Clay and Alumina Grain Size Effect on Highalumina Refractories

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Abstract. There is an attempt to produce a synthetic mullite by using the domestic raw materials as Klokoti fireclay and metallurgical electrofiltered alumina made in the Alumina Plant ″Birač″ - Zvornik. In this regard, specific methods are being developed to make the four types mixtures of clay and alumina. These mixtures contain raw or benefited clay with nonmilling or milling alumina. Two class of mixtures: (1) raw clay at 1700°C and (2) benefited clay at 1580°C have obtained the best properties of synthetic mullite. An effect of milling alumina is not so significant like an influence of benefited clay. The sintering process in the industrial furnaces during two hours at the highest temperature has not been enough for the fully mullitization reaction. The increase amorphous phase is found in the structure of mixtures with benefited clay because these mixtures types contain much more impurities. By a careful control of the production steps and sintering time extend, a synthetic mullite could be obtained by using fine grained raw clay and also fine grained alumina.

Introduction

The highalumina refractory materials of mullite composition can be produced with a synthetic mullite [1]. One of methods to obtain synthetic mullite is hightemperature treating of mixtures clay and alumina [2]. The mullitization process is slow and depends on composition and purity of components in mixtures, consistently with homogeneity, grain size, selected method of mixture preparation, temperature and duration of sintering [3].
The synthetic mullite refractory with cca 70 % Al2O3 has obtained from the mixture contents Klokoti fireclay and metallurgical electrofiltered alumina made in the Alumina Plant „Birač“.- Zvornik. The raw clay contains a low amount Al2O3 and its beneficiation has carried out by a sedimentation and on this way an elimination of grains over 20 μm. The electofiltered alumina has grains mostly between 15 μm and 45 μm. The coarse grains alumina has milled to fine grains bellow 30 μm (50 % its grains was bellow 5 μm). During experiment the four types of specimens have made as following:

1. Mixture with sieved clay and nonmilling electrofiltered alumina (″SN″).
2. Mixture with sieved clay and milling electrofiltered alumina (″SM″).
3. Mixture with benefited clay and nonmilling electrofiltered alumina (″BN″).
4. Mixture with benefited clay and milling electrofiltered alumina (″BM″).

In industrial furnace circumstances all mixture types have treated at temperatures 1580°C and 1635°C, while specimens marked ″SN″ and ″BN″ have an additional treatment at 1700°C. At the highest temperature the specimens have been hold up cca two hours.
The present study is dedicated to analyze how the grain size change influences on synthetic mullite properties in production scale.

Materials and Experimental Procedures

The experiments were carried out on mixtures of clay and alumina with following characteristics [4-6,8-11].

Clay. The Klokoti fireclay from stocks was sieved bellow 1 mm (mark ″S″). To obtain clay with higher alumina content it was used dry and crushed up clay. Distillate water with 0.74 g/l sodiumpyrophosphate was added into it and one hour stirring. According the Stokes law and experimental conditions, the sedimentation time of grains over 20 μm was calculated. After that time the suspension with clay component bellow 20 μm was decanted and dried to finally benefited clay (mark ″B″). The chemical composition of raw and benefited clay is listed in Table 1 and the grain size distribution of raw clay in Table 2. The refractoriness of raw clay is 1520°C, and the benefited clay 1660°C.

Alumina. The Alumina Plant ″Birač″ - Zvornik produces a metallurgical alumina with maximum 12% α- Al_2O_3 and minimum 90% grains over 45 μm. This alumina is not suitable for a synthetic mullite, thereby providing it an electrofiltered alumina (mark ″N″) which chemical composition is listed in Table 1 is used. Since this alumina has 98.3% grains between 15 μm and 45 μm and only 1.7% bellows 15 μm, it was milled to increase its activity. The grain size distribution of milling alumina (mark ″M″) is listed in Table 2.

Table 1. Chemical composition of raw and benefited clay and alumina

Component	Chemical composition [%]		
	Raw clay	Benefited clay	Electrofiltered alumina
Al_2O_3	17.14	31.49	98.14
SiO_2	73.05	52.01	0.021
Fe_2O_3	2.51	3.30	0.017
CaO	1.22	0.56	0.027
MgO	0.36	0.62	-
Na_2O	0.35	0.27	0.74
K_2O	2.78	4.68	-
ZnO	-	-	0.031
LOI	5.58	9.67	1.02

Table 2. Grain size distribution of raw clay and milling alumina

Percentage content [%]	Grain size [μm]	
	Raw clay	Milling alumina
10	2.8	0.98
20	5.27	1.52
30	8.07	2.30
40	11.7	3.29
50	16.6	5.05
60	23.4	7.90
70	33.7	12.00
80	49.4	16.1
90	73.8	21.2
100	300	50

Mixture. Four types of mixture according to grain size and two types according to chemical composition were made:

1. Mixture ″SN″ with sieved raw clay (34%) and nonmilling electrofiltered alumina (66%).
2. Mixture ″SM″ with sieved raw clay (34%) and milling electrofiltered alumina (66%).
3. Mixture ″BN″ with benefited clay (42%) and nonmilling electrofiltered alumina (58%).
4. Mixture ″BM″ with benefited clay (42%) and milling electrofiltered alumina (58%).

The calculated chemical compositions of dry mixtures are given in Table 3. The preparation mixtures was performed by hand mixing of dry components then adding water to get the 20% moisture and sulphite alcali cca 1% for better binding and finished by mixing. The green mixture cylinder specimens ϕ 50 × 45 mm were formed on a hydraulic press with pressure cca 20 MPa and dried.

Anneling. Anneling was carried out in industrial furnaces at the Plant ″Enker″ Tešanj. All mixtures were treated at 1580°C and 1635°C in the tunnel furnace within the cycle of 36 hours. The specimens ″SN″ and ″BN″ were further treated in the chamber furnace at 1700°C in the cycle of 44 hours. The anneling duration on the highest temperature has been cca two hours.

Examination. The determination of true density was according to JUS B.D8.302 (1984.) [7]. The bulk density, water absorption, true, apparent and closed porosity have been determined according to JUS B.D8.302 (1958.) and JUS B.D8.312 (1983.). The compressive strength could not take out according to standard because there were not enough specimens, so an unlogical result at specimen ″BM″ at 1580°C was obtained. Crystalline content was determined by using 20% HF during one hour at 25°C. The acid dissolves glassy phases and undissolved rest is crystaline phase.

Results and discussion

Table 3. Experimental resuts

Properties		Type of specimen									
		SN			SM		BN			BM	
Anneling temp. [°C]		1580	1635	1700	1580	1635	1580	1635	1700	1580	1635
Volume shrinkage [%]		28.25	30.79	36.51	29.56	30.35	47.85	43.34	42.24	48.25	43.50
Loss of mass [%]		5.316	5.255	5.05	5.37	5.385	6.555	6.535	6.67	6.7	6.825
Bulk density [g/cm^3]		2.09	2.18	2.39	2.32	2.33	2.77	2.53	2.42	2.84	2.60
True density [g/cm^3]		3.118	3.165	3.102	3.077	3.052	3.228	3.183	3.235	3.275	3.181
Compressive strength [MPa]		92.5	110	136	99	111	159	45	21	84	46
Crystalline content [%]		81.02	81.60	79.53	80.75	81.53	71.65	70.76	69.97	71.25	77.79
Ratio crystal/amorphous		80/20	80/20	80/20	80/20	80/20	70/30	70/30	70/30	70/30	75/25
True porosity [%]		33	31	23	25	24	14	20	25	13	18
Apparent porosity [%]		31	28	17	24	22	0	2	4	0	3
Closed porosity [%]		2	3	6	1	2	14	18	21	13	15
Water absorption [%]		14.5	13.3	7.1	10	9.4	0.05	0.8	1.45	0.11	1.0
Chemical composition [%]	Al_2O_3	68.5	72.4	68.6	69.4	72.8	69.4	73.6	67.5	68.1	74.8
	SiO_2	24.8	24.5	23.6	24.5	24.0	21.4	21.2	21.5	22.7	21.5
	Impurities	6.67	2.98	7.62	5.95	3.06	9.15	5.09	10.88	9.12	3.64
Calculated chemical composition [%]	Al_2O_3	70.6					70.147				
	SiO_2	24.85					21.856				
	Impurities	2.97					5.164				

The results of examination are given in Table 3.

Macroscopic appearance. The appearance of specimens is shown in Figure 3 and Figure 5. The white specimens with orange spots were made of raw clay and the orange and brown specimens were made of benefited clay. The specimens of raw clay have had a lot of surface cracks and less volume shrinkage.

The specimens of benefited clay treated at 1700°C (the specimens number 4 and 5 in Figure 3) have shown some deformations in form like buckling. The temperature 1700°C was too high for these types of specimens due to the presintered products with so much closed pores were produced.

The darkness of specimens has increased with increasing annealing temperature. There were no significant differences in appearance between nonmilling and milling alumina specimens.

Shrinkage and bulk density. The alumina grain size has not effected to a shrinkage, while the clay state had a great rule on shrinkage. The specimens of benefited clay have had rather high shrinkage and higher than of raw clay. Bulk density was depended of alumina and clay grain sizes such fine grains mixture could be easily detected by higher density than coarse grains. The temperature dependence of bulk density is shown in Figure 1. The shrinkage and bulk density specimens of raw clay have increased with increasing temperature and vice versa decreased at specimens of benefited clay.

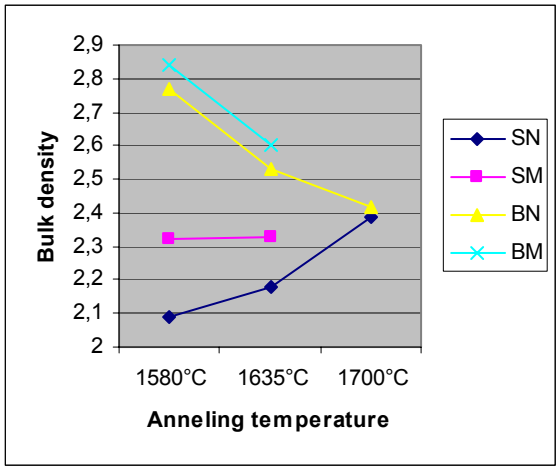

Fig. 1. Bulk density versus temperature

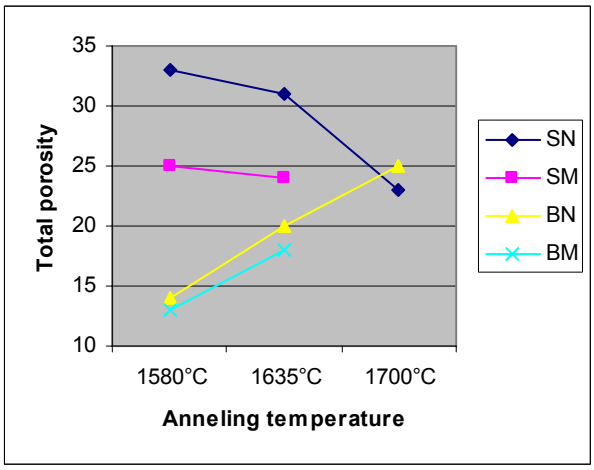

Fig. 2. Total porosity versus temperature

Compressive strength. The results of compressive strength have shown the very close dependence as bulk density except the ″BM″ at 1580°C (see Table 3). As it is mentioned there weren´t enough specimens to get real examination of compressive strength.

Crystaline content. The alumina grain size and temperature have not much effected to crystaline content. It has depended of a clay state so the specimens of raw clay have contained more crystaline phase than them of benefited clay because the benefited clay has contained more impurities.

There is a difference between calculated and tested chemical composition due to additions water and sulphide alcali. There is also increased content of Al2O3 and decreased content of impurities in specimens treated at 1635°C. There were some reaction between specimens and strewing powder of electromelted corundum during this treatment that caused these results. At 1700°C these reactions have intensified but results have shown the effect of carefully sampling when the cylinder bottom have not taken for chemical analyze.

Porosity. The total porosity has decreased with decreasing granulation of mixtures. For details, a total porosity dependence of temperature and mixture type is shown in Figure 2. Because of great number of cracks in specimens of raw clay they have had a high apparent porosity and it decreased with temperature increasing. Specimens of benefited clay have had a low apparent porosity but it increased with temperature increasing.

The differences in closed porosity between specimens of nonmilling and milling alumina were small. Closed porosity was low in specimens of raw clay and increased with temperature increasing. It also has increased with temperature in specimens of benefited clay, as can be seen in the Figure 4 and Figure 6. The specimens of benefited clay have had a great amount of closed pores and their dimension particularly increased with temperature increasing.

Fig. 3. Specimens treated at 1580 and 1700°C 1+2-″SN″ at 1700°C; 8+9-″SN″ at 1580°C; 15-″SM″ at 1580°C; 4+5-″BN″ at 1700°C; 11+12-″BN″ at 1580°C; 18-″BM″ at 1580°C)

Fig. 4. Destroyed ″BM″ at 1580°C

Fig. 5. Specimens treated at 1635°C (3+7-″SN″; 13+14-″SM″; 6+10-″BN″; 16+17-″BM″)

Fig. 6. Destroyed ″BM″ at 1635°C

Conclusion

The present work has demonstrated the importance of differences in grain size distribution in raw materials for a synthetic mullite production. The differences between specimens of raw and those of benefited clay have been significant speciality at volume shrinkage, mass loss, bulk density, compressive strength, crystaline content, porosity and water absorption. The differences between specimens of nonmilling and milling alumina have not been so significant except at a bulk density. The specimens of raw clay have had less deleterious components and higher SiO_2 content, so they have had more mullite content, higher degree of mullitization and lower mass loss. On the other hand they have had more pores, they have had smaller bulk density and volume shrinkage than the specimens of benefited clay.

The specimens of milling alumina have shown a slightly higher mass loss, bulk density and volume shrinkage and a slightly lower deleterious content and porosity than the specimens of nonmilling alumina.

The strength, bulk density and volume shrinkage have increased with temperature increasing at the specimens of raw clay and decreased at the specimens of benefited clay.

The beneficiation of raw clay, that is decreasing the grain size, has a significant effect on refractory properties more than effect of decreasing grain size of electrofiltered alumina.

For a production good synthetic mullite these experiments have separated two proceedings: (1) at lower temperatures the mixtures of benefited clay and fine grains alumina with a smaller amount of crystaline and (2) at higher temperatures the mixtures of raw clay and fine grains alumina with increasing crystaline. Therefore these experiments have to be continued and balanced effects of these processes.

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