Almatis Expands its Calcined Aluminas into a Higher Purity Range

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In this article, the authors discuss the need for improved purity levels of specialty alumina for emerging and developing technical applications. They discuss the impact of the overall purity level of alumina on its properties and how specific impurities or dopants impact specific properties more severe than other impurities or dopants. The dielectric loss is given as an example property that is significantly influenced by specific impurities. The awareness that specific impurities and certain combinations thereof have a larger impact on the properties of alumina than the overall purity opens up the possibility for a more economical solution to selectively avoid or remove impurities in alumina that are harmful for the targeted properties, depending on the application.

Higher purity alumina

Alumina is the most extensively used ceramic material. A major reason for the success of alumina over other technical ceramic materials is its excellent material properties in combination with its lower price, which is based on the use of the Bayer process.

For the vast majority of alumina applications a purity range of 99,6–99,8 % is sufficient to achieve the desired properties. Some specialty applications require higher purities to achieve the desired properties. The demand for higher purity alumina has been increasing recently due to new emerging applications such as 5G and Li-ion batteries, as well as due to the advancement of existing applications, for example semiconductor processing equipment.

An increase in purity to >99,9 % typically comes at a significantly higher cost, e.g. by an order of magnitude, caused by either more expensive feed that has to be used, or complex processing steps to remove impurities from the alumina. For example, purities of 99,99 % or greater are typically produced by methods that use ammonium alum, aluminium metal, or aluminium salts as feed instead of cost effective Bayer feed from a refinery.

In an effort to address the increasing need for higher purity alumina of >99,9%, Almatis focused on improving the purity levels of Bayer based materials to generate cost effective alumina powders with purities greater 99,9 %. A proprietary process allows us to selectively remove impurities to reach purity levels of 99,6–99,99 % using a Bayer-based feedstock, specifically targeting impurities that are most harmful for individual applications.

In previous work is was reported how impurities and dopants such as Na_2O, SiO_2, CaO, and MgO affect the sintering behaviour and microstructure evolution in specialty aluminas derived from the Bayer process [1–3]. However, only little work has been done on how impurities in this concentration range affect properties of alumina.

For applications in semiconductor processing and 5G the dielectric loss tangent is an important property, and it is reported that the impurity concentration in the alumina has a major impact on it [4–6]. Therefore, we investigated the dielectric loss tangent of alumina with different purity levels and impurities.

Higher purity specialty calcined aluminas produced at Almatis

Tab. 1 shows the overall purity of five alumina powders and the concentration of their impurities. The five powders are chosen to cover the a purity range of 99,78–99,97 %. Note that MgO is typically not considered an impurity due to its use as a sintering aid. MgO was intentionally added to powders 1, 2 and 5 for this reason. The physical parameters of the five powders are shown in Tab. 2.

Microstructures and densities of higher purity Bayer alumina

Fig. 1 shows microstructures of samples prepared from Bayer process alumina with purities of A) 99,78 % (powder 1) and B) 99,97 % (powder 3). The samples were prepared by freeze granulation, uniaxial pressing of freeze granulated powder at 90 MPa and firing at 1600 °C for 1 h.

It can be seen that the impact of the overall purity on the microstructure of the samples investigated here is small. The grain size and shape of samples with a purity level of 99,78 % A) are similar to samples with

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Tab. 1 Purity levels of five alumina powders used for dielectric measurements

[ppm]	Na_2O	Fe_2O_3	B_2O_3	SiO_2	MgO	TiO_2	CaO	Li_2O	Al_2O_3 [mass-%]
Powder 1	790	184	12	204	761	34	241	2	99,78
Powder 2	80	133	14	214	563	15	105	2	99,89
Powder 3	150	67	11	60	14	4	19	20	99,97
Powder 4	70	193	10	79	16	34	59	2	99,95
Powder 5	80	187	8	83	595	34	63	2	99,89

Tab. 2 Particle size values by laser diffraction and specific surface are measured by the BET method

	d_{10} [µm]	d_{50} [µm]	d_{90} [µm]	d_{100} [µm]	BET [m^2/g]
Powder 1	0,12	0,5	2,11	10	6,56
Powder 2	0,09	0,45	2,08	12	7,92
Powder 3	0,1	0,49	1,62	12	4,80
Powder 4	0,08	0,43	1,84	10	8,57
Powder 5	0,08	0,43	1,93	10	8,28

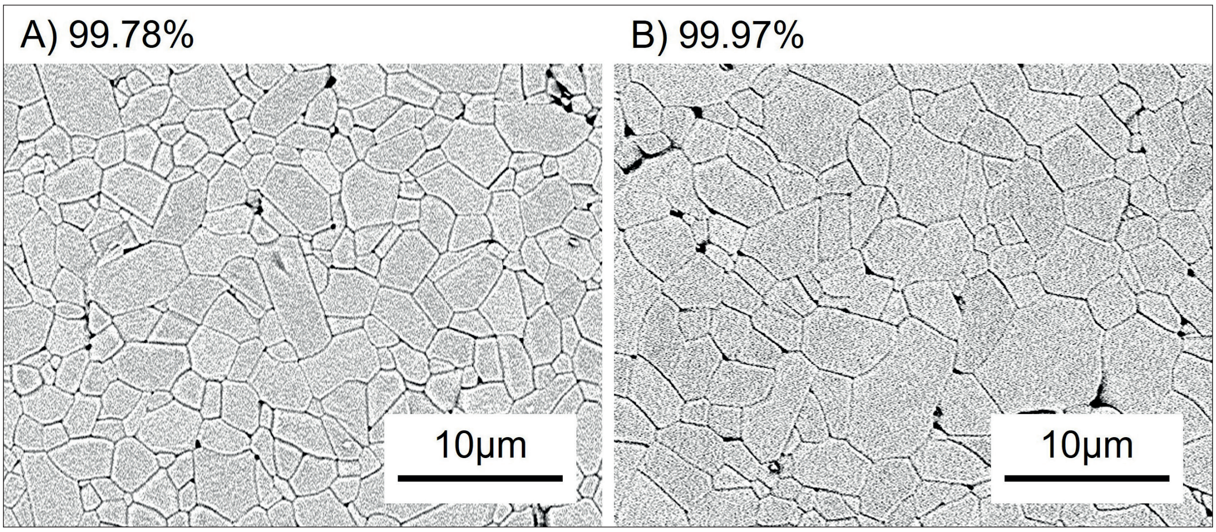

Fig. 1 Microstructures of alumina with a purity of A) 99,78 % and B) 99,97 %

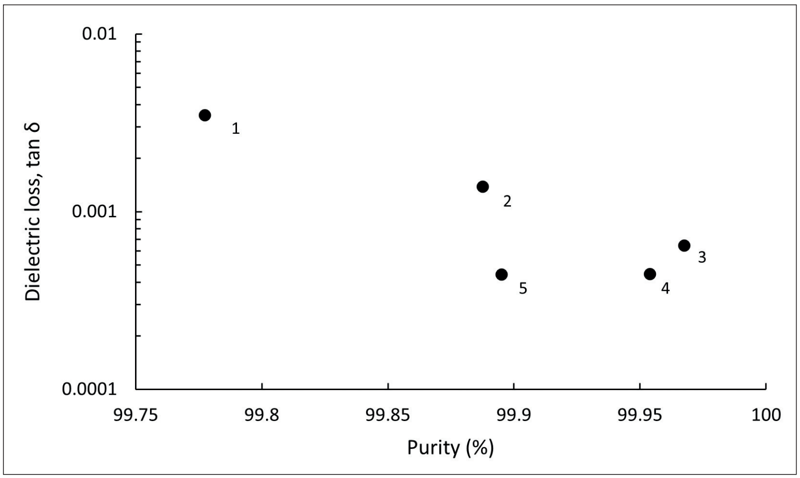

Fig. 2 Loss tangent and purity of the alumina; the numbers indicate the powders used to prepare the samples

a higher purity level of 99,97 % B). After investigating a larger sample area a higher number of facetted grains similar to the grain in the center of image A) in Fig. 1, was observed in the alumina with lower purity.

The formation of a small amount of second phases, most likely sodium aluminate, calcium aluminate, and spinel phases [2–3, 7], was observed in samples with the lower purity (99,78 %). No second phase formation was observed in the sample with a higher purity of 99,97 %.

To determine the impact of the purity on the sintered density ten pellets of each powder were uniaxially pressed at 90 MPa and sintered at 1600 °C for 1 h in an electric kiln. The samples made from the powder with a purity of 99,78 % had an average density of 3,91 g/cm^3 (SD = 0,01 g/cm^3), whereas the samples made from the powder with a purity of 99,97 % had an average density of 3,93 g/cm^3 (SD = 0,01 g/cm^3).

The difference in the sintered density can be attributed to effects of the impurities on the sintering mechanisms, as described in the literature [1–3, 7].

Effect of impurities on properties: example dielectric loss tangent

Fig. 2 shows the dielectric loss tangent of samples that were prepared from the five alumina powders described in Tab. 1 and Tab. 2. The dielectric loss tangent was determined at 10 GHz using split-cylinder resonator measurements as described by Janezic and Baker-Jarvis [8]. The authors estimate the accuracy of this measurement to be ~10 %. It can be seen that the dielectric loss tangent decreases with increasing purity.

The sample prepared from powder 1 (99,78 % purity) has a dielectric loss tangent of $3,5 \times 10^{-3}$, whereas the samples prepared from powders with a purity of 99,89 % or higher have dielectric loss values that are one order of magnitude lower.

However, it can also be seen that the dielectric loss tangent does not solely depend on the overall purity of the alumina, i.e. it is not the purest sample (made from powder 3) that has the lowest dielectric loss tangent. This indicates that the type of impurities present is more important for the dielectric loss than the total amount of impurities. Powder 3 has the lowest overall impurity concentration and the lowest impurities for every individual impurity except for Na_2O and Li_2O. This indicates that Na_2O and Li_2O have a more severe impact on the dielectric loss tangent than other impurities.

Powder 1 has the highest Na_2O concentration with 790 ppm and also shows the highest loss tangent, which further supports the claim that Na_2O has a significant impact on the dielectric loss tangent. It is also apparent that Na_2O and Li_2O are not the only impurities that affect the dielectric loss.

Samples from powders 1 and 2 have a higher SiO_2 and CaO concentration than samples from powders 3, 4 and 5. This indicates that higher SiO_2 and CaO concentrations lead to higher dielectric loss tangents as well. Powder 4 and powder 5 have similar impurity levels except for the MgO concentration. Powder 5 was intentionally doped to the reported MgO level, as it is common practice for reactive aluminas due to the positive effect of MgO on the sintering behaviour and microstructure development of alumina (Fig. 1A). Powder 4 was not doped with MgO and the difference in MgO concentration did not affect the dielectric loss tangent at 10 GHz for these samples. This contradicts the observation by Molla et al. [4] who reported a negative effect of MgO on the dielectric loss tangent of alumina.

However, further investigations are necessary to understand this discrepancy. The data analysed in this study shows no indication that Fe_2O_3, TiO_2 or B_2O_3 have any impact on the dielectric loss tangent at 10 GHz within the impurity ranges (Tab. 1).

Summary

The data presented here suggests that Na_2O, CaO, SiO_2 and Li_2O are the main contributors to impact the dielectric loss tangent at 10 GHz. The dielectric loss tangent can be reduced from $3,5 \times 10^{-3}$ to $4,4 \times 10^{-4}$ by avoiding/removing the mentioned impurities. However, more detailed investigations are necessary to fully understand the effects of single impurities and cross-effects of different impurities with each other and how they influence the dielectric loss tangent over a wider range of frequencies of alumina.

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