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Effect of Mullite Formation on Properties of Aluminosilicate Ceramic Balls

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Abstract

In order to study the effect of mullite phase on the physico-mechanical of the aluminosilicate ceramic balls, 3 ceramic balls made of clay, feldspar and quartz were prepared. However, in this work, the clays were selected from i.e.,Trong, Perak (TC), Simpang Pulai, Perak (SP) and Selendang, Pahang (SC) and were identified as CBT, CBP and CBS, respectively. The formulation of each clay was fixed to 30 wt.% clay; 40 wt.% potash feldspar; 40 wt.% silica sand. The mixtures later,were dried for 6 hours under 25 ºC of room temperatures. Prior to shape balls, 30 wt.% of water was added to the mixtures in order to form dough. The dough was aged for 24 hours to homogenous the plasticity before shaped to 19 mm of spherical balls. The balls were dried in an oven at 110 °C for 24 hours before fired at 1250 °C for 2 hours. The phase formation of each mixture was investigated via X-ray diffraction analysis (XRD). Meanwhile, the physico-mechanical of ceramic balls was determined according Universal Oil Products (UOP). It is found that CBT exhibited outstanding physico-mechanical which has crushing strength 1270 kg compared to CBP and CBS due to the presence of mullite phase. This enables their use for ceramic balls as catalyst bed support in refining applications.

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*Keywords:*Mullite;aluminosilicate

1. Introduction

Ceramic balls in the shape of spherical of varying sizes, are popular to be used in ball valves, bearings, mechanical devices that provide linear or rotary motion, grinding media and also as bio-ceramic filters, purifiers,

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humidifiers and softeners. Besides the above mentioned application, the ceramic ball also is widely used as catalyst bed support especially in oil and gas refining applications. It is due the balls that can serve for both; to support and to protect catalyst from gas flows at various pressures, temperatures and rates, respectively. For that reason, they must have i) high impact resistance so that they do not break during loading into a reactor and ii) the ability to withstand rapid changes in pressure[1]. For this purpose, Universal Oil Product (UOP) are responsible to evaluate the ceramic ball characteristic so that they could meet the specifications set by UOP (as shown in Table 1).

The literatures indicated that there are two types of ceramic balls that served as catalyst bed supports;i) alumina and ii) aluminosilicate, respectively [2]. However, due to high sintering temperature (1500ºC) of α-alumina[3] most of catalyst bed supports are made of aluminosilicate. In addition, aluminosilicate price are also cheaper compared to α-alumina[4] since the kaolin[5] (one of the ingredients requires to produce aluminosilicate) can be obtained easily at low-priced. Furthermore, aluminosilicate also exhibit a low thermal expansion coefficient, good high-temperature strength and creep resistance, low density and good chemical inertness[6]. Besides, having low sintering temperature (< 1300 ºC), aluminosilicate also possess high mechanical strength which is comparable to the α-alumina ceramic ball. Although aluminosilicate holds various magnificent characteristic, there are several factors must be considered (i.e., mullite phase formation, temperature and soaking time[7]**)** so that the above mentioned characteristic can be achieved.

The formation of mullite phase during fabrication of the aluminosilicate ceramic balls is crucial because the phase could provide a strong bonding to exhibits good physico-mechanical properties[8]. Various approaches have been applied to synthesize mullite such as solid state reaction. However, the inter diffusion rates of Si^{4+} and Al^{3+} within the mullite lattice are relatively slow, the kinetics of mullite formation is depend on the precursor mixing strongly[5]. For example, the mullitization temperature for the solid state reaction between Al_2O_3 and SiO_2 particles is at 1650 ºC but when sol-gel technique is applied, the mullite can be formed at a temperature around 1150 ºC[5]. Thus, a careful selection on the suitable techniques to produce mullite-aluminosilicate must be taken into account. Among the available approaches, kaolin (kaolinite clay) is used.Thus, in this work, the aluminosolicate ceramic balls were synthesized using kaolinite clay as the main raw material while others such as silica sand and potash feldspar were added appropriately to improve the quality of aluminosilicate ceramic balls (based on UOP standard)

Table 1: Main specification of Inert Ceramic Ball by Universal Oil Product (UOP)

Dimension	UOP Specification
Chemical composition	
$Al_2O_3 + SiO_2$	≥ 90% (check font !)
SiO_2	≤ 80%
Physical requirement	
Shape	Spherical
Water absorption	≤ 0.9 %
Density	≥ 2.160 g/cm^3
Drop test (6 meter)	No fractured or spalling
Crushing strength (min.)	
- 19 mm Ø	430 kg

2. Materials and experimental procedures

2.1. Materials

The materials used in this work are clay, potash feldspar and silica sand. The chemical compositions of these materials are given in Table 2. Three Malaysian clay was used in this study i.e. Trong clay, Perak (TC), Simpang Pulai clay, Perak (SP) and Selendang clay, Pahang (SC). Trong clay (TC) and Simpang Pulai clay (SP) were supplied by Uniteck Agency Sdn. Bhd. Selendang Clay (SC) was supplied by Sri Hisham Holdings Sdn. Bhd. Beside clays, both potash feldspar and silica sand were obtained from Sibelco Malaysia Sdn. Bhd. were used to formulate the ceramic ball bodies.

2.2. Experimental procedures

Each powder mixture with different types of kaolin consist of 30 wt.% clay, 40 wt.% potash feldspar and 40wt.% silica sand were mixed for 6 hours via ball mill. Approximately 30 wt.% of distilled water (H_2O)added into the mixtures to form dough before aged for 24 hours to obtain homogenous plasticity of the dough. The dough (12 gram) was rolled manually using hand to produce 19 mm of balls diameter. The balls were dried in an Memmert UN260 oven at 110 °C for 24 h. before fired at 1250 °C for 2 h in Yudian 1600 furnace.

Various characterization techniques relative to physic-mechanical properties namely bulk density (g/cm^3), porosity (%), water absorption (%) and crushing strength (kg) of fired ceramic balls were used to measure the fired balls according to ASTM standard specifications[10,11]. For phase determination X-ray diffraction (XRD) analysis (Bruker AXS D8 Advance, Germany) was used and the results were analyzed using PAN Analytical X'pertHighScore Plus software. The XRD pattern of each ball from 10° to 90° at 2-theta scale were obtained using CuKα radiation (wavelength, λ = 1.5406 Å) with a scan speed of 2°/min. The morphology of the ceramic ball surfaces were observed using field emission scanning electron microscope (FESEM-Carl Zeiss Supra 35) that is equipped with energy dispersion X-ray EDX.

3. Results and discussion

The phase formation of aluminosilicate ceramic balls synthesized from a combination powder of kaolinite clay, silica sand and potash feldspar were determined via XRD analysis and the patterns obtained is shown in Fig. 1. It is found that a large amount of quartz phase is detected meanwhile other phase such albite, orthoclase and microcline were present in a minute amount. Fig.1 also shows the transformation of ceramic ball bodies after sintering process. From the patterns obtained and previous studies, the formulated bodies underwent of phase transformations as the temperature was raised from room temperature to 1250 ºC. Transformations of these phase are when T ≥1000ºC,

$$2SiO_2.Al_2O_3.2H_2O \text{ (kaolinite)} \rightarrow 3Al_2O_3.2SiO_2 \text{ (mullite)} + 4SiO_2 \text{ (amorphous)}$$

Mullite phase appears in two ceramic balls of CBT and CBS and no mullite phase detected in CBP except quartz phase which has less crystallinity. To further confirm this observation, quantitative XRD analysis was carried out through Rietveld refinement method using PAN Analytical X'PertHighScore Plus software. The results are shown in Table 3 which shows the weight R profile and the goodness of fit (GoF) values of ceramic balls. This approximates shows the reliability of the percentage concentration of identified phases obtained during refinement process. For acceptable refinement of the sintered samples, the weighted R profile for each observed peak needs to be below 20%, whereby GoF values needs to be less than 2.9 [12, 13].The phase transformations are expressed in the form of chemical reactions for the ease of explanation. However, the above equations are not exactly balanced for many ceramic products and are more or less non-stoichiometric[5]. Furthermore, the impurities in the starting powder can induce a liquid phase during firing.

Table 2 Chemical analyses data of the starting materials and formulated bodies

Constituents (wt.%)	Raw materials					Ceramic ball body types		
	TC	SP	SC	Potash Feldspar	Silica Sand	CBT	CBP	CBS
SiO_2	47.06	48.06	62.36	67.00	98.00	72.68	73.28	78.21
Al_2O_3	37.60	37.38	27.75	19.00	1.20	18.98	18.41	15.06
Fe_2O_3	0.95	0.70	0.54	0.12	0.05	0.37	0.28	0.24
TiO_2	0.54	0.02	0.81	0.02	0.03	0.17	0.02	0.26
Na_2O	0.01	0.02	0.09	2.00	0.15	0.30	0.31	0.34
K_2O	1.37	1.36	3.04	12.00	0.5	3.37	3.42	3.93
CaO	0.05	0.02	0.02	0.22	0.02	0.12	0.11	0.11
MgO	0.10	0.06	0.23	-	-	0.05	0.03	0.09
L.O.I	12.01	12.09	4.90	0.42	0.18	3.81	4.01	1.66

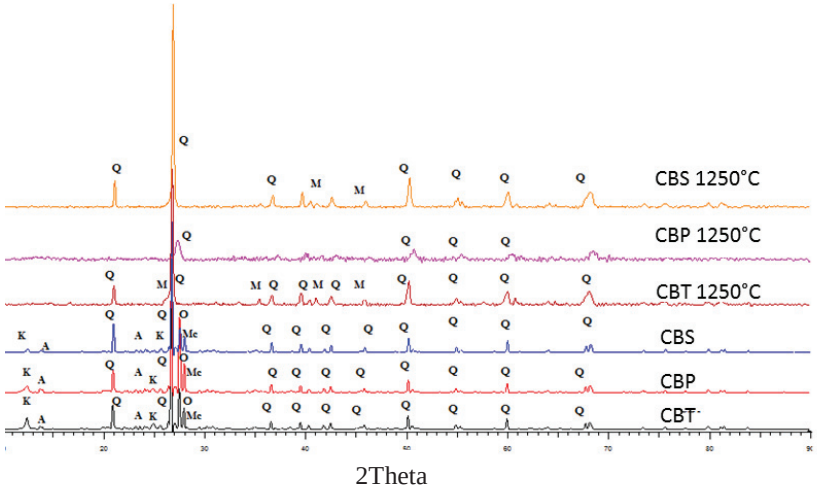


Fig. 1: X-ray diffractograms of ceramic ball bodies before and after sintering at 1250ºC. (Note: K=kaolinite, Q= quartz, Mc= microcline, O=orthoclase, A=albite, M=mullite)

Table 3 Quantitative analysis of secondary phases (mullite, quartz) presence in ceramic balls after sintering 1250 ºC through Rietvield refinement method

Ceramic ball designation	Percentage of mullite (%)	Percentage of quartz (%)	Peaks profile			
			R expected (error factor)	R profile (reliability factor)	Weighted R profile	Goodness of fit (GOF)
CBT	14.0	86.0	10.8631	13.2958	15.8552	2.1303
CBP	-	100.0	16.5215	17.9964	19.6477	1.4143
CBS	1.6	98.4	10.6708	12.7617	15.7207	2.1704

Bulk density, porosity, water absorption and crushing strength of ceramic balls were determined for balls fired at 1250 ºC. Fig.2 shows the bulk density value decrease accompanied by a decrease in the value of porosity. The decrease in porosity is related to the decomposition of the clay minerals, calcite, and organic matter initially present in ceramic balls. When ceramic balls were fired at 1250 ºC, the quartz remained undissolved, the potassium feldspar partly fused, and the kaolinite fully dehydroxylated. During densification process, the pore spaces gradually become filled with molten material which on cooling solidifies to form a glassy matrix. CBS has less porosity and water absorption (Fig.3) than other ceramic balls (CBT; 7.61%, 0.68% and CBP; 6.25%, 1.07%) of 5.91 % and 0.44 %, respectively due to densification process. The difference in the densification behaviour of ceramic ball bodies were mainly related to the dehydration of kaolinite, mullite formation and the liquid phase which mainly derived from SiO_2 and Al_2O_3 at higher temperatures[14]. Fig. 4 shows CBT has the highest crushing strength, 1,270.7 kg compared to other ceramic balls. It is 100% higher than the value set by UOP of 430kg for ball-sized 19 mm. CBT has the highest crushing strength due to the highest mullite content in the body [9].Crushing strength is related to the formation of mullite phase that forms a network of mullite needles which strengthens the structure at high temperature[8]. From the Table 3, CBT has a mullite content higher than other ceramic balls of 14.0%.

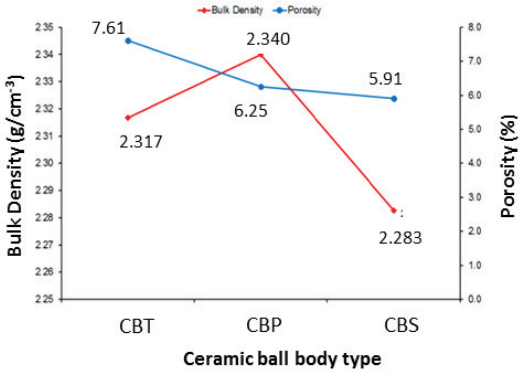


Fig. 2: Bulk density and porosity of the ceramic balls fired at 1250 ºC.

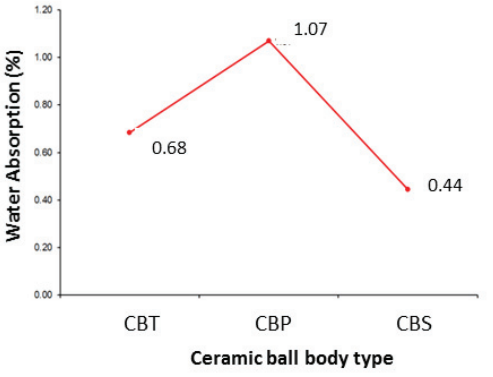


Fig. 3: Water absorption and porosity of the ceramic balls fired at 1250 ºC.

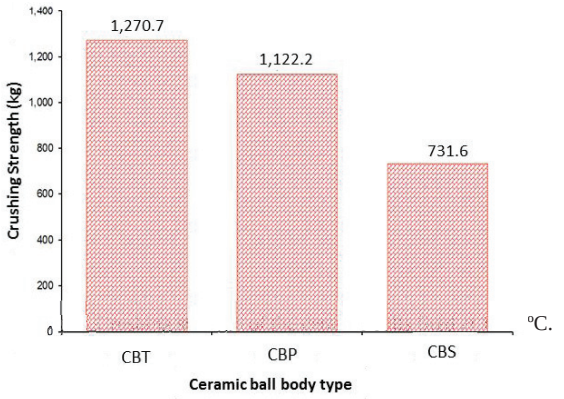
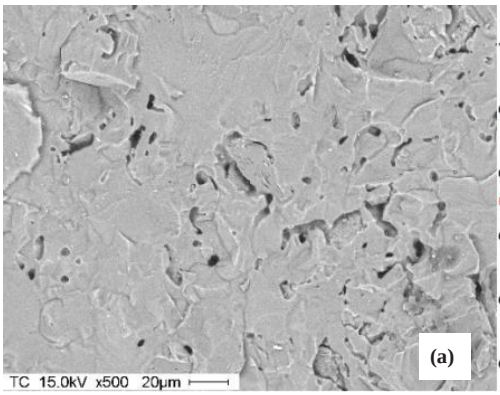
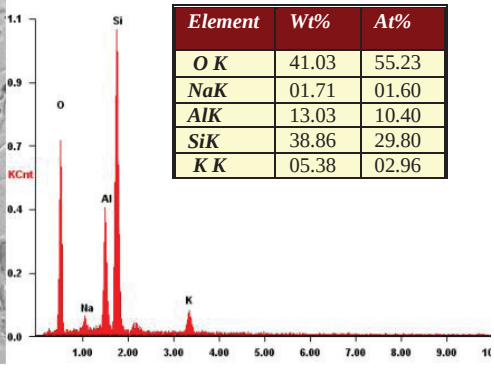


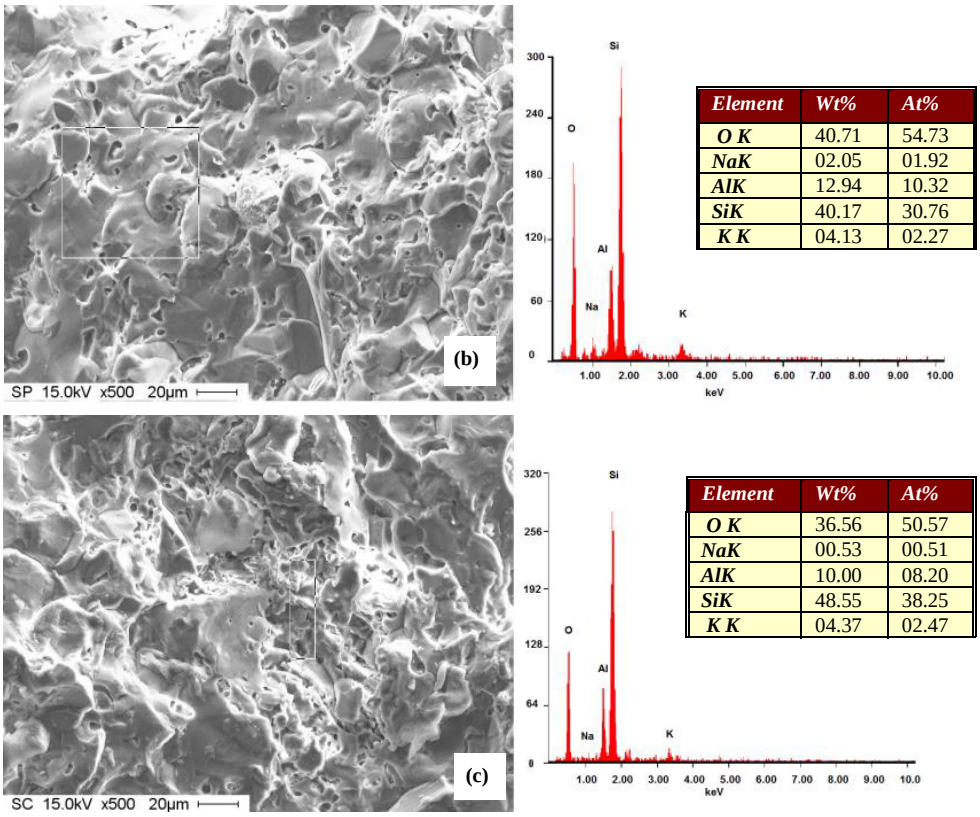
Fig. 4: Crushing strength of the ceramic balls fired at 1250 ºC.

The microstructure of the three ceramic balls as observed on FESEM are shown in Fig.5. The microstructures exhibit homogeneous matrix with relatively high porosity. The matrix has a relatively high Si/Al ratio, revealed by EDS spectra analyses.The fracture surface is characterised by the presence of round pores, essentially closed porosity. Spherical pores indicate a mature microstructure, where a sort of equilibrium was reached, from the equilibrium between the vapour pressure of gas and the viscosity of the liquid phase[7]. The microstructures of CBT and CBP do not present substantial differences among them, while CBS shows a less compact microstructure, with a lot of pores due to incomplete densification process during sintering.





Element	Wt%	At%
O K	41.03	55.23
NaK	01.71	01.60
AlK	13.03	10.40
SiK	38.86	29.80
K K	05.38	02.96



Element	Wt%	At%
O K	40.71	54.73
NaK	02.05	01.92
AlK	12.94	10.32
SiK	40.17	30.76
K K	04.13	02.27

Element	Wt%	At%
O K	36.56	50.57
NaK	00.53	00.51
AlK	10.00	08.20
SiK	48.55	38.25
K K	04.37	02.47

Fig.5. EDX spot analysis of: (a) CBT, (b) CBP and (c) CBS heat treated at 1250 °C for 2 h. (Micrographs showing selected areas for elemental composition analysis and quantitative compositions are given in the insets.)

4. Conclusion

Physico-mechanical of aluminosilicate ceramic balls is found to be highly dependent on the transformation mullite phase in the bodies. The presence of mullite in CBT is higher than CBP and CBS. CBT containing 14.0% mullite show outstanding physico-mechanical after firing at 1250 ºC which has highest crushing strength, 1270.7 kg and 100% better than the crushing strength set by UOP and met other specifications. These excellent properties of such ceramic balls enable their use in various refining applications.

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