IOP Conf. Series: Materials Science and Engineering **385** (2018) 012038 doi:10.1088/1757-899X/385/1/012038

Raw materials for mullite grog manufacturing

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Abstract. The starting raw materials for aluminosilicate grog manufacturing are fissile claystones and shales. These raw materials are available in the Czech Republic and grogs with up to 45 % aluminium oxide content are manufactured. However, refractory production cannot do without higher-Al_2O_3 -content grogs. This group includes grogs with alumina content of 45 % to 70 %, which constitute a transition between fire clay and mullite grogs. Because of the high market price of these grogs, however, there is an effort to seek ways to manufacture these in the Czech Republic. The primary condition for manufacturing is the correct choice of raw material, a suitable treatment facility, and a kiln capable of firing at temperatures above 1400 °C. This paper assesses some local raw materials for grog manufacturing and compares the results with a mullite grog of similar properties that is available on the European market.

1. Introduction

Refractory materials can be divided according to the dominant oxide content (silica, aluminosilica, alumina, magnesia, etc.), the manufacturing technology (shaped or unshaped), the temperature they can withstand, materials they contain (corundum, mullite, sillimanite, etc.), bulk density (dense, insulating), etc. The refractoriness of these aluminosilicate grogs depends mainly on Al_2O_3 content, which is also how they are classified; see table 1. The grog with a high Al_2O_3 content is used in the manufacturing of a great many shaped, as well as unshaped, refractories. The properties of the final product are determined by the chemical and mineralogical composition of the grog and its density. This paper discusses an aluminosilicate with Al_2O_3 content above 45 %. Currently, this grog is being imported to the Czech Republic and is used in the production of a number of refractory materials, such as blast furnace stack lining, torpedo ladles, backup lining in steel ladles, reheating furnaces in ferrous metallurgy, lime kilns, melting and holding furnaces, pot furnaces, anode baking furnaces in aluminium metallurgy, and many other areas where the use of these refractories is unavoidable [2].

This paper assesses several local raw materials suitable for grog manufacturing and compares the results with mullite grogs available on the European market.

2. Mullite Characterization

The only aluminosilica crystalline phase which is stable at high temperature is mullite, most commonly expressed as $3Al_2O_3.2SiO_2$. Mullite is a very stable compound with a high melting point. It also has very low thermal expansion, good strength, and high modulus of elasticity. This is why it is usually desirable that the mullite content be as high as possible. The mullite content of a material is determined primarily by the chemical composition of raw materials and firing temperature. Mullite begins to form typical needle crystals (figure 2) at temperatures above 1300 °C.

Sintered mullites are produced from different raw materials which are mixed in powdered form and then sintered at an optimum temperature after compaction. Oxides, hydroxides, salts and silicates are used as starting materials. Mullitization takes place by solid-solid or transient liquid phase reactions of the starting materials by aluminium, silicon and oxygen atom inter-diffusion [2]. These mullites tend to have "stoichiometric", i.e., 3/2 - composition ($3Al_2O_3 \cdot 2SiO_2$, ≈72 wt. % Al_2O_3).

Fused mullites are commercially produced by melting the starting materials above 2000 °C, casting the aluminium silicate melt into the ingot moulds and cooling it to room temperature. Raw materials with low impurity levels, e.g. Bayers alumina, quartz sand and fused silica are used. For lower quality mullite, bauxite and a mixture of alumina and kaolinite have also been used. These mullites tend to be Al_2O_3-rich with approximate 2/1-composition ($2Al_2O_3 \cdot SiO_2$, ≈ 78 wt. % Al_2O_3).

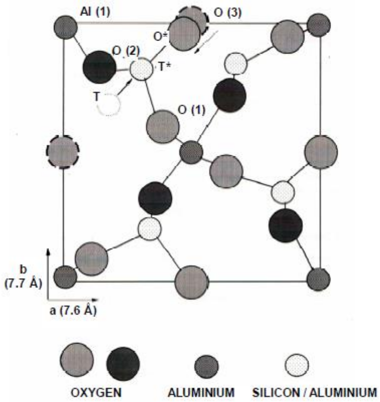

Figure 1. Atom positions in unit cell of mullite [4].

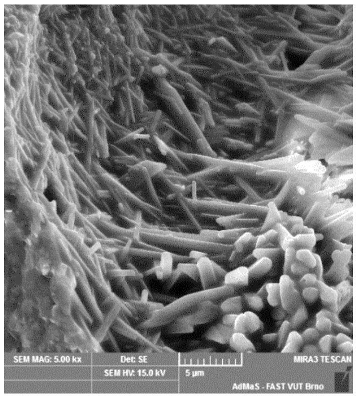

Figure 2. Scanning electron micrograph of mullite, firing temperature 1420 °C.

Chemical-mullites are produced by heat treatment of organic or inorganic precursors prepared by advanced processing techniques, such as sol-gel, hydrolysis, precipitation, spray pyrolysis, chemical vapour deposition, etc. The composition of such mullites strongly depends on the starting materials and the temperature treatment. Extremely Al_2O_3-rich compounds (>90 wt.% Al_2O_3) have been identified at synthesis temperatures <1000 ◦C [1].

Mullite has orthorhombic crystal structure with unit cell dimensions a = 0.7540 nm, b = 0.7680 nm and c = 0.2885 nm for the stoichiometric composition [3]. Mullite is intermediate in composition between alumina (Al_2O_3) and sillimanite (Al_2SiO_5). It can be seen from figure 1 that mullite consists of chains of AlO_6 octahedra at the edges and the centre of the unit cell. These chains are joined by Al_2SiO_4 tetrahedra [4].

3. Mullite grogs available on the European market

3.1. Symulox

Mullite identified as M72 contains 72 % Al_2O_3 and is typically extremely high in purity, which is its primary difference from natural aluminosilicates. Products made with clinkered mullite have a high chemical resistance and excellent refractory properties. Good strength combined with a low thermal expansion results in outstanding thermal shock resistance. The products can be applied at temperatures up to 1700 °C. The bulk density of Symulox is 2800 kg·m^{-3}, water absorption is around 1 %, and open porosity is 1.5 %. It contains 90-95 % mullite, 5-10 % glass phase and 1% corundum [5]. Other products from this product line are sintered mullite Z72 or reactive aluminium oxide named M 672.

Table 1. Chemical and mineralogical composition of mullite grog Symulox M72.

Oxide	Content [%]
Al_2O_3	72.00
SiO_2	26.00
TiO_2	0.20
Fe_2O_3	0.30
CaO	0.05
Na_2O	0.20

Mineral	Content [%]
Mullite	90 - 95
Glass phase	5 - 10
α-corundum	1

3.2. Virginia Mullite

This type of mullite is produced by kyanite calcination at a temperature of 1450 °C. The material thus produced, known as Virginia Mullite, consists of approx. 80 % mullite, 11 % amorphous glass, 7 % quartz and less than 1 % cristobalite. It differs from other synthetic mullites in particle shape and material purity, which is higher than in mullites produced by clay mineral calcination [6].

Table 2. Chemical and mineralogical composition of Virginia Mullite grog.

Oxide	Content [%]
Al_2O_3	58.00
SiO_2	40.20
TiO_2	1.10
Fe_2O_3	0.50
CaO	0.04
Na_2O	0.10

Mineral	Content [%]
Mullite	79-85
Glass phase	8-12
Quartz	4-8
Cristobalite	<1

3.3. Vulcasil H

Vulcan Refractories produce a broad spectrum of materials containing 55-99.5 % of Al_2O_3. Their fused mullite is known for its high purity, resistance to thermal shock and chemical resistance. The HRP group of grogs contains 79 % Al_2O_3 and 21 % SiO_2. The bulk density is 2700 kg·m^{-3} and apparent porosity is around 18 % [7].

Table 3. Chemical composition of Vulcasil H.

Oxide	Content [%]	Oxide	Content [%]
Al_2O_3	78.0	Fe_2O_3	< 0.5
SiO_2	20.0	CaO	< 0.5
TiO_2	< 0.5	Na_2O	< 0.5

3.4. Henan Cunse Refractory - M47

The Chinese company Henan Cunse Refractory from Dengfeng offers a great many products and materials suitable for refractory roles. Grogs containing mullite are identified with an M followed by a number that specifies the average content of Al_2O_3. The company also offers grogs with a reduced Fe_2O_3 content; they are identified by the letters DM followed again by a number denoting the content of Al_2O_3.[8] Grog M47 has a bulk density of 2600 kg.m^{-3}, apparent porosity of 3 % and a refractoriness of 1780 °C.

Table 4. Chemical and mineralogical composition of a mullite grog from Henan Cunse Refractory.

ID	Al_2O_3 [%]	Fe_2O_3 [%]	K_2O+Na_2O [%]	Mullite content [%]
M47	45-49	<1	<0.3	55-65
M60	58-62	<1.3	<0.3	70-80
M70	68-72	<1.5	<0.3	85-90

DM45	43-47	<0.4	<0.3	50-60
DM60	58-62	<0.5	<0.3	70-80
DM70	68-72	<0.6	<0.3	85-90

4. Testing raw materials for suitability in grog production

Aluminosilicate grogs are typically produced from refractory clays, claystones, shales and kaolin.

4.1. Raw materials

This investigation tested passing fractions of W Super claystone, which had been heaped for half a year, 5 years and 10 years. Since claystone W Super contains a maximum of 44 % of Al_2O_3, a waste mullite produced by MOTIM Electrocorundum Ltd. was also tested as a potential source of Al_2O_3. Tables and diagrams refer to the waste mullite Motim by the letter M.

Table 5. Chemical and mineralogical composition of waste mullite Motim, claystone W Super and a test mixture containing 90 % of W Super and 10 % of Motim.

Motim	Content [%]	W Super	[%]	90 % W Super 10 % Motim	Content [%]
Al_2O_3	73.470	Loss on ignition	-13.51	Al_2O_3	46.78
SiO_2	22.710	SiO_2	52.92	SiO_2	49.67
TiO_2	0.014	Al_2O_3	43.17	TiO_2	1.63
Fe_2O_3	3.295	TiO_2	1.83	Fe_2O_3	1.02
CaO	0.008	Fe_2O_3	0.73	CaO	0.14
Na_2O	0.080	CaO	0.16	Na_2O	0.07
Mullite	93	MgO	0.13		
Glass	4	K_2O	0.63		
		Na_2O	0.07		
α-corundum	3				

The first set of specimens was made with a passing fraction of claystone W Super of varying age. The second set of specimens contained a passing fraction of W Super (90 %) and waste mullite Motim (10 %). The passing fractions of W Super were identified as Super 0.5, Super 5 and Super 10, with the number indicating heaping time in years.

The specimens were pressed using a hydraulic press at 20, 25 and 30 MPa. The mixture's water content was 8%. Once pressed, the specimens were dried in a laboratory dryer and fired in a laboratory superkanthal furnace at 1500 °C with a holding time of 4 hours.

4.2. Laboratory tests

The freshly pressed specimens were weighed and measured to determine their bulk density. After firing at 1500 °C, they were tested using the hydrostatic weighing method to measure their bulk density, apparent porosity, water absorption and apparent density. Selected specimens were tested for pore size distribution by high-pressure mercury intrusion porosimetry. The mineralogical composition was determined by XRD analysis. A scanning electron microscope was used to examine the internal structure of the claystone used in the specimen production. The values listed in the tables represent an average of three independent measurements.

Table 6. Properties of claystone W Super after firing at 1500 °C.

100 % W Super	Pressure	Water absorption	Bulk density	Apparent porosity	Apparent density	Overall shrinkage
	[MPa]	[%]	[kg.m^{-3}]	[%]	[kg.m^{-3}]	[%]
Super 0.5	20	2.0	2390	4.7	2507	-10.1
Super 0.5	25	3.2	2346	5.5	2535	-10.2
Super 0.5	30	2.5	2341	5.9	2489	-9.8

Super 5	20	3.6	2358	8.4	2575	-9.3
Super 5	25	2.3	2401	7.6	2543	-9.7
Super 5	30	2.6	2368	6.2	2524	-9.5
Super 10	20	3.7	2298	8.5	2510	-10.0
Super 10	25	4.3	2249	9.8	2493	-9.8
Super 10	30	4.2	2271	9.6	2512	-10.0

Table 7. Properties of the mixture of 90 % of W Super and 10 % of Motim after firing at 1500 °C.

90 % W Super 10 % Motim	Pressure	Water absorption	Bulk density	Apparent porosity	Apparent density	Overall shrinkage
	[MPa]	[%]	[kg.m^{-3}]	[%]	[kg.m^{-3}]	[%]
M-Super 0.5	20	2.3	2443	5.6	2588	-9.5
M-Super 0.5	25	2.6	2407	6.4	2571	-9.6
M Super 0.5	30	3.2	2390	7.6	2588	-9.3
M- Super 5	20	4.1	2368	9.7	2624	-8.1
M- Super 5	25	4.6	2365	10.9	2653	-8.2
M- Super 5	30	3.9	2428	9.4	2680	-8.1
M- Super 10	20	4.4	2336	10.3	2604	-8.9
M- Super 10	25	4.5	2359	10.7	2643	-8.8
M- Super 10	30	3.4	2378	8.1	2586	-8.9

4.3. Result discussion

Claystone W-Super was observed for the influence of heaping time and compaction pressure on the resulting material's mineral composition and pore structure. The apparent porosity of specimens made with claystone SW-Super 0.5 ranged from 4.5 to 5.5 %. The claystone which was heaped for 10 years reached values of apparent porosity between 8.5 and 9.8 %. As its heaping increases the porosity of the fired material (figure 4), the results show that it is best to use freshly mined claystone for dense grog manufacturing. The porosity of the fired grog is also affected by the pressure at which it was compacted; it is necessary to set an optimal pressure for each raw material. W-super 0.5 was the most suitable for manufacturing, with an optimal compaction pressure of 20 MPa. The firing temperature decisively influences the grog's density and mineralogical composition. 1500 °C is sufficient for achieving the desired mineralogical composition. The content of low-temperature quartz is 5-6 % and mullite content is 66 % for Super 5, and 70 % for M Super 5 sample.

W-Super contains the fissile mineral kaolinite. If a 30-mm passing fraction of claystone is heaped for several years, the kaolinite contained in it degrades, which manifests itself in fissures in its structure, thereby increasing the number of pores in the claystone; figure 3. Ten years of heaping causes kaolinite particle size to drop below 1 μm; the layers no longer have sharp edges and the structure is "aerated", figure 3 c). This “aeration” reduces density and increases porosity both after pressing and after firing.

a b c

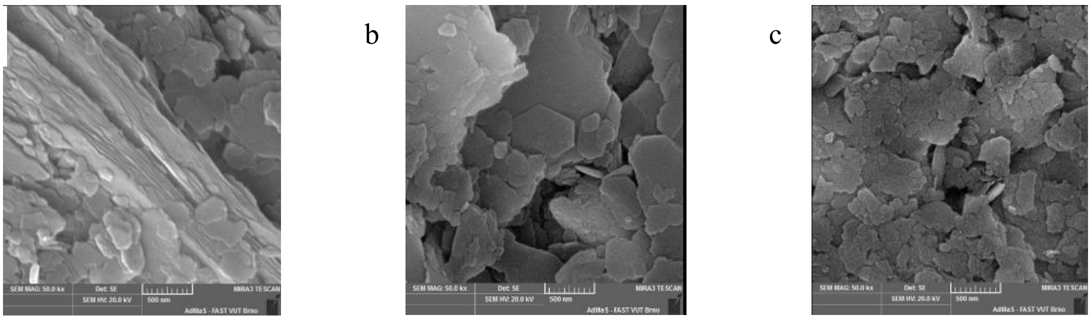

Figure 3. Morphology of kaolinite a) half a year, b) 5 years, c) 10 year; magnified 50 000x.

Given its chemical and mineralogical composition, clay W-Super is suitable for high-alumina grog; however, it must be combined with a material with a high Al_2O_3 content. This study identified waste mullite Motim (aluminium oxide content of 73-75 %) to be a suitable source of Al_2O_3; table 1. The dosage of 10 % meant the total Al_2O_3 content in the mixture was 46.8 %. For details on the properties of the grog fired at 1500 °C see table 7. In some cases, the addition of waste mullite increased apparent porosity by 10 - 20 %.

The test results indicate the following:

- The application of the waste mullite Motim increases the apparent porosity of the fired product, figure 4, 5.
- The waste mullite causes the formation of 5-10 μm pores and increases the average pore size of the fired grog.
- The addition of Motim increases mullite content in the fired grog.

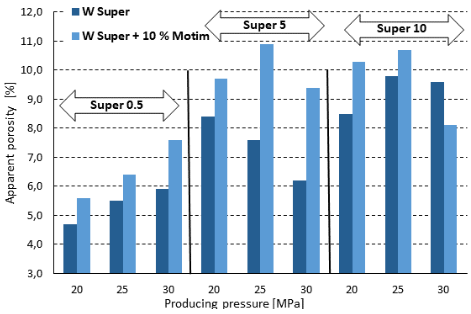

Figure 4. Influence of 10 % of waste mullite on apparent porosity of fired grog.

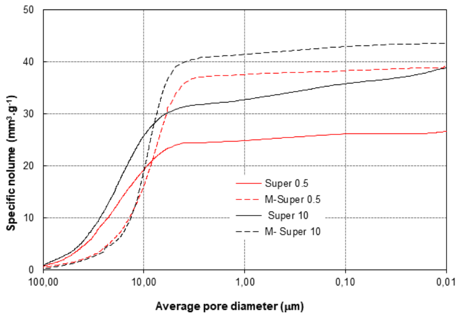

Figure 5. Comparison of pore size distribution.

5. Conclusion

The study demonstrates that the raw materials considered herein are well suited for mullite grog manufacturing. Grog W Super 0.5 with a 10 % addition of waste mullite was found to be the most suitable. The chemical composition (Al_2O_3 content = 46.7 %) meets the requirement for grogs with a high Al_2O_3 content. The lowest porosity achieved by any of the specimens was 5.6 %. This value approaches grog M47 with an apparent porosity of 3 %. The porosity can be further decreased by firing at a lower temperature, or by modifying the fresh mixture's composition. This will be subject to further research.

Acknowledgements

The paper was created within the project no. 2016TH02020321 "Production of Mullite Grog in a Shaft Kiln" sponsored by the Technical Agency of the Czech Republic.

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