The Effect of SiO₂ and Na₂O Content on the Sintering Behavior of Calcined Specialty Aluminas for the Ceramics Industry

Abstract: The ceramics industry encompasses a wide variety of applications, including advanced ceramics, technical ceramics, honeycomb ceramics, spark plugs, high voltage insulators, wear parts and many more. Calcined alumina is a commonly used raw material in all of these ceramic applications due to its robust mechanical, electrical, thermal and chemical properties. These properties are highly dependent on the physical and chemical characteristics of the alumina itself. Therefore, the focus of this research was to evaluate the role of chemical characteristics on the physical and mechanical properties of four commercially available calcined reactive aluminas. Specifically, this work aims to quantify the effect of the trace impurities SiO₂ and Na₂O on alumina shrinkage, shrinkage rate, sintered density and flexural strength.

Keywords: calcined alumina, reactive alumina, specialty alumina, ceramics, impurities, sintering

Calcined aluminas for the ceramic industry

Alumina begins as bauxite ore, which is mined and transported to refineries where the purified mineral gibbsite is extracted via the Bayer process [1]. While the vast majority (> 90 %) of the alumina hydrate is calcined for eventual use in the production of aluminum metal, a smaller percentage is used in non-metalurgical applications, such as the production of specialty aluminas. Calcined alumina is one type of specialty alumina, with distinguishing characteristics of predominantly α-phase content, and carefully controlled primary crystal size, morphology, surface area and chemistry. The physical and chemical properties of a given alumina, such as particle size distribution, surface area, green density and trace impurity levels, often dictate performance in a final application. Calcined alumina producers can control physical properties more directly than chemical impurities by altering certain processing conditions, such as temperature and time. Generally, the maximum chemical purity for aluminas processed with Bayer feedstock is less than 99.9 % on an oxide basis. Certainly, production of higher purity alumina products is possible, even to levels greater than 99,999 %, but only through wet chemical processing or the use of high purity aluminum feedstocks [2]. Since most of the impurities are chemically bound in the Bayer crystal, they are not readily available for removal by conventional methods, either prior to or during the calcination process. More comprehensive summaries of alumina production can be found in the literature and won’t be duplicated here [1–3].

Controlling impurities is one of the main challenges for a specialty alumina producer. The most common impurities that are available for control during processing are Na₂O and SiO₂. Though soda control typically refers to a removal process, overall impurity control in specialty alumina processing doesn’t explicitly imply removal. Some impurities need to be controlled because of the potential for addition during processing. An example of impurity addition during processing is the increase in SiO₂ content during grinding operations. The content of these impurities, whether removed or added during processing, can impact alumina performance in an end-use ceramic application.

Considering the various calcined and reactive alumina products available in the market, and each with varying impurity levels, ceramic manufacturers are interested in understanding the effects of specific impurities on the performance of a given alumina. Some common application-based reasons for this are:

- End-use product is subjected to harsh chemical environments that tend to etch specific impurities.
- The direct impact of small impurity differences on performance, and moreover variability, is difficult to quantify. Even with repetitious laboratory testing on multiple samples, conclusions are often still constrained by experimental variance. This can be especially true for ground reactive aluminas.
- While some research has focused on understanding the effects of various physical parameters on alumina properties, much has been dedicated to understanding the impact of chemical impurities on sintering kinetics, grain growth and microstructure development. Most of these chemical studies have evaluated high purity systems using specific addition levels of selected impurities, such as SiO₂ [6], TiO₂ [7, 8], Fe₂O₃ [9], MgO [10, 11], and various combinations [12, 13].

Fundamental research using high purity systems does provide a plat-
form for mechanistic understanding; however the findings don’t always translate to industrial systems. From a practical point of view, knowledge of impurity effects on specialty alumina systems is critical since the sales volume of high purity aluminas (99.9% purity or higher) accounts for only about 1% of the global ceramic industry demand, whereas specialty aluminas (99.8% purity or less) accounts for almost 90%. Due to this, the following study was put together to help quantify the effects of impurities on aluminas that are not considered high purity.

**Commercially available specialty aluminas**

Four commercially available specialty alumina powders capable of being used in equivalent ceramic applications were evaluated. Each powder is considered a 99.8% calcined reactive alumina with 0.5 μm median particle size. The powder samples were selected to have similar overall particle size distribution, specific surface area and chemical purity. The major difference between the aluminas was the level of the specific impurities, mainly Na₂O and SiO₂. Overall, the Na₂O range of the alumina samples was 0.02–0.10%, while the SiO₂ range was 0.01–0.04%. Characterization data of all as-received powder samples, using Alnatis standard test methods, is shown in Tab. 1.

The shrinkage behavior of each powder was evaluated by dilatometry and the strength by four-point bending method. In an effort to eliminate the effects of sample preparation and compaction differences between powders, each powder was uniaxially pressed at 15.6 MPa and then cold isostatically pressed (CIP) at progressively higher pressures from 50 MPa to 300 MPa. The green density, fired density and shrinkage of each compact was measured and, as shown in Fig. 1, a CIP pressure of 300 MPa was determined to be the point at which the impact on shrinkage becomes sufficiently de-coupled from the CIP pressing pressure. The pressed density achieved for each powder at a CIP pressure of 300 MPa was 2.33–2.34 g/cm³. Compacts were prepared for four-point bending analysis by pressing the aluminas into 25 mm x 2 mm x 2,5 mm bars and sintering at 1540°C. The four-point bending method was performed in accordance with DIN EN 843-1, with bending rates at 0.5 mm/min. The Weibull statistics were calculated based on ISO 20501 with at least 30 sample bars evaluated for each alumina powder.

**Shrinkage and strength results**

Dilatometry was used to evaluate the shrinkage and sintering behavior of each powder up to 1580°C. The
Process Engineering

![Graph](image)

**Fig. 3** Weibull plot for each alumina powder

![Graph](image)

**Fig. 4** Shrinkage rate as a function of temperature for each alumina powder

Dilatometry results for linear shrinkage (PLC, %) of each powder as a function of temperature (°C) are shown in Fig. 2. The shrinkage behavior of each powder follows a stacked pattern of curves that initially appear to behave similarly up to 1580 °C, only revealing slight differences in overall shrinkage. As shown in Tab. 2, the highest shrinkage observed by dilatometry at 1580 °C was 13.3 % for CT3000 LS SG, followed by 12.7 %, 12.4 % and 11.9 % for samples B, A and C, respectively. The fired density of each powder at 1540 °C, as given previously in Tab. 1, followed the same trend, with CT3000 LS SG achieving the highest density at 3.95 g/cm³, followed again by samples B, A and C at 3.89 g/cm³, 3.90 g/cm³ and 3.88 g/cm³, respectively. The sintered density of a powder compact is often an indicator of relative strength. Therefore the strength of each powder was evaluated by four-point bending to determine if the flexural strength showed the same trend as density and shrinkage. Tab. 3 shows the Weibull parameters for each alumina powder, including the characteristic strength and modulus. The characteristic strength of each sample indeed trended with the aforementioned shrinkage and fired density results, though not in a linear relation. CT3000 LS SG had the highest characteristic strength at 434 MPa, followed by samples B and A at 372 MPa and sample C at 369 MPa.

The Weibull modulus followed a different trend than shrinkage, fired density and characteristic strength. Sample A achieved the highest modulus at 11.6, followed by samples C, B and CT3000 LS SG with values of 7.8, 7.6, and 6.3 respectively. The complete Weibull data for each powder is shown in Fig. 3. The characteristic strength and modulus values observed in this study agree with the ranges reported in previous work on comparable alumina powders [13, 14].

Tuan et al. observed flexural strength and Weibull modulus values of 332–380 MPa and 5.2–10.6, respectively, for a 99.8 % calcined alumina powder sintered at 1580 °C [14]. Similarly, Quinn reported on a global Round Robin study of MIL STD method using Coors AD-999 alumina powder and reported an average flexural strength of 374 ± 17 MPa and modulus of 9.8 ± 2.7 [15].

**Sintering kinetics**

In an effort to better understand the shrinkage kinetics of each powder, the shrinkage rate [%/min] of each compact was evaluated as a function of temperature (°C), as shown in Fig. 4. The graph clearly shows that CT3000 LS SG has the highest shrinkage rate of each powder followed by samples, B, A and C. The graph also shows that the powders do not follow a similar shrinkage pattern as might be interpreted by Fig. 2, but rather diverge dramatically around 1150 °C. The shrinkage behavior and moreover sintering behavior of each powder is therefore quite different, especially between 1150 °C and 1500 °C. The divergence in behavior between 1150 °C to 1500 °C encompasses the transition from intermediate to final stage sintering. During these stages of sintering, the microstructure is developing rapidly through grain growth, pore elimination and boundary movement. The observable changes in sintering kinetics indicates that the densification behavior of each powder is different. The effect of impurities on microstructure and grain development during sintering has been studied for many years, and though competing theories exist, research clearly shows that impurities directly impact sintering behavior [16–21].

Previous work by Louet et al. [17] reported on the effect of silica content on sintering kinetics. Louet’s work showed that increased silica content resulted in a significant decrease in the rate of densification during sintering. Further, the divergence in Louet’s rate of density plot begins near 1150 °C, similar to what is observed here. Though different impurities are present in specialty aluminas, and much research has been dedicated to quantifying their impact on sintering, [6–20] both of these works identify SiO₂ as an impurity that directly reduces the densification rate. For a more direct
comparison, Fig. 5 shows the relation of silica content and shrinkage of each alumina as measured in this study. Despite the presence of other oxides (Na₂O, CaO, Fe₂O₃, MgO etc.) that have been shown to influence sintering behavior, the linear correlation between silica and shrinkage is obvious. Given that the pressed density of each compact was equivalent, the noted silica relation is also valid in relation to fired density. While an equivalent relation could not be established between Na₂O content and shrinkage or fired density, the data does show the powder with the lowest SiO₂ and Na₂O contents, CT3000 LS SG at combined 0.03 %, achieved the fastest sintering rate, highest fired density and highest characteristic strength. The other three powders evaluated had considerably higher impurity levels than CT3000 LS SG and concurrently displayed slower sintering rates, achieved lower densities and lower characteristic strengths.

**Summary**

Four commercially available 99.8% pure specialty aluminas capable of being used in equivalent ceramic applications were evaluated by dilatometry and four-point bending methods. The powders had similar particle size, surface area, green density and overall purity, but differed in their SiO₂ and Na₂O contents. Silica content in the aluminas was found to directly correlate to shrinkage and density. Further, silica was determined to negatively influence shrinkage and sintering rates between 1150 °C and 1500 °C, an observation supported by previous literature. A direct correlation could not be made between soda content of the alumina and shrinkage, density or strength during this study. However, as a general statement, the alumina powder with the lowest individual and combined SiO₂ and Na₂O impurity levels, CT3000 LS SG, achieved the highest shrinkage rate, fired density and characteristic strength.

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**References**