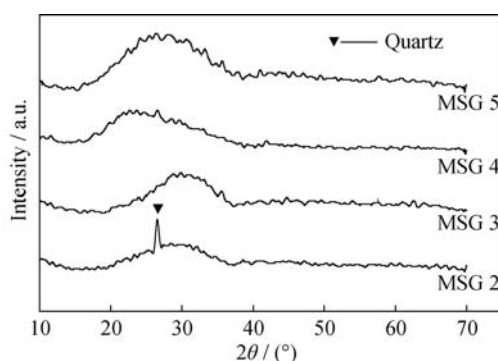


Fig. 3. XRD patterns of MSGs.

As the experiment results shown, the scum present in MSG 2 was silica. Low calcium oxide and high silica contents resulted in an increase in the glass melting temperature. As a result, the reaction between quartz and alkali earth metal oxides could not be completed, resulting in some quartz remaining on the surface of MSG. Owing to an increase in the content of calcium oxide, MSG 3 exhibited high transparency, uniform color, and good chemical and mechanical properties, indicating that the process of melting was better than that for MSG 2. Compared to MSG 3, MSG 4 was darker due to a continuous increase in the slag content; however, the color in some parts of MSG was uneven, indicating the formation of a glass subphase that caused the changes in XRD peaks that resembled glass features.

Owings to a continual increase in calcium oxide content, MSG 5 was of the deepest color, which implied that a glass subphase was obviously present. Because the viscosity of melts increased rapidly in the process of pouring, a large amount of similar ions gathered together, forming a glass subphase [11].

Calcium oxide could destroy the network of quartz units and act as a glass stabilizer, which increased the chemical stability and mechanical strength of MSG [12-13]. Because the Ca–O bond energy (135 kJ/mol) was significantly less than the Si–O bond energy (444 kJ/mol), the Ca–O bond was easily dragged by the Si–O bond and broken up; in other words, O²⁻ ions would easily be attracted around the Si–O bond, weakening the network. As a result, the melt viscosity was reduced, and the rates of various reactions were improved greatly, leading to the formation of a more stable MSG. However, if the content of calcium oxide was too high, the crystallization of glass would tend to decrease and internal energy could not be released quickly, making the MSG unstable and brittle. The network was too weak to drag all the Ca²⁺ ions as calcium oxide content was significantly high; hence, more and more Ca²⁺ ions were being deposited, forming a Ca-rich phase. During the annealing process, the microcracks were formed easily due to a difference in the coefficients of thermal expansion between the Ca-rich phase and the main glass phase, making the MSG fragile.

3.4. SEM analysis

In order to observe the microstructures, MSGs were investigated using SEM, as shown in Figs. 4-7. The size of crystal present in MSG 2 was small, as shown by energy dispersive X-ray spectroscopy (EDS), implying that the content of Si in the crystal was higher relative to that of glass; MSG 3 and MSG 2 had the similar microstructures, except that the size of crystal in MSG 3 was much smaller than that in MSG 2. Some glass subphases were present in MSG 4 (Fig. 6); the size of glass subphase in MSG 5 was larger relative to that in MSG 4, which contained a small amount of Fe (evident from EDS results).

As the XRD and EDS results shown, the crystal present in MSG 2 was quartz. With an increase in calcium oxide content, the reactions among raw materials became more complete. For example, the size of the remaining crystal in MSG 3 was much smaller than that in MSG 2. The possibility of crystallization in MSG 4 decreased with the increase of calcium oxide content, and a glass subphase was formed to reduce the internal energy. Owing to a continuous increase in the calcium oxide content, the size of the glass

subphase in MSG 5 was larger than that in MSG 4. Meanwhile, as a kind of crystal nucleating agent, ferric oxide introduced in the melt from slag [14-16] also induced Ca²⁺ and Mg²⁺ to gather together when the slag content increased,

aiding in the formation of glass subphase. Therefore, although the calcium oxide could help in the melting process, it could also induce the formation a glass subphase under the relatively high concentration in MSG.

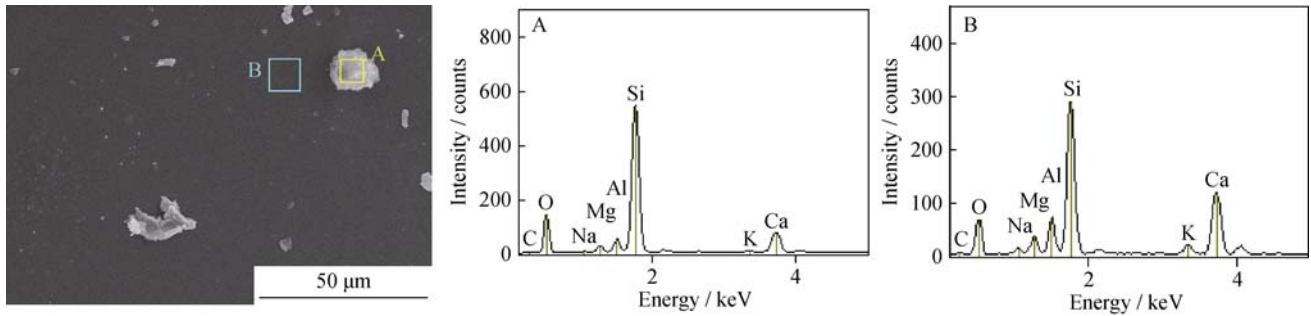


Fig. 4. SEM image and EDS spectra of MSG 2.

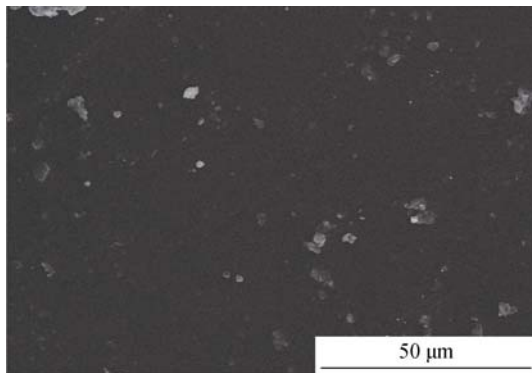


Fig. 5. SEM image of MSG 3.

To sum up, the microstructure of MSG 3 was finer than that of MSG 2, because calcium oxide could lower the viscosity of the melt to accelerate reactions among batches, leading to the formation of a homogeneous melt. Because of

a difference in the coefficients of thermal expansion between the glass subphase and parent phase, the tensile stress was increased in MSG 4 and 5 during the annealing process, leading to the inferior mechanical properties.

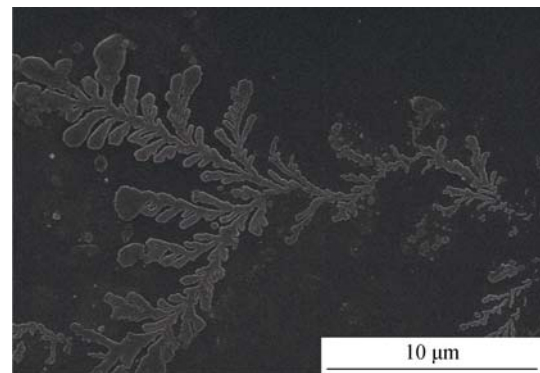


Fig. 6. SEM image of MSG 4.

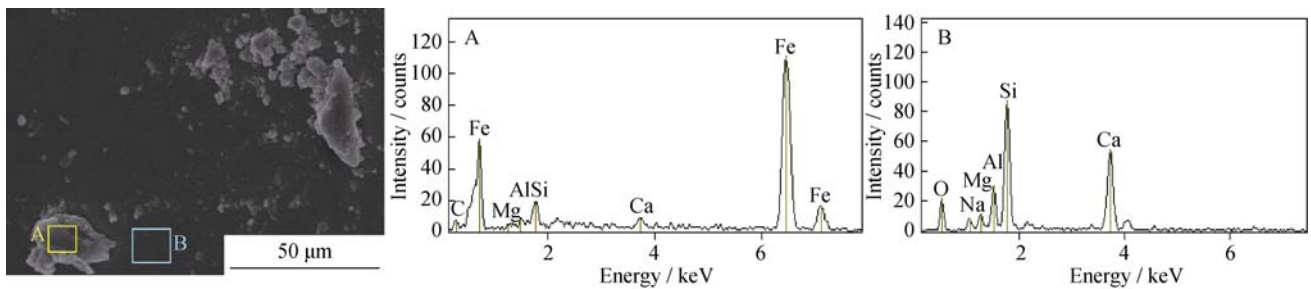


Fig. 7. SEM image and EDS spectra of MSG 5.

3.5. Performances tests

Performances of an MSG with respect to various mechanical and chemical properties are shown in Table 3. Bending strength of MSG 3 is the highest (33.23 MPa) among MSGs 3-5; those of MSG 4 and 5 are 29.13MPa and

22.88 MPa, respectively. This indicates that the mechanical properties of MSG 3 were better than those of others when the molten slag content of MSG was 67.37wt%. The performances of MSG 3, such as bending strength, acid and alkali resistance, and water absorption, are better than the ordinary ceramic and marble, as shown in Table 3.

Table 3. Performances of materials

Material	Bending strength / MPa	Acid resistance / %	Alkali resistance / %	Water absorption / %
MSG	36.15	0.52	0.09	0.00
Ceramic	27.01	12.01	8.00	11.00
Marble	17.02	10.30	0.28	0.04

4. Conclusions

MSG was prepared from the molten industrial slag, using appropriate reactions and techniques, which was uniform in color and showed superior performance. Based on experimental results, the following conclusions can be drawn.

(1) Chemical composition of MSG obtained from the ternary phase diagram and based on test results is as follows: CaO, 27wt%-33wt%; SiO₂, 42wt%-51wt%; Al₂O₃, 11wt%-14wt%; MgO, 6wt%-8wt%; and Na₂O+K₂O, 1wt%-4wt%. The optimum amount of molten slag in the MSG is 67.37wt%.

(2) Thermodynamics analysis of the glass melting process shows that, alkali metal oxides, which served as fluxes, react with silica easily; as a result, the Si-O network tends to break, inducing the glass melting. The extent of reaction between calcium oxide, which served as a stabilizer, and silica varies greatly.

(3) XRD and SEM results show that the melting process is more complete and the melt viscosity is lowered with an increase in calcium oxide content, indicating that calcium oxide can be a better choice for inducing glass melting. The melt viscosity and ion migration rate decrease rapidly during the annealing process when the calcium oxide content is too high, which causes the similar ions to gather together, forming a glass subphase. In addition, ferric oxide present in slag acts as an effective nucleating agent, which can induce crystallization, aiding in the glass subphase formation.

(4) Mechanical properties of MSG are superior when the molten slag content is 67.37wt%; the bending strength of MSG 3 is the highest among MSGs 3-5, and the performances of MSG 3, with respect to bending strength, acid and alkali resistance, and water absorption, are better than those of the ceramic and marble.

Acknowledgments

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