EFFECT OF GRAIN SIZES OF PREHEATED ANDALUSITE AGGREGATE ON THE PROPERTIES OF MULLITE-BASED REFRACTORY

Qingfeng Wang[1], Wei Tang[2], Xiaoyu Wang[1], Liusheng Li[1], Guihua Liao[1], Guotian Ye[2]

[1]Luoyang Institute of Science and Technology, Luoyang, China; [2]Zhengzhou University, Zhengzhou, China

ABSTRACT

In this work, the different grain sizes (5-3mm, 3-1mm, ≤1mm) of andalusite aggregate were preheated at 1400°C for 3h to substitute the same size of mullite aggregates in mullite-based refractory. The cold mechanical strength and thermal shock resistance of these mullite-based samples, after firing at 1450°C for 3h, were investigated in the light of phase evolution and microstructure development. The results showed that the residual andalusite in the preheated andalusite aggregate played the role on the properties of fired samples. And the increased grain size of andalusite aggregate induced the improved thermal shock resistance and the deceased mechanical strength, due to the micro-cracking network resulting from the anisotropic characteristic of andalusite crystals.

INTRODUCTION

In general, andalusite refractory products are used satisfactorily when thermal shock resistance is required. It is suggested that the improved thermal shock resistance of andalusite refractories could be largely due to the high thermomechancial resistance of primary and secondary mullite generated by the transformation of andalusite at high temperatures[1]. Apart from this aspect, some researchers pointed out that the improved thermal shock resistance could be attributed to the shielding effects of viscoelastic crack bridging by silica glassy phase, which not only healed the initial cracks but also stopped the new cracks created by the thermal shocks[2]. In addition, the impurities of andalusite[3] and the micro-sized alumina addition which influence the mullitization process of andalusite can also affect the thermal shock resistance of andalusite refractories. These results indicate that there is a closely relationship between the mullitization process and the thermal shock resistance of andalusite refractories, resulting from the composite microstructure developed during the mullitization process[2].

However, the mullitization process of andalusite is not too fast at temperature below 1550°C. And the complete mullitization of a fine grain would be more rapidly achieved than the one of a large grain[3]. These features show that the large grains of andalusite, such as andalusite aggregates, are not fully transformed into mullite in comparison with fine or ultrafine andalusite powders under the same firing condition. At the same time, it is found that andalusite aggregates, used in refractory materials, are typically made of a single crystal or of a fragment of single crystal. Moreover, andalusite crystal presents the anisotropic coefficient of thermal expansion (CTE) of $12.9\times10^{-6}K^{-1}$ along a axe, $9.6\times10^{-6}K^{-1}$ along b axe and $3.1\times10^{-6}K^{-1}$ along c axe[4, 5]. Considering the above factors as well as the low linear thermal expansion coefficient ($4.5\times10^{-6}K^{-1}$) of mullite[6], it is very interest to address that the thermal expansion mismatch among the partly mullitized andalusite aggregates and matrixes would generate thermal stress during heating or cooling, which can bring about the network of micro-cracks and thus can strongly affect the thermal shock resistance of mullite based refractories.

Although many works have been devoted to study the thermomechancial behavior of refractories with andalusite aggregate[7, 8], few researches took into account the thermal shock resistance behaviors of mullite based refractories associated with the anisotropic behavior of partly mullitized andalusite aggregates in comparison with mullite aggregates and matrixes. Therefore, the aim of this paper is to investigate the thermal shock resistance behavior of mullite based refractories with emphasizing on the thermal expansion mismatch between the preheated andalusite aggregates and matrixes.

MATERIALS AND METHODS

As shown in Table 1, mullite (5-3mm, 3-1mm, ≤1mm and 325 mesh, Jinghui), reactive alumina (CL370, Almatis), microsilica (U951, Elkem) and calcium aluminate cement (Secar 71, Kerneos) were used as starting materials. Sodium tripolyphosphate (STPP) were used as water reducer. The commercial andalusite aggregate (5-3mm, 3-1mm and ≤1mm, Imerys Refractory Minerals) were preheated at 1400°C for 3h.

Then, the different grain sizes of mullite aggregate were substituted by the same size of preheated andalusite aggregates.

All batches were dry-mixed for 1 min before water addition, followed by 4 min wet mixing in a laboratory mixer. After that, the mixtures were cast under vibration into the moulds of 4cm×4cm×16cm. Then all the samples were dried at 110°C for 24h, followed by heat treatment at 1450°C×3h. After firing, bulk density (BD) and apparent porosity (AP), firing linear change (FLC) and modulus of rupture (MOR) were measured. And the thermal shock damage test was conducted as follows: the fired (1450°C×3h) samples were subjected to 5 cycles of heating at 950±10°C for 30 min and cooling down in air from 950°C to room temperature. The bending strength of the samples after thermal shock was measured. And the thermal shock resistance was evaluated by residual strength ratio of the samples. The phase composition of preheated andalusite aggregates was determined by X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Germany) and the approximate abundance of crystalline phases was calculated by means of X' Pert plus software. The morphology of the fired (1450°C×3h) samples after 5 cycles of thermal shock were observed by field-emission scanning electron microscopy (SEM, ΣIGMA HD, ZEISS, Germany). To remove glass phase, the fractured surfaces of the samples were etched by 5 wt% HF solution for 15s and then washed and dried at 100°C. In addition, the values of above results were the average from three bars.

Tab. 1: Formulation of mullite based castables.

Raw materials		M	MB	MM	MS
Mullite aggregate	5-3mm	30	0	30	30
	3-1mm	23	23	0	23
	≤1mm	15	15	15	0
Preheated andalusite aggregate	5-3mm	0	30	0	0
	3-1mm	0	0	23	0
	≤1mm	0	0	0	15
Mullite	0.048mm	20	20	20	20
CL370		3	3	3	3
Microsilica		3	3	3	3
CAC		6	6	6	6

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern and the relative contents of residual andalusite and mullite of andalusite aggregates with different grain sizes after preheating at 1400°C for 3h. It can be observed from Figure 1a that andalusite, mullite and small quantities of quartz were detected in all the preheated andalusite aggregates (1400°C×3h). However, the intensities of mullite were increased on the expense of andalusite with the decreasing grain sizes of andalusite aggregates after preheating at 1400°C×3h, which was consistent with the relative contents development of residual andalusite and mullite for the preheated andalusite aggregates with different grain sizes (shown in Figure 1b). These results confirmed that there is a slower mullitization rate of coarse andalusite aggregates than the one of fine aggregates with the firing temperature up to 1400°C.

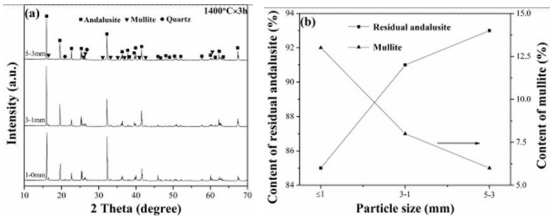

Fig. 1: XRD patterns and relative contents of residual andalusite and mullite for the preheated andalusite aggregates at 1400°C for 3 h.

Figure 2 shows that bulk density (2.63 g/cm^3) of the samples with coarse preheated andalusite aggregate (5-3mm) was slight higher than the one (2.62 g/cm^3) of the samples without preheated andalusite aggregate. However, bulk density of the preheated andalusite aggregates was decreased from 2.63 g/cm^3 (MB) to 2.59 g/cm^3 (MS) with the decreased the grain size of the preheated andalusite aggregate from 5-3mm to ≤1mm, accompanied with the increased apparent porosity (AP) of samples from 13.4 % (MB) to 13.6 % (MS). These results should be attributed to faster mullitization rate of small grain size of andalusite aggregates in comparison with the ones of large andalusite aggregate (shown in Figure 1), which led to the obvious volume expansion during the mullitization process[1].

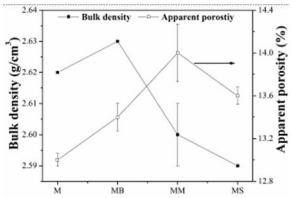

Fig. 2: Effect of the grain size of preheated andalusite aggregates on BD and AP of the castables fired at 1450°C×3 h.

As shown in Figure 3, the firing linear change (FLC) of the castable samples without the preheated andalusite aggregates was the largest (-0.63%) among the samples with preheated andalusite aggregate, resulting from the volume expansion[1] of preheated andalusite continuous mullitization process. For the samples with the preheated andalusite aggregates, however, the samples with fine preheated andalusite aggregates (≤1mm) showed the largest shrinkage

(-0.47%), the samples with the mediate size (3-1mm) of preheated andalusite aggregates had a larger shrinkage (-0.41%), and the samples with large grain size (5-3mm) of preheated andalusite aggregate present the smallest shrinkage (-0.22%). It is reported that the amount of silica-rich glass available on the surface of andalusite is depended on the size of andalusite grain, and more silica glass can be made available on the surface of fine andalusite grain than the large ones[1]. Therefore, the liquid phases yielded from the continuous mullitization of the fine preheated andalusite aggregates would assist more sintering and accordingly counterbalance the volume expansion of mullitization, compared with the large preheated andalusite aggregates.

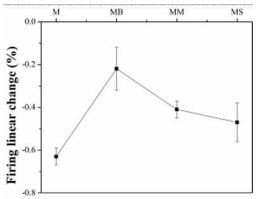

Fig. 3: Effect of preheated andalusite aggregates on FLC of the castables fired at 1450°C×3 h.

As shown in Figure 4, it can be observed that the large grain size (5-3mm) of preheated andalusite aggregates addition can decrease the cold modulus of rupture from 2.62 MPa (the samples without preheated andalusite aggregates) to 8.7 MPa (the samples with 5-3mm preheated andalusite aggregates). However, with the small grain sizes of preheated andalusite aggregates addition, cold modulus of rupture was increased from 12.4 MPa (the samples with 3-1mm preheated andalusite aggregates) to 26.4 MPa (the samples with ≤1mm preheated andalusite aggregates). It is known that there are two typical factors can notably affect the mechanical strength of andalusite refractories. The first one is related to the volume expansion induced by andalusite mullitization[1]. The second one is the expelled amorphous silica phase from the decomposition of andalusite which can act as the sintering additive during the densification process[9]. Therefore, these results should be attributed to the interaction between the volume expansion of mullitization and silica liquid aided sintering. For the large grain size of preheated andalusite aggregates, the volume expansion of mullitization should have an advantage over the liquid sintering to deteriorate the mechanical strength development. Nonetheless, the small grain size of the preheated andalusite aggregate would induce much more expelled silica-rich liquid[1], which not only brought about the obvious sintering shrinkage (as shown in Figure 3) but also enhanced the bending strength of the samples.

After thermal shock experiment, the residual strength of the samples without the preheated andalusite aggregate decreased sharply to 10.4 MPa. The samples with small (≤1mm) and mediate (3-1mm) grain size of preheated andalusite aggregates decreased to 13.3 MPa and 11.3 MPa, respectively. However, the residual bending strength of the samples with large grain size (5-3mm) of preheated andalusite aggregates increased from 8.7 MPa (before thermal shock) to 9.6 MPa (after thermal shock). As a result, the residual strength ratios of the samples with preheated andalusite aggregates were all higher than the ones without preheated andalusite aggregate. And the residual strength ratio (111.2 %) of the samples with large grain size of preheated andalusite aggregate was the highest in comparison with the ones containing mediate preheated andalusite aggregate (47.2 %) and small preheated andalusite aggregate (65.6 %).

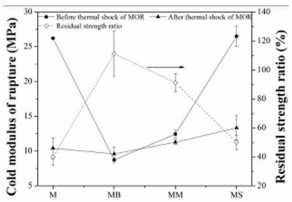

Fig. 4: Effect of the grain size of preheated andalusite aggregates on firing linear change of the castables fired at 1450°C×3 h.

To illustrate the difference among the thermal shock resistance behaviors of the above samples, the samples with large (5-3mm) preheated andalusite aggregates and the ones without preheated andalusite aggregates were selected, and the micrographs of these samples after 5 cycles of thermal shock were shown in Figure 5.

It can be observed from Figure 5a that the interfacial debonding between mullite aggregate and matrix were not obvious. Conversely, there were some large micro-cracks located at the interfaces of the preheated andalusite aggregates and matrix after 5 cycles of thermal shock, as shown in Figure 5b. Because of the highest amount of residual andalusite in the large preheated andalusite aggregate (shown in Figure 1), the micro-cracks present in the samples with large (5-3mm) preheated andalusite aggregates should be the result of the large thermal expansion mismatch between the residual andalusite aggregate and the castable matrix, which should be responsible for the increased thermal shock resistance of the sample with large grain size of preheated andalusite aggregates (shown in Figure 4).

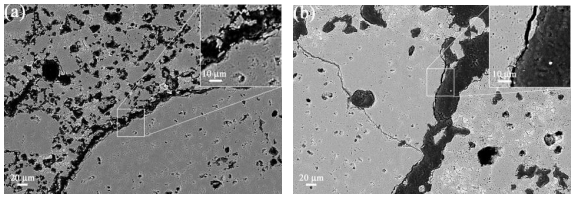

Fig. 5: Microstructure of the fired samples without (a) and with preheated andalusite aggregates (b) after thermal shock.

CONCLUSIONS

Considering the mullitization process influenced by the particle size of andalusite and the anisotropy of thermal expansion of andalusite crystal, the preheated andalusite aggregate addition in the mullite based refractory not only influence the bulk density and sintering linear change of the sample, but also control the thermomechancial behavior of the mullite based castable samples. In particular, the high content of residual andalusite in the preheated andalusite aggregate induced the large thermal expansion mismatch between the preheated andalusite aggregates and matrixes of the castable samples. This feature brought about the increased network of micro-cracks around the aggregates, which can obviously enhance the thermal shock resistance of mullite based refractories.

ACKNOWLEDGEMENTS

The authors acknowledge the Foundation of the State Key Laboratory of Advanced Refractories of China (grant number 201301 and 201502), Foundation of Key Scientific Research Projects in Colleges and Universities of Henan Province (grant number 16A430021) and Foundation of High Level Talent Research Project of Luoyang Institute of Science and Technology (grant number 2015BZ05) for the financial support.

REFERENCES

[1] Rebouillat L, Rigaud M. Andalusite-based high-alumina castables. J Am Ceram Soc. 2002;85(2):373-8.

[2] Bouchetou ML, Poirier J. Behaviour of andalusite and mullitized andalusite under thermal shock. Refract Appl News. 2009;14(5):14-8.

[3] Bouchetou M-L, Ildefonse J-P, Poirier J, Daniellou P. Mullite grown from fired andalusite grains: the role of impurities and of the high temperature liquid phase on the kinetics of mullitization and consequences on thermal shocks resistance. Ceram Int. 2005;31(7):999-1005.

[4] Kakroudi MG, Huger M, Gault C, Chotard T. Anisotropic behaviour of andalusite particles used as aggregates on refractory castables. J Eur Ceram Soc. 2009;29(4):571-9.

[5] Moehmel S, Frulli D, Ahouanto F, Heever Dvd. Properties and applications of andalusite based refractories and the influence of mineral impurities on the behaviour of refractories made thereof. In: Proceedings of the 7th International Symposium on Refractories (ISR 2016); 2016 Sept 20-22;. Xi'an, China; 2016.

[6] Schneider H, Fischer RX, Schreuer J. Mullite: crystal structure and related properties. J Am Ceram Soc. 2015;98(10):2948-67.

[7] Chuanyin Z, Guotian Y, Kunpeng L, Yajuan W, Dan H. Influence of mullitization of andalusite with different particle size on high-temperature properties of high-alumina bricks. In: Proceedings of the 57th International Colloquium On Refractories 2014; 2014 Sept 24-25; Aachen, Germany; 2014. p. 211-3.

[8] Ribeiro GC, Resende WS, Rodrigues JA, Ribeiro S. Thermal shock resistance of a refractory castable containing andalusite aggregate. Ceram Int. 2016;42(16):19167-71.

[9] Zadeh Hayati E, Mohammad Moradi O, Ghassemi Kakroudi M. Investigation the effect of sintering temperature on Young's modulus evaluation and thermal shock behavior of a cordierite–mullite based composite. Mater Des. 2013;45:571-5.