Comparison of Fused and Sintered High Alumina Refractory Aggregates - Perceptions, Characteristics, and Behaviour in Different Refractories

Dale P. Zacherl[1], Marion Schnabel[2], Sebastian Klaus[2], Andreas Buhr[2], Dagmar Schmidtmeier[3], Shankha Chatterjee[4],
Jerry Dutton[5]
[1]Almatis Inc., Leetsdale, Pennsylvania, USA
[2]Almatis GmbH, Frankfurt, Germany
[3]Almatis GmbH, Ludwigshafen, Germany
[4]Almatis Alumina Pvt. Ltd, Kolkata, India
[5]Stourbridge, United Kingdom

INTRODUCTION

The refractory community continuously strives for better and deeper understanding of materials, their reactions and applications. Studies conducted in the past, plus individual experiences, positive or negative, have created many perceptions in the market about the most appropriate refractory aggregate for a particular application.

With regard to the use of fused and sintered aggregates in both refractory bricks and castables, opinions are set and are difficult to discuss and refute. These include:

- Fused raw materials are more dense and therefore more resistant to corrosion
- Fused raw materials have a rounder grain shape that is better for densification and flowability
- Fused raw materials exhibit better creep resistance
- Sintered aggregates are more reactive and develop higher strength during firing. Therefore the thermal shock resistance is lower when compared to fused aggregates

However, something that applied in the past does not necessarily have to be still valid today.

Fused and sintered versions of most synthetic high alumina materials exist in the market. High alumina aggregates with > 99 % Al_2O_3 are white fused alumina (WFA) and sintered Tabular alumina. Brown fused alumina (BFA) was for a long time the only aggregate with 95% Al_2O_3 content. With the development of BSA 96, an alternative sintered aggregate was introduced to the market in 2010 [1].

The purpose of this paper is to outline the differences between high alumina fused and sintered raw materials and show their influence on the final properties of refractory formulations such as bricks, castables or dry vibratable mixes (DVMs). The focus will be on white and brown fused alumina and sintered Tabular alumina and BSA 96. Other aggregates such as Spinel and Mullite also exist as fused and sintered versions but are not discussed in this paper.

PRODUCTION OF HIGH ALUMINA AGGREGATES

Fusion process

Typically, white fused alumina (WFA) is produced by batch melting of a Bayer alumina feedstock in an electric arc furnace. After melting at temperatures >2000°C, cooling of the blocks takes place and Na_2O is segregated as β-alumina in the upper central portion of the fused block. Due to the inherent cooling of the molten alumina block, WFA properties differ between the inner and the outer part of the block. Apart from the differences in Na_2O content, the crystal size and the open porosity also vary in different sections of the block.

Brown fused alumina is produced by fusing pre-calcined non-metallurgical bauxite in a batch or semi-batch furnace. During the fusion process oxides of silicon and iron are reduced to metal by the addition of coke and are removed as ferrosilicon. Iron scrap is added to facilitate the gravimetric separation of ferrosilicon [2].

A shortening of the melting and separation process in order to reduce production cost will have a significant impact on the quality of the fused product. Unless the fusion process is carefully controlled, the product may contain residual carbides, metallic inclusions and other impurities.

Sintering process

The production of sintered high alumina aggregates such as Tabular alumina and BSA 96 follows the same process steps as practised in the advanced ceramics industry. In principle, they consist of raw material grinding, forming, drying and sintering [3].

CHEMICAL PURITY

The impurity levels of fused and sintered aggregate are generally similar. The major difference is the location of the impurities. Because of the ceramic processing the impurities of sintered aggregates are homogenously distributed within the structure. As a consequence all size fractions have the same chemical composition as shown in Tab. 1. Even the fine milled materials have the same chemical composition as coarser fractions.

This is different to fused aggregates where impurities often accumulate in the fine fractions. These impurities may react with water and have a negative impact on the flow and setting behaviour of castables or influence the sintering behaviour as described by Büchel et al. [4].

Tab. 1: Chemistry of BSA 96 by fraction

Chemistry [%] per fraction [mm]						
	6-15	3-6	1-3	0.5-1	0-0.5	<90µm
Na_2O	0.28	0.31	0.29	0.32	0.27	0.30
Fe_2O_3	0.16	0.18	0.20	0.21	0.19	0.16
SiO_2	0.54	0.58	0.62	0.61	0.51	0.51

DENSITY AND POROSITY

It is often stated that fused grains show a better chemical resistance when compared to sintered aggregates of similar chemical composition due to high density, low open porosity and large crystal size.

White and brown fused alumina samples of different origin (European and Chinese) and Tabular alumina and BSA 96 were tested at the DIFK, Höhr-Grenzhausen by using the mercury-intrusion method in accordance with DIN 66133. The bulk density, open porosity and mean pore diameter are shown in Tab. 2. The bulk density and the open porosity of all WFA samples are higher than for Tabular alumina. This can be attributed to the differences in microstructure between fused and sintered alumina. (Fig. 1)

The ceramic sinter process permits a well-controlled development of microstructure where small pores are entrapped inside and between the crystals. These pores are mainly closed and are the reason for the lower bulk density and lower open porosity of Tabular alumina. However, even more important than the absolute value of open porosity is the difference in the mean pore diameter between WFA and Tabular alumina. The average pore size of the tested white fused alumina varied between 30.7 - 47.3 µm whereas Tabular alumina exhibits a mean pore diameter in the submicron range of 0.71 µm. There are virtually no pores present in Tabular alumina with a diameter larger than 10 µm. Brown fused alumina has a significantly higher bulk density and slightly lower open porosity by mercury intrusion method when compared to BSA 96. But the mean pore diameters for the brown fused samples range between 14.7 – 28.0 µm whereas the mean pore diameter of BSA 96 is only 0.38 µm.
The total open porosity of a refractory material is a critical value, because open pores increase the surface area of the refractory material that can be attacked and will therefore contribute to accelerated corrosion.

Tab. 2: Comparison of open porosity and mean pore diameter of fused and sintered refractory aggregates

		Tabular alumina	White Fused Alumina (WFA)		
		T60/T64	supplier A	supplier B	supplier C
		5 – 8 mm	3 – 5 mm	3 – 6 mm	3 – 6 mm
Mean pore diameter	µm	0.71	47.3	30.7	43.9
Open porosity	vol.-%	1.51	5.56	5.77	5.22
Bulk density	g/cm³	3.60	3.66	3.66	3.71

		BSA 96	Brown Fused Alumina (BFA)			
			supplier A	supplier B		supplier C
		5 – 8 mm	3 – 5 mm	3 – 6 mm	6 – 10 mm	3 – 6 mm
Mean pore diameter	µm	0.38	28.0	14.7	27.0	24.9
Open porosity	vol.-%	4.40	0.85	1.84	1.99	1.24
Bulk density	g/cm³	3.52	3.88	3.88	3.85	4.00

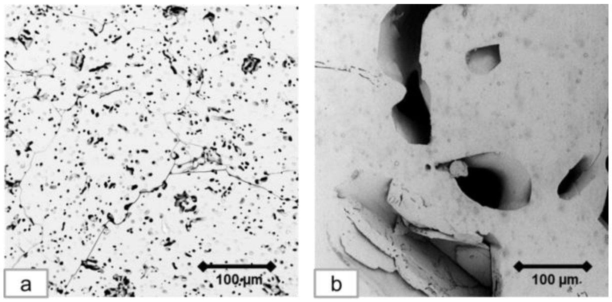

Fig. 1: Microstructure of Tabular alumina (a) and white fused alumina (b)

However the pore size is also important in order to judge the resistance of a material against corrosion. As shown by Borovikov the calculated infiltration speed of a pore with a size of 50 µm by a typical steel slag is more than 100 times higher than for a pore of 1 µm [5]. Small pores <1 µm can almost not be infiltrated by typical steel slags or metals and do not therefore support corrosion by offering additional surface area.
Although the bulk density of fused aggregates is generally higher than for the comparable sintered aggregate their porosity is mainly open with large pores that can be easily penetrated. Tabular alumina and BSA 96 show a clear advantage over fused materials with regard to corrosion because of their closed porosity and the very fine pore structure of the open pores.
The closed porosity of sintered high alumina aggregates is also the reason for their good thermal shock resistance when compared to fused materials. The pores prevent the propagation of cracks which have been generated by the thermo-mechanical stress induced by the thermal shock. As described in previous papers the percentage of undamaged grains of Tabular alumina after 20 thermal shock cycles is four to five times higher than for fused aggregates with comparable chemical composition [3].

GRAIN SHAPE

The grain shape of fused and sintered high alumina aggregates was measured with an optical analyser, CAMSIZER P4 using Dynamic Image Analysis (DIA) from Retsch Technology. DIA analyses the shadow projections of particles and a variety of size parameters can be measured.
For this study the focus was on

- Aspect or width/length ratio, as a function of the largest diameter and the smallest diameter. With increasing aspect ratio the grains are rounder; low values indicate elongated, splintery grains.
- Sphericity of sintered and fused particles.
- Corner roundness as mean radius of all corners divided by the radius of the largest in-circle. Higher values indicate a smoother surface whereas sharp-edged particles have typically low values.

As shown in Fig. 2 the average aspect ratio of WFA, BFA and Tabular alumina are very close - 0.64 for the fused aggregates and 0.65 for sintered alumina. BSA 96 shows a slightly higher average aspect ratio of 0.68 representing more cubic shaped grains.

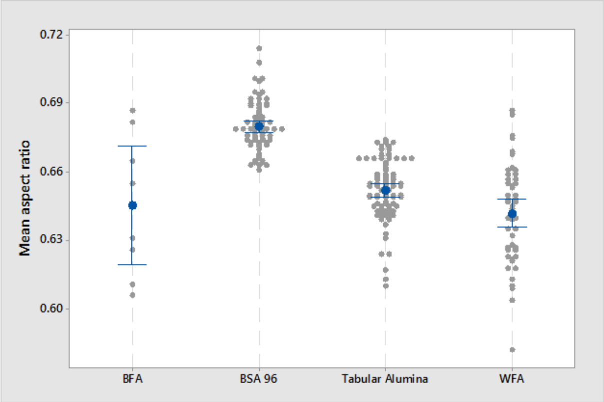

Fig. 2: Mean aspect ratio of fused and sintered refractory aggregates

The influence of these apparently small differences of the grain shape on the flowability of a refractory castable is shown in Fig. 3. Selected Tabular fractions with different aspect ratios from 0.62 to 0.68 were tested in a formulation of a self-flowing castable. Particle size distribution and matrix composition were kept constant. The flowability was measured 10 min after mixing.
For the same water content the flowability improves from 228 mm to 252 mm with an increase of the aspect ratio from approximately 0.63 towards more cubic particles with an aspect ratio of approximately 0.68.

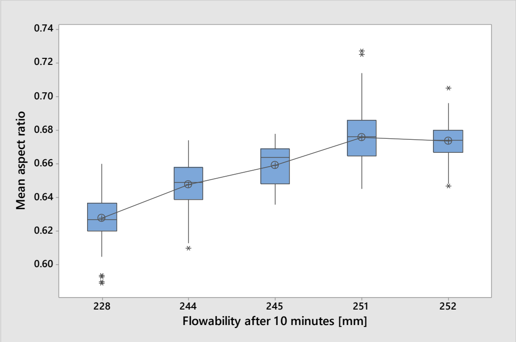

Fig.3: Relationship of aspect ratio of refractory aggregate to flowability of a self- flowing castable

A well-established method for determination of the shape of sand and sediments in geological analyses is the manual analysis of roundness and sphericity according to Krumbein & Sloss. The corner roundness on the x-axis is plotted against the sphericity on the Y-axis, and therefore allows a more complex description of the particle shape. Fig. 4 provides this analysis between fused and sintered refractory aggregates.

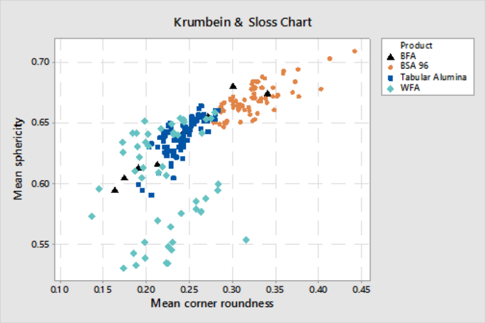

Fig. 4: Krumbein & Sloss Chart of fused and sintered refractory aggregates

The mean sphericity of the tested WFA has a wide spread from below 0.52 to 0.66. The two visible major areas can be attributed to the different suppliers of the material. All WFA samples have a low mean corner roundness below 0.3 which means sharp-edged grains. As the primary application of these aggregates is in the abrasion market, this property is required to achieve good cutting results.

The size parameters of Tabular alumina almost overlap with those of the more rounded WFA samples. A slight shift can be noticed in corner roundness which is on average higher for the sintered aggregate. The origin for this may well be in the microstructures which result in different fracture behaviour.

The BSA 96 results are positioned more in the upper right corner of the chart which represents the roundest grains with the smoothest surface of the tested materials. The BFA results are wide spread for both sphericity and roundness, but there are not enough data points to draw sound conclusions. It seems that as in the case of WFA the shape parameters for BFA are also much dependent on the supplier.

CREEP RESISTANCE

High temperature creep resistance is an important indicator for the volume stability of materials under high pressure and elevated temperatures. It has been shown that the creep resistance of Tabular based Mullite-bonded 90% Al_2O_3 bricks is superior when compared to bricks based on white fused alumina [5]. For this special application fine Tabular is beneficial for in-situ Mullite formation which results in a strong bonded matrix and a lower creep rate accordingly.

To test the creep resistance of the aggregate itself high alumina castables were investigated. The matrix composition was kept constant for Tabular and WFA. To exclude ternary phases to influence the creep behaviour, a calcia free mix with Alphabond 300 (hydratable alumina) as a bonding agent was chosen. However, it has to be considered that, due to the lack of calcia, the bond in the matrix is less pronounced resulting in lower strength and higher open porosity[6]. The WFA sizes had a low amount of impurities and BSGs >3.6 g/cm^3. The samples were pre-fired at 1500°C and sent to Tata Steel Ijmuiden for creep investigations. The samples were heated up to 1600°C followed by a 50 h holding time as shown in Fig. 5. A constant pressure of 0.6 MPa (87 psi) was applied during whole treatment time. This pressure is three times higher than the usually applied 0.2 MPa in order to show different behaviour of materials.

The results show with -0.088 %/h$_{2h\text{-}50h}$ a more pronounced creep rate for the Tabular based castable when compared to the castable based on WFA (-0.039 %/h$_{2h\text{-}50h}$). The higher creep for Tabular may be explained by two mechanisms:

1. A Tabular alumina grain can be defined as a polycrystalline material comparable to a ceramic body. Such materials are more sensitive to high temperature creep due to grain boundary sliding at microscopic scale [7].
2. Fused materials exhibit lower sinter reactivity when compared to sintered materials. With regards to Tabular alumina this leads to a more intense interaction between the aggregate and the surrounding matrix. The ongoing densification caused by sinter reactions at 1600°C is reflected in a higher creep rate for Tabular.

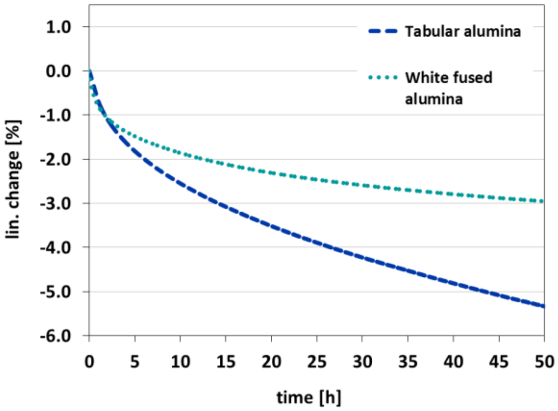

Fig. 5: Creep tests for 50 h holding time at 1600°C and a constant pressure of 0.6 MPa.

SINTER REACTIVITY

Various studies have been conducted to compare the differences in reactivity of fused and sintered aggregates. Klewski et al. [8] investigated the influence of various alumina aggregates on the spinel formation during firing and on the final properties of AMC bricks. It was found that bricks based on BSA 96 show a more intense and homogeneous spinel formation than those based on BFA. Sintered aggregates show an earlier and more even spinel formation in AMC bricks when compared to fused aggregates due to their higher sintering activity. BSA 96 contains less and more evenly distributed impurities than BFA. Therefore BSA 96 shows predictable and consistent behaviour in spinel formation and PLC.

Munuswami et al. presented a study where high purity fused and sintered alumina aggregates are compared in spinel forming dry vibratable mixes (DVMs) [9]. The particle size distribution of the Tabular alumina fractions were adjusted to take into account the differences in bulk density of WFA (around 3.70 g/cm³) and Tabular alumina (around 3.55 g/cm³). It was found that, although the rammed density of the Tabular alumina mixes was lower, the densification level for Tabular alumina was comparable to WFA. This proves that, contrary to what is often claimed, the particle shape of WFA does not allow better densification. As mentioned above the aspect ratio of particular cubic WFA and Tabular alumina are almost identical.

After firing at 1600°C for 3 h, the expansion of the Tabular alumina mix was much higher at 6.9 % when compared to WFA at only 5.4%. This confirms the higher thermal reactivity of Tabular alumina compared to that of WFA. Mineralogical analysis by XRD found no spinel formation at 1000˚C, but a significantly higher amount for the Tabular DVM at elevated temperatures (1200-1600˚C).

In a second Tabular containing DVM mix, the reactive components of the spinel formation, Tabular alumina fines and MgO, were reduced to control the overall reactivity and to achieve similar expansion levels as obtained with the fused aggregate. The adjustment of the recipe resulted in similar physical properties for a mix based on sintered aggregate to the traditionally used white fused alumina.

Studies conducted at the Luoyang Institute of Refractories Research (LIRR) in China compared high purity corundum bricks based on Tabular alumina, white fused alumina, and also combinations of both aggregates [10].

Due to the higher reactivity of sintered aggregates, the Tabular alumina containing bricks show much higher density, lower apparent porosity, higher compressive and tensile strengths than WFA bricks at identical firing temperatures.

In corrosion tests with oil cracking slag, the Tabular alumina bricks outperformed WFA based bricks. This result can be explained by the better densification in addition to evenly distributed small pores and a good link between matrix and sintered grains. The strong interconnection of sintered aggregates and matrix also results in an improved abrasion resistance of the Tabular alumina bricks when compared to the white fused alumina bricks. The abrasion loss according to ASTM C704 was 4.4 cm³ for Tabular alumina but 8.7 cm³ for WFA.

CONCLUSION

The different process routes of fusing and sintering do not only influence the energy balance of the manufactured raw material but also have an impact on the material properties of the high alumina aggregates.

In general it can be stated that, depending on the cooling conditions and the quality of the grading process, fused aluminas are more inhomogeneous products when compared to the sintered aggregates. The sintering process route enables both a homogeneous distribution of the impurities in the product and stable physical properties, e.g. density, porosity and microstructure.

The bulk density of fused aggregates is generally higher than for comparable sintered aggregates, but their porosity is mainly open with very large pores of >50 µm. Sintered aggregates exhibit high closed porosity and very fine open pores of less than 1µm that can hardly be penetrated by corrosive media. The lower bulk density is even an economic advantage as less material is required for a given application.

Shape analysis has shown that WFA particles have a wider range of shapes, many of which are less round than sintered aggregates. This was also shown by identical densification levels in sensitive dry vibrating mixes. BSA 96 has the roundest grains of the tested refractory aggregates and also the highest corner roundness.

The creep resistance was tested for a very pure WFA based castable with a higher creep resistance as the Tabular alumina based one. The higher creep rate for Tabular alumina can be explained by the higher sinter reactivity and by its polycrystalline nature.

Sintered aggregates such as Tabular alumina and BSA 96 are more reactive than fused aggregates of similar chemistry.

In AMC bricks and dry vibrating mixes sintered aggregates show an earlier and a more even spinel formation when compared to fused aggregates. To reduce excessive expansion of the refractory materials adjustment of the recipes is required. Typically slight modifications, especially in the matrix, are sufficient to lower expansion reactions to a level similar to the one observed with fused aggregates. The earlier spinel formation can also be used to achieve a moderate spinel formation over a wider temperature range.

The better interconnection of the matrix with sintered aggregates increases the abrasion resistance of high alumina bricks and improves the penetration of slag.

REFERENCES

[1] Amthauer K, Buhr A, Schnabel M, Freundlich S, Dutton J: New European Sinter Aggregate with 96 % Al_2O_3, 54. International Colloquium on Refractories, Aachen, 2011, 95-98.

[2] Cichy P: Fused Alumina – pure and alloyed – as abrasive and refractory material, in Alumina science and technology handbook ed. by L.D. Hart, American Ceramic Society, ISBN0-916094-33-2 (1990), 393-426

[3] MacZura G: in Alumina science and technology handbook ed. by L.D. Hart, American Ceramic Society, ISBN0-916094-33-2 (1990), 109-170

[4] Büchel G, Liu X, Buhr A, Dutton J: review of Tabular Alumina as High Performance Refractory Material, interceram Refractories Manual 2007; 6-12

[5] Borovikov R: Dissertation; TU Freiberg „Untersuchungen zum Verschleiß hochtonerdehaltiger Feuerfestmaterialien für die Pfannenmetallurgie im Stahlwerksbetrieb; 2002

[6] Long B, Buhr A, Xu G: Thermodynamic evaluation and properties of refractory materials for steel ladle purging plugs in the system Al_2O_3-MgO-CaO; Ceramics International, 2016, 42, 11930-11940

[7] Porter J, Blumenthal W, Evans A: Creep fracture in ceramic polycrystals - I. creep cavitation effects in polycrystalline alumina; Acta Metallurgica, 1981, 29, 1899-1906

[8] Klewski M, Maracha G, Buhr A, Schnabel M, Dutton J: “Spinel formation and technical properties of AluMagCarbon bricks with different alumina aggregates”; UNITECR (2015)

[9] Munuswami M, Chatterjee S, Mukherjee S: Role of Tabular Alumina as a suitable aggregate for emerging applications – focus on dry ramming mix; IREFCON 2014, 97-103

[10] Liu X, Yanqing X, Keming G, Buhr A, Büchel G: Tabular Alumina for High Purity Corundum Brick; The Fifth International Symposium on Refractories (ISR'2007)