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High Purity Mullite-Corundum Thermal Insulating Firebricks

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Abstract: Laboratory and industrial experiments were carried out to study the possibility of producing high purity mullite-corundum thermal insulating firebricks. The results show that by using industrial alumina, natural powder quartz, coal gangues and a small amount of additives, high purity mullite-corundum thermal insulating firebricks can be produced. The service temperature of these brick can be up to 1780℃ with low thermal conductivity and good thermal shock resistance.

Key words: mullite; corundum; thermal insulating; firebricks

Thermal insulating firebricks of Al_2O_3-SiO_2 system with good thermal insulating ability usually have a service temperature below 1 700℃ [1–3]. Other firebricks, such as alumina bubble firebricks, zircon bubble firebricks have higher service temperature up to 1800 and 1 900℃ [4–5]. But these bricks have much higher costs, lower thermal insulating ability, lower thermal shock resistance ability and heat capacity is still not satisfactory due to their higher bulk density. Mullite has very high melting temperature (above 1 850℃) [6–9] and pure mullite materials are characterized by high strength at high temperature, low thermal conductivity and good thermal shock resistance [10–15]. Pure mullite-corundum composite will have a service temperature up to 1 800℃. But very high purity chemical materials can not be used to produce largely consumed refractories due to their high costs. This paper is to discuss a possibility of using relatively low cost materials including coal gangues and natural powder quartz to produce mullite-corundum thermal insulating firebricks with relative high purity and good ability of high temperature service.

1 Raw Materials And Green Body Preparation

1.1 Raw materials

The chemical analysis of three raw materials is listed in table 1.

The α-Al_2O_3 shown in table 1 is produced by heating industrial γ-Al_2O_3 at 1 700℃. During heating the γ-Al_2O_3 is transformed into α-Al_2O_3. Due to the α-Al_2O_3 has higher density than the γ-Al_2O_3, such a transformation will cause a volume shrinkage of 12% for individual mineral grains. Subsequently, the particles composed of millions of individual mineral grains will have volume shrinkage. On the other hand, impurities such as Na_2O, SiO_2 and Fe_2O_3 decrease due to the high temperature evaporation. So the raw material of alumina is purified during heating.

The coal gangues are the organic bearing clay layers sandwiched between coal layers. The mineral and chemical composition varies for the different mining area. The major mineral composition in most of the coal gangues is kaolinite which has a theoretical composition of $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$. The content of other minor minerals including chlorite, illite, montmorillonite, iron sulphides, carbonates, quartz, feldspars, micas and carbon-bearing materials are mostly between 3%–10% in mass fraction. In some special cases, the content of these minor minerals can be up to 40%. The coal gauges used in this study are composed of nearly pure kaolinite apart from about 4% carbon-bearing combustibles. There is a large reserve of such coal gangues in China. The coal gangues used in this study come from

Table 1 Chemical composition of raw materials (mass fraction in %).

Material	Al_2O_3	SiO_2	Fe_2O_3	MgO	CaO	TiO_2	K_2O	Na_2O	Loss on ignition
α-Al_2O_3	99.12	0.52	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.13	0.20
Coal gangue	35.92	45.75	0.31	< 0.02	< 0.02	0.14	0.15	< 0.10	17.28
Natural powder quartz	1.02	98.36	0.12	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.23

Yangquan, China.

The natural powder quartz comes from Jiangxi province, China. The deposits of this natural powder quartz are formed by weathering of siliceous limes. The grain sizes of the quartz grains are mostly in the range of 5–50 μm and are highly purified by natural weathering. The natural powder quartz used in this study has been graded and further purified by water separation. The natural powder quartz used in this study contains only grains of smaller than 30 μm in diameter.

1.2 Raw materials mixing

The mixing and milling of the raw materials are carried out in a high efficiency stirring milling machine with a wet method. Before milling, the coal gangues have to be crushed into small grains not bigger than 0.5 mm. The milling machine has very high efficiency when average grain sizes is above 5 μm. The milling efficiency decreases rapidly when average grain size is smaller than 5 μm. It is clear that 8 h milling is necessary to obtain a mixture with average grain sizes of less than 5 μm.

1.3 Green body preparation

When the mixtures are milled to an average grain size of less than 5 μm, the kaolinite in the coal gangues is mostly separated into individual mineral grains. The grain sizes of part of the α-Al_2O_3 and quartz are in the range of gel-forming sizes. So after 8 h milling, the mixture has a good ability of suspension. The mixture fluid is pumped into a de-watering filter press. In this machine the water content of the mixture is reduced from 60% to 25%. After de-watering the mixture becomes plastic mud. The mud is drawn from the machine, and mixed with organic materials in a screw-mixing machine for 30 min. The organic materials added in this process will be burned out during sintering. The space originally occupied by these organic materials will exist in the final product as pores, which can keep the final products having low bulk density and low thermal conductivity. After the mud mixed with organic materials, it is put into an extruding machine to form green bodies with designed size.

There is a vacuum room in the extruding machine. Before the mud is extruded to form a green body, the air in the mud is extracted to a vacuum of 0.01 MPa. With such a vacuum extent, the undesirable pores and fissures can be exempted. The distance between some of the grains can be decreased. Subsequently, the strength of green body products can be largely increased. The wet green body is dried in a tunnel kiln with a temperature – time curve shown in **figure 1**.

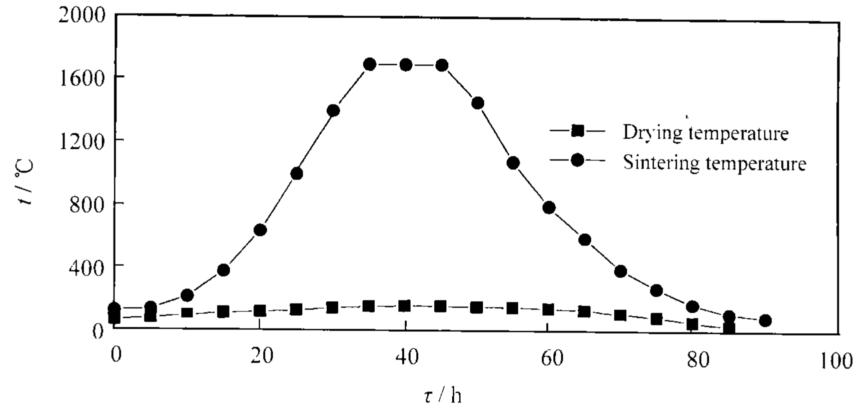

Figure 1 Temperature–time curve of green body drying and sintering.

2 Sintering of Mullite-Corundum Thermal Insulating Firebricks

2.1 Temperature – time curve of sintering

The sintering is a key process in the producing of the mullite-corundum thermal insulating firebricks. Due to the existence of large amount of organic materials in the green body the temperature increase rate before 200℃ should be very low. During this period, evaporates in the organic materials escapes from the green body. If the temperature increase is not slow enough, evaporates will escape fast, resulting in the strength decrease of green bodies or even leading the cracking of the green bodies. Between 200 and 400℃, the temperature increase also cannot be fast. The sintering is carried out in a 30 m^3 drawer kiln. Due to the large space in the kiln, it is very difficult to confine the temperature difference within a small range in this stage, for example ±10℃. In such a low temperature stage, that is, when the temperature reading on the monitor is 200℃, some low temperature corner is still far below 200℃, and large amount of gaseous composition in the green bodies is still to be evaporated. In such a case, if the temperature increase is too fast, these parts of green bodies can still be damaged. Also, most of carbon lifted in the green body will be burned out in this temperature range. Between 400 and 1 600℃, the rate of temperature rise can be increased to 100℃/h. Between 1 600 and 1 700℃, it is also necessary to keep low rate of temperature rise. In this temperature range, part of the raw materials melted, certain amount of melted liquid exists between mineral grains. Various chemical reactions and physical transformation happen in this temperature range. The volume shrinkage is quick in this temperature due to the high temperature sintering. If the temperature increase is too fast in this temperature range, there will be a big temperature difference between the surface and the center of the green body. The temperature difference will cause a big difference of shrinkage between the center and the surface of the green body. After the constant temperature at 1 700℃ there should be a controlled temperature decrease. The slow decrease of temperature allows most of the liquid or glass phases crystallize into mullite, corundum or other minerals, which can upgrade the physical properties of the final products. When the temperature is lowered to 1 200℃, the burners can be shut down, and the temperature can be lowered at a higher rate. The temperature — time curve of sintering is also shown in figure 1.

2.2 Phase change during high temperature sintering

To decide a premium sintering temperature, the sintering experiments are carried out in the laboratory with an electric stove. The samples are sintered at 1400, 1 600, 1 700 and 1 750℃ for 10 h, respectively, the sintered samples are examined by XRD for their phase composition. The results are shown in **figure 2**. The figure shows that when sintering temperature increases, the mullite content in the samples increases steadily and corundum decrease. Above 1 700℃, the ratio of mullite/corundum nearly keeps constant. This means that the formation reaction of mullite is nearly finished at 1 700℃.

3 Factors Affecting Physical Properties of Mullite-Corundum Thermal Insulating Firebricks

3.1 The effect of organic materials

While the bulk density is kept constant, the sizes and shapes of the organic materials have a great effect on the strength and thermal shock resistance of the mullite-corundum thermal insulating firebricks. The organic materials used in this study include particles of styrofoam and saw powder. As shown in **table 2**, when the density is kept 1.2 g/cm^3 and the Al_2O_3 content is kept 75.0% in mass fraction, the physical properties are quite different between the two type of firebricks which use pure particles of styrofoam with mixed grain sizes and saw powders with mixed grain sizes as organic materials respectively.

It is shown in table 2 that the bricks using particles of styrofoam as organic materials have higher strength, higher thermal conductivity, and lower ability of ther-

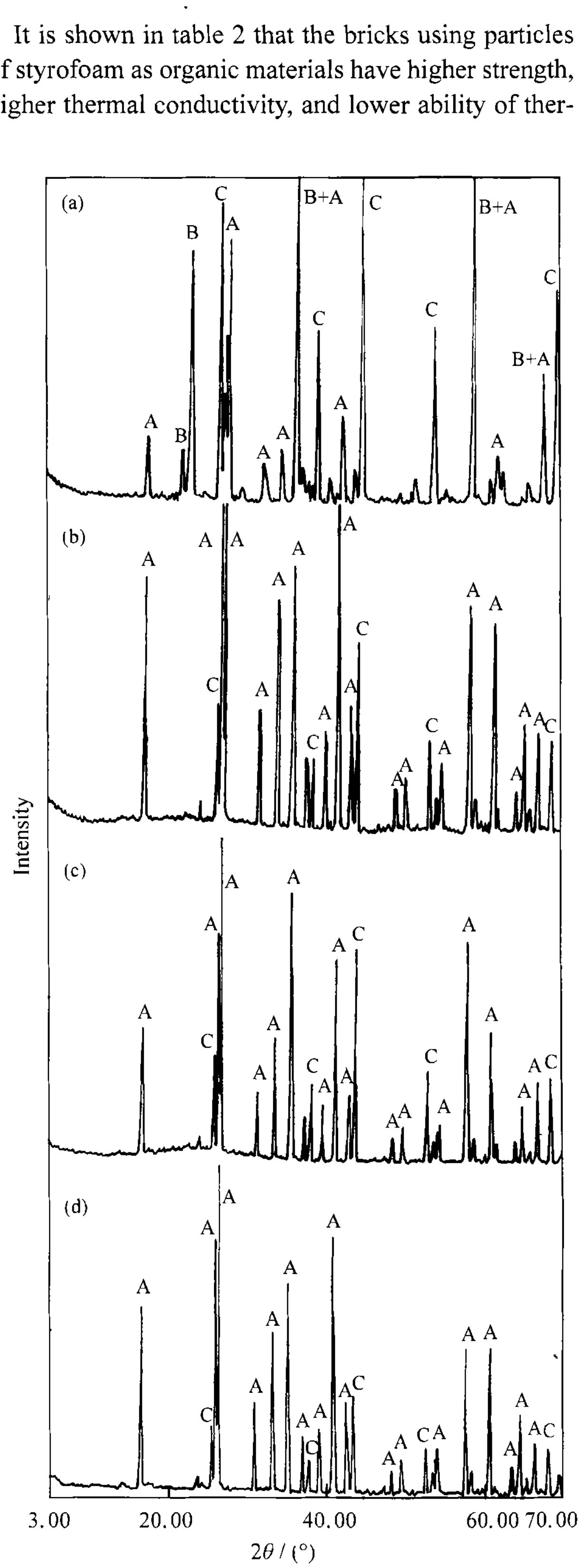

Figure 2 XRD spectrum of samples sintered at different temperature. (a) 1 400℃, 10 h; (b) 1 600℃, 10 h; (c) 1 700℃, 10 h; (d) 1 750℃, 10 h. A–mullite, B–crystobalite, C–corundum.

Table 2 Physical properties of mullite-corundum firebricks using the particles of styrofoam and saw powder as organic materials.

Organic materials	Cold crushing strength / MPa	Flexural strength / MPa	Thermal conductivity (at 800℃) / W(m·K)$^{-1}$	Thermal shock resistance / times	Re-heating linear change (at 1750℃, 24 h) / %
Particles of styrofoam	7.8	2.5	0.67	6	−0.12
Saw powder	2.2	1.6	0.55	28	−0.18

mal shock resistance and smaller reheating linear change than those using the other one. When using pure saw powder as organic materials, the grain sizes of the saw powder also have some effects on the physical properties of mullite-corundum firebricks. The experiment shows that the bricks using coarse saw powder as organic materials have higher strength, higher thermal conductivity, higher thermal shock resistant ability and smaller re-heating linear change.

When using a mixture of particles of styrofoam and saw powder as organic materials, the mullite-corundum thermal insulating firebricks will have physical properties between two end members, but there is an optimum ratio of styrofoam particles to saw powder. **Figure 3** shows the properties change of the mullite-corundum thermal-insulating firebricks, when the volume ratio of saw powder to styrofoam particles varies. In these experiments, the brick density is kept at 1.2 g/cm^3. The grain sizes of the styrofoam particles are between 0.1–2.0 mm. The longest dimension of saw powder is between 2.0–5.0 mm.

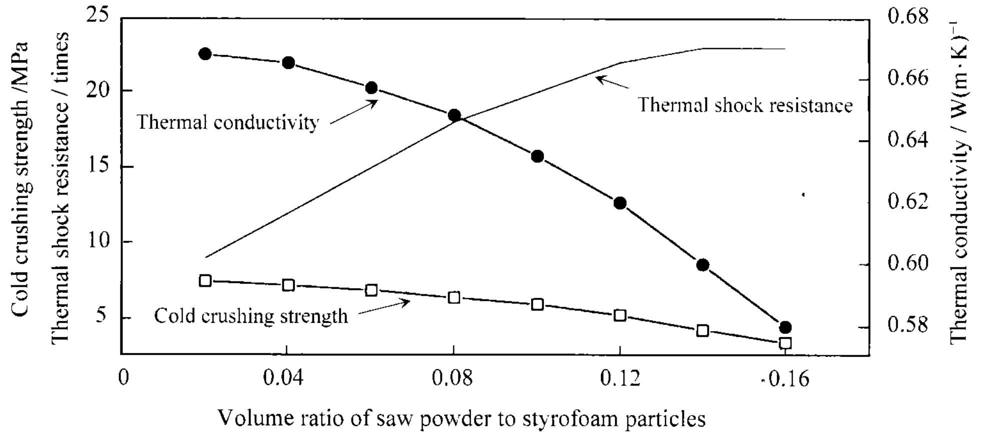

Figure 3 Property change of the final products when the volume ratio of saw powder to styrofoam particles varies.

It is shown in figure 3 that when the volume ratio of saw powder to styrofoam particles is smaller than 0.11, the ability of thermal shock resistance increases rapidly with the increase of the ratio. Other properties change slowly. The continuing increase of the ratio has a smaller effect on the properties of the final products.

3.2 The effect of Al_2O_3 content on the properties of the mullite-corundum thermal insulating firebrick

The theoretical Al_2O_3 content in mullite is 71.8% in mass fraction. At high temperature, there is an extra Al_2O_3 content in its crystal lattice due to its solid solution ability. This situation occurs when the Al_2O_3-SiO_2 melts cool down and mullite crystallizes from the melt. Once mullite forms at lower temperature with its composition near to the theoretical composition, it will be very slow for mullite to solve more Al_2O_3 into its crystal lattice at higher temperature. So when the Al_2O_3 content of the bricks is above 71.8% in mass fraction, there will be corundum left in the final products. The ratio of mullite to corundum will have apparent effects on the properties of the final products. **Table 3** shows the effects of Al_2O_3 content on the properties of samples. In these experiments, the density of the bricks is kept at 1.2 g/cm^3, the grain sizes of styrofoam particles between 1.0–2.0 mm, the longest dimension of saw powder between 2.0–5.0 mm, and the volume ratio of saw powder to styrofoam particles at 0.11.

It is shown in table 3 that when the Al_2O_3 content is above 75.0% the ability of thermal shock resistance decreases quickly and the thermal conductivity increase rapidly. The linear change of sintering and re-heating decrease continuously but slowly. The reason of strength and the ability of thermal shock resistance decreasing are that when Al_2O_3 content is above 75.0% the ratio of mullite to corundum in the firebricks will decrease rapidly. Firstly, this will cause the porosity increase because the corundum mineral has a higher density than the mullite mineral. When the density of firebricks is kept at 1.2 g/cm^3, the smaller of the mullite to corundum ratio, the higher of the porosity inside the fir-

Table 3 Effect of Al_2O_3 content on the properties of samples.

mass fraction of Al_2O_3 / %	70	72	74	76	78	80	82	84	86
Cold crushing strength / MPa	5.77	5.77	5.77	5.74	5.65	5.52	5.30	5.12	4.99
Thermal shock resistance / times	21	21	21	20	19	18	16	15	14
Thermal conductivity / $W(m \cdot K)^{-1}$	0.57	0.57	0.58	0.59	0.61	0.63	0.67	0.71	0.74
Linear change of sintering (at 1 700℃, 10 h) / %	−5.6	−4.2	−3.5	−3.2	−3.0	−2.9	−2.9	−2.9	−2.9
Linear change of re-heating (at 1 750℃, 24 h) / %	−0.88	−0.44	−0.22	−0.10	−0.09	−0.08	−0.07	−0.07	−0.07

ebricks. Secondly, the corundum mineral has a much higher thermal expansion rate than the mullite mineral [2]. When the ratio of mullite to corundum decrease, the thermal expansion rate of the firebricks will increase. Subsequently, the ability of thermal shock resistance will decrease. Because the corundum mineral has a much higher thermal conductivity than the mullite mineral, when the ratio of mullite to corundum decrease, the thermal conductivity of the fire bricks will increase slowly. The decrease of sintering linear change and re-heating linear change is mainly because that the increase of Al_2O_3 in the system will increase the sintering difficulties of the samples. Thus, the maximum service temperature can be slightly increased.

4 Properties of Final Products and Their Application

The chemical composition of the mullite-corundum thermal insulating firebricks is Al_2O_3, 75.02%; SiO_2, 24.65%; Fe_2O_3, 0.12%; CaO, 0.01%; MgO, 0.01%; TiO_2, 0.08%; Na_2O, 0.07%; K_2O, 0.01% in mass fraction. The mineral composition is corundum, 6.28%; mullite, 91.25%; others, 2.47% in mass fraction.

The final products of the mullite-corundum thermal insulating firebricks have following physical properties: The density is 1.2 g/cm^3; the cold crushing strength is 5.7 MPa; the flexural strength is 2.3 MPa; the thermal conductivity at 800℃ is.0.59 W/(m·K); the thermal shock resistance is 21 times; the re-heating linear change after 1 750℃,24 h is −0.13%; the maximum service temperature is 1 780℃.

The mullite-corundum thermal insulating firebricks can be used in various furnaces, kilns, and stoves that use oil, gas or electricity as heating sources as fire-contact linings. The maximum long time service temperature is above 1 750℃. Compared with alumina bubble firebricks, the mullite-corundum thermal insulating firebricks have much higher ability of thermal shock resistance and lower thermal conductivity. Consequently, the service lifetime can be significantly prolonged. Compared with zirconia bubble firebricks, the costs are largely reduced.

5 Conclusions

High purity mullite-corundum thermal insulating firebricks can be produced by using α-Al_2O_3, coal gangues and natural powder quartz. The most economic sintering is 1 700℃,10 h with a controlled slow cooling down process. The best selection of the ratio of saw powders to styrofoam particles is 0.11. With a density of 1.2 g/cm^3, the mullite-corundum thermal insulating firebricks have a maximum service temperature of 1 780℃.

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