Essential Readings in Light Metals: Alumina and Bauxite.
Edited by Don Donaldson and Benny E. Raahauge.

ON ALUMINA POWDERS FOR CERAMICS

Yukio Oda, Hidetoshi Okamoto, and Susumu Shibusawa

Showa Denko K.K.

8, Ebisucho, Kanagawa-ku, Yokohama City

Kanagawa Prefecture 221 Japan

Abstract

The Yokohama Works of Showa Denko, which suspended production of smelter grade alumina in 1985, is now one of the few plants in the world specializing in the production of non-metallurgical grade aluminas.

In view of the wide variety of applications including ceramics, abrasives, refractories and fillers, alumina is required to have various powder properties to meet respective demands.

As alumina producer, Showa Denko has been engaged in the development of diversified grades of alumina fitting respective areas of application.

This time, alumina powders for ceramics will be taken as an example to introduce Showa Denko's improved technology for evaluation of calcination degree and powder properties.

Introduction

This year marks the 58th anniversary of the start of alumina production in Japan on a commercial scale. While alumina was manufactured in the initial stage as raw material for aluminum smelting, it now has a very wide applications as raw materials for ceramics, abrasives, refractories and other products.

The Yokohama Works of Showa Denko was the first in Japan to produce alumina. It suspended production of smelter-grade alumina following the suspension in 1985 of aluminum smelting. It now specializes in the production of non-metallurgical grade aluminas.

Since non-metallurgical grade aluminas have a wide variety of applications, they are required to have diversified powder characteristics depending on respective applications.

Control of Linear Shrinkage and Ultimate Crystal

When we take ceramics application as an example, dimensional accuracy is given the utmost importance as illustrated in the case of alumina substrates. Users accordingly demand aluminas that can easily secure dimensional accuracy of alumina ceramics.

① Ultimate Crystal of Alumina

As shown in Figure 1, thousands of ultimate crystals of alumina generally agglomerate to form one particle. Alumina ceramics is produced by forming and sintering alumina which has been pulverized to a size close to that of ultimate crystal.[1), 2)] It is therefore necessary to strictly control the size, distribution and shape of those ultimate crystals.

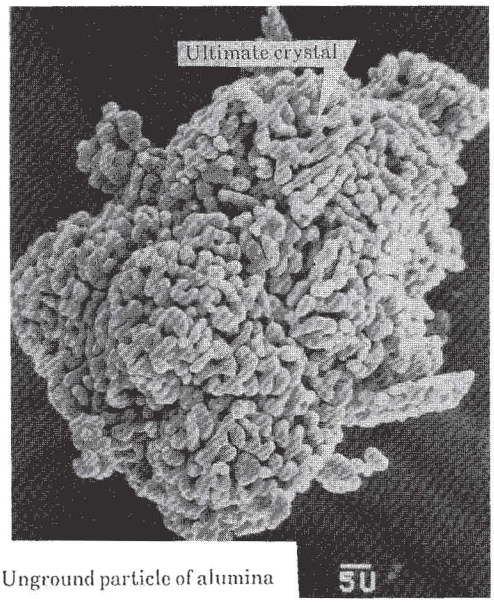

Figure 1: Unground particle of alumina

② Control of Linear Shrinkage

In order to secure dimensional accuracy of products, it is necessary to control the linear shrinkage of ceramics when it is sintered. Shrinkage factor is a function of green density and fired density and the relationship of the two is almost linear for aluminas made of the same production method. (Figure 2)

Thus green density should be controlled for the purpose of controlling the shrinkage factor. Since the green density reflects the compactibility of powder, control of linear shrinkage is equivalent to control of compactibility of powder.

It is therefore necessary for alumina powders for ceramics to have particle size distribution and compactibility of powder that are controlled in a very narrow range under given grinding conditions.

Compactibility of powder is a kind of characteristics affected by the size, distribution and shape of particles constituting the powder (ultimate crystals in this case).

Size, distribution and shape of ultimate crystals of alumina are also influenced by the characteristics of aluminum hydroxide, raw material of alumina. If the same type of raw material is used, the above characteristics of alumina can be controlled by the conditions of calcination (temperature, retention time and atmosphere).

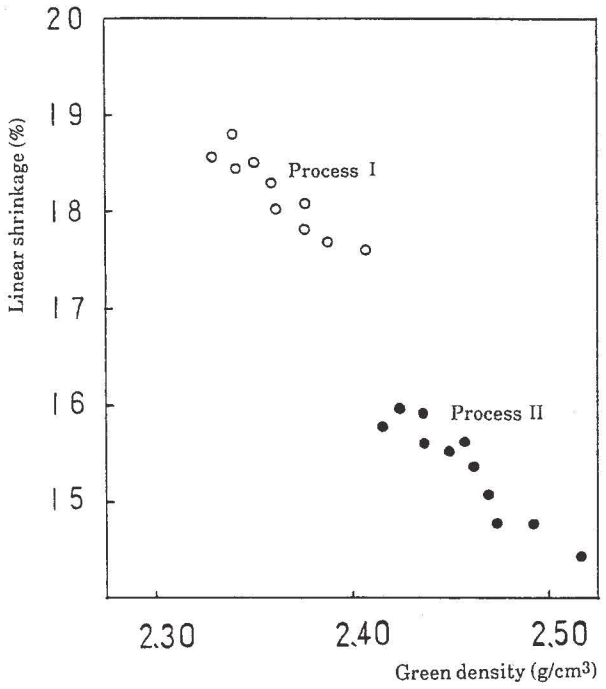

Figure 2: Relationship between green density and linear shrinkage

From the above, it can be concluded that linear shrinkage of alumina ceramics can be controlled by controlling the degree of calcination (size, distribution and shape) of ultimate crystals through manipulation of calcination conditions.

Quality Control Items for Alumina Powders for Ceramics

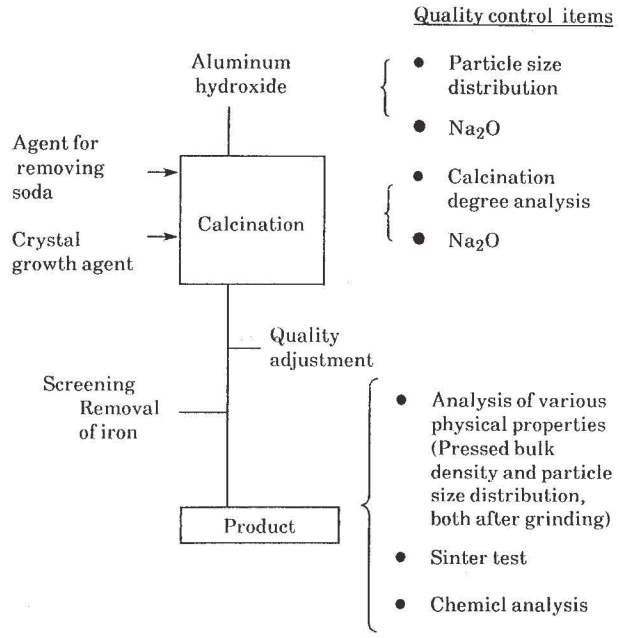

Figure 3: Quality control items for alumina for ceramics

Figure 3 shows items for quality control when alumina powders for ceramics are produced. The following two are the most important points for the production of alumina for ceramics:

① Evaluate the degree of calcination of alumina in the calcination process as quickly as possible and feed it back to calcination conditions.

② Measure the pressed bulk density (measure for evaluation of compactibility of powder) as accurately as possible and make it compatible with calcination degree.

We therefore studied development of a simple method for analyzing calcination degree and ways to improve the accuracy of measuring pressed bulk density.

Development of Simple Method for Calcination Degree Analysis

Evaluation of calcination degree of alumina is usually performed by measuring the BET specific surface area or by measuring the particle size distribution after grinding. However, it takes 2-6 hours in the latter case and 0.5-1 hour in the former. Thus development of a method enabling evaluation of calcination degree in a shorter time has been hoped for.

When aluminum hydroxide is pressurized, secondary particles are reduced to primary particles[3]. We applied this method to alumina. Namely, we put unground alumina 6 g into a 20mmØ mold, pressurized it, and measured the bulk density. We call it "the unground powder pressed bulk density method."

Experiment 1

We adopted two levels of samples--Sample A (Alumina A) with large-sized ultimate crystals and Sample B (Alumina B) with smaller ultimate crystals. (Mean particle size measured after four hours of dry grinding was used to determine the level.) Using those two levels of samples, we measured the change in bulk density under different pressures.

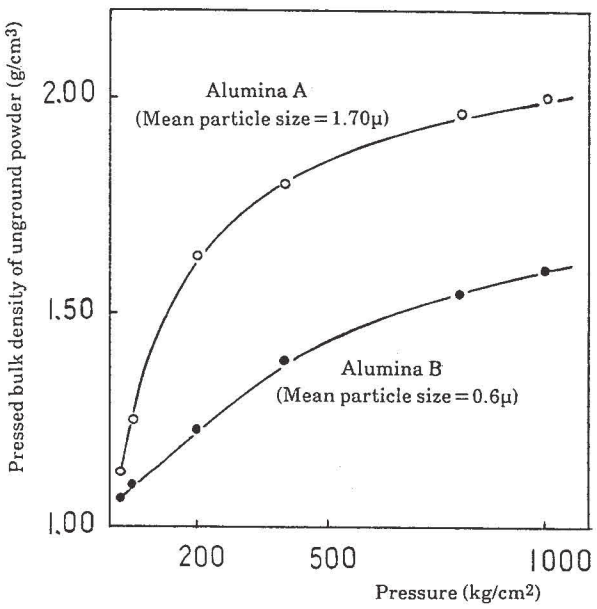

Figure 4: Change in pressed bulk density of unground powder with the change in pressure

The test results are shown in Figure 4. As the pressure increases, the pressed bulk density of unground powder Alumina A suddenly increases compared to that of Alumina B. When pressure exceeds 200 kg/cm^2, the pressed bulk density of both Alumina A and Alumina B increases in the same manner.

Experiment 2

Pressed bulk density of unground alumina powder was measured in the same manner as in Experiment 1 except that the pressure was fixed at 300 kg/cm^2. As shown in Figure 5, the pressed bulk density of unground powder increases in proportion as the ultimate crystal grows in size.

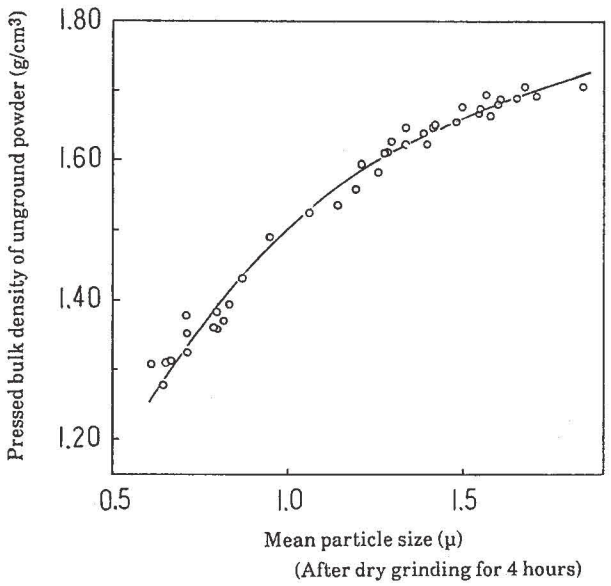

Figure 5: Relationship between the size of ultimate crystals of alumina and pressed bulk density of unground powder

Experiment 3

In Experiment 1, the pressed bulk density of unground powder Alumina A and that of unground powder Alumina B were widely different. To determine the reason, we compressed Alumina A and Alumina B at the pressure of 300 kg/cm^2 to compare the particle size distribution. The comparison was made before and after pressurization.

The results are shown in Figure 6. Both Alumina A and Alumina B presented finer distribution after pressurization, indicating that collapse of agglomerated particle into ultimate crystals has taken place.

Meanwhile, Alumina A with larger ultimate crystals compared to Alumina B shows finer and broader particle size. This corresponds to the fact that its pressed bulk density increases.

This phenomenon can be construed as meaning that the alumina with larger ultimate crystals have less number of contacts between ultimate crystals and therefore smaller total contact areas, thereby giving more chance of collapse of agglomerated particles.

Moreover, when ultimate crystals are large, the neck between ultimate crystals grow and the total contact areas between ultimate crystals become even smaller.

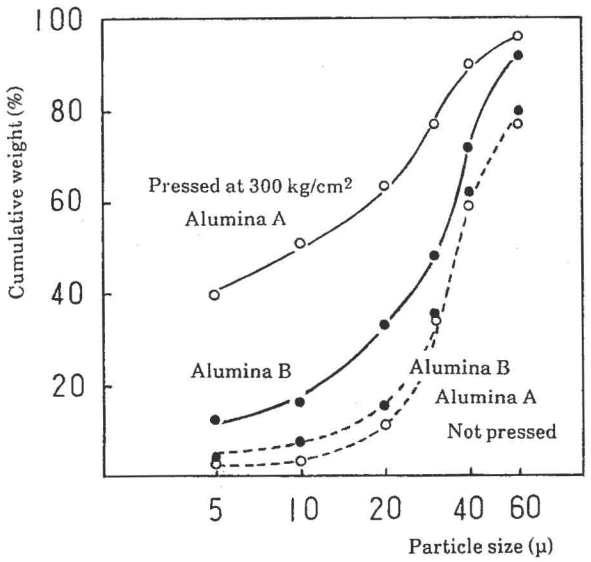

Figure 6: Change in particle size distribution when alumina is compressed

Thus it is now clear that ultimate crystals of alumina can be evaluated by measuring the pressed bulk density of unground powder after pressurization at more than 200 kg/cm^2.

Furthermore it only takes 5-10 minutes. This demonstrates that the unground powder pressed bulk density method is very useful as a simple method for analyzing the calcination degree.

Improvement of Measurement Accuracy of Pressed Bulk Density

As explained earlier, it is very important to secure dimensional accuracy of ceramics, especially in the case of electro-ceramics for applications as IC packages and HIC substrates. Users therefore demand aluminas with stabilized linear shrinkage at the time of sintering.

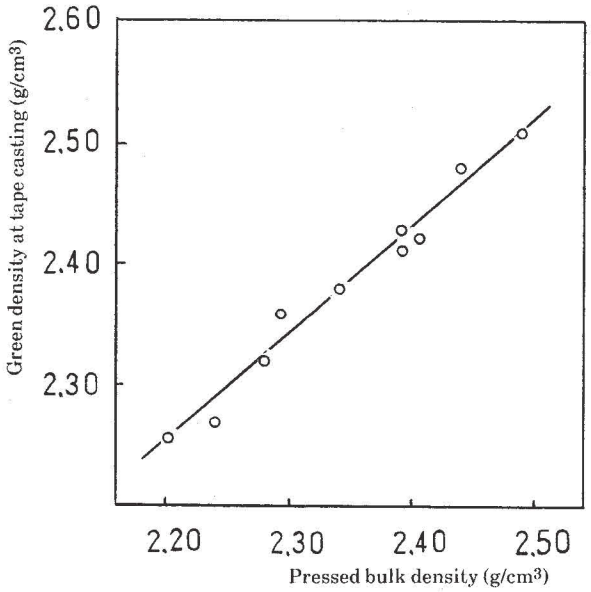

Figure 7: Relationship between pressed bulk density of ground alumina powder and green density at tape casting

As shown in Figure 7, the pressed bulk density of ground alumina powder (a measure of evaluating powder compactibility) has good correlation with green density.

We therefore need to control the pressed bulk density of ground alumina powders in order to control the linear shrinkage of ceramics at the time of sintering.

Method for measuring pressed bulk density: Ground alumina 6 g is put into a 20mmØ mold, pressed at 1 ton/cm^2. Then its bulk density is measured.

Controlled Scope of Pressed Bulk Density

When alumina substrate is taken as an example, its dimensional tolerance is generally ±1%. If this fluctuation is all due to green density, its scope of change should be approximately ±0.05 g/cm^3.

Actually, however, there are other factors causing the change and the scope of fluctuation is strictly controlled. In the case of alumina for substrate applications, it is required to control the pressed bulk density after grinding within the fluctuation scope of ±0.02 g/cm^3.

Measurement Accuracy Before Improvement

Before improvement, the measurement accuracy of pressed bulk density was σ=0.005g/cm^3. This was not sufficient from a viewpoint of users' requirements. And its reproducibility tended to decline after interval of days although the reproducibility within the same day was good.

We thus investigated the yearly fluctuations of pressed bulk density using standard samples. As shown in Figure 8, there is a tendency that pressed bulk density is large in summer and small in winter. This suggests a seasonal influence, especially the influence of relative humidity.

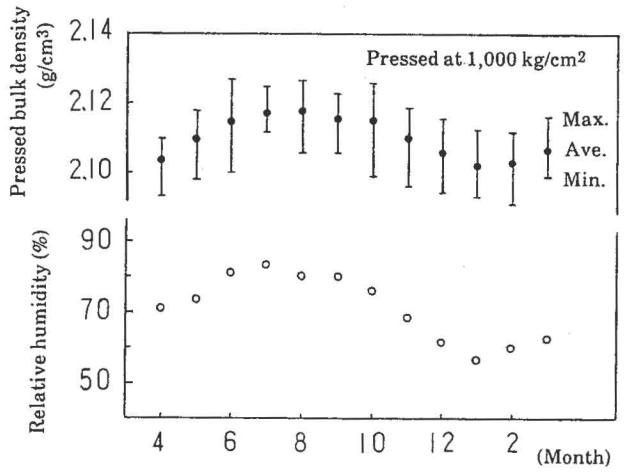

Figure 8: Yearly changes in measurements of pressed bulk density of standard samples; and yearly changes in relative humidity (monthly average) of environment for measurement

Influence of Humidity on Pressed Bulk Density

Alumina C was dried for two hours at 110°C and left to stand for fixed hours in the places with relative humidity of 50%, 65% and 80%, respectively. Then the pressed bulk density was measured.

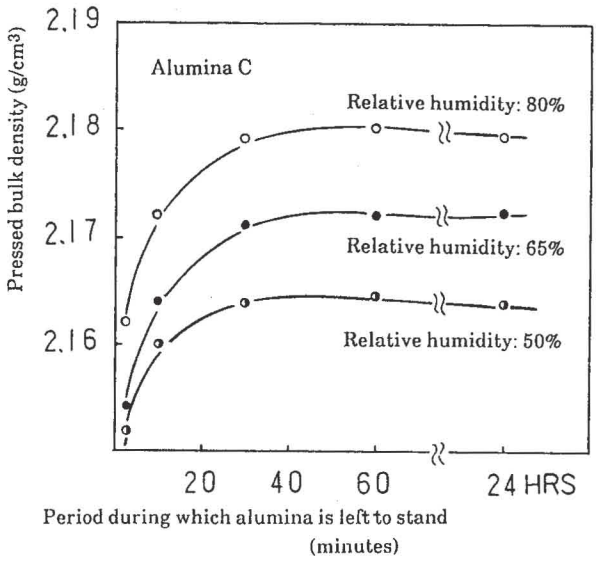

Figure 9: Period during which alumina is left to stand and relative humidity: Their influence on pressed bulk density

As shown in Figure 9, pressed bulk density increases as the sample is left to stand for longer time. The pressed bulk density also increases as the relative humidity increases. Measurements are stabilized after the lapse of one hour after drying.

Measurement Accuracy After Improvement

Based on the above results, we decided to measure the pressed bulk density after drying the sample for two hours at 110°C and leaving it to stand for one hour or more in the atmosphere of 23°C and relative humidity of 65%.

As a result, the measurement accuracy has improved from the previous σ=0.005g/cm^3 to σ=0.001g/cm^3.

Relationship between Pressed Bulk Density and Calcination Degree

Figure 10 shows the relationship between pressed bulk density (pressure: 1 ton/cm^2)--measure of evaluating compactibility of powder--and pressed bulk density of unground powder (pressure: 300 kg/cm^2) under the simple analysis method for calcination degree.

Since the two have extremely good correlation, degree of calcination can be specified as long as the target value of pressed bulk density is fixed.

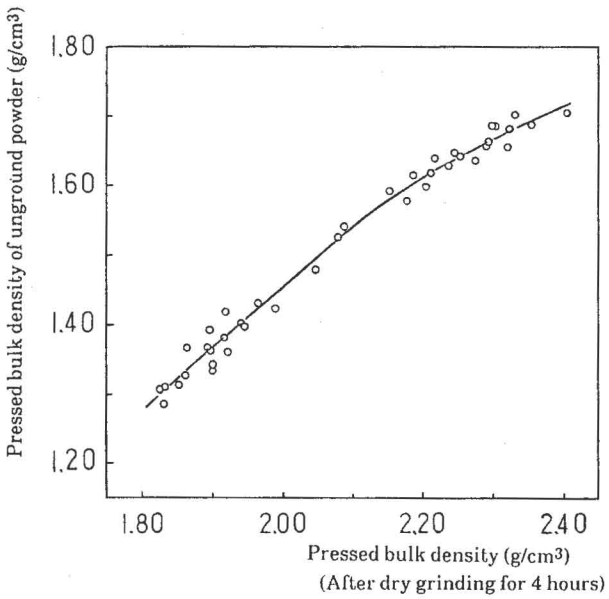

Figure 10: Relationship between pressed bulk density (measure of evaluating powder compactibility) and pressed bulk density of unground powder (simple measure of evaluating calcination degree)

That is, alumina powders for ceramics meeting the users' requirements can be produced by:

① setting the target scope of pressed bulk density based on the relationship between the linear shrinkage of ceramics at the time of sintering and the pressed bulk density of ground alumina powders; and determining the scope of calcination degree corresponding thereto from the pressed bulk density of unground powder, and

② frequently measuring the pressed bulk density of unground powder, feeding it back to calcination conditions, thereby controlling the calcination degree within the said scope.

Conclusion

The most important quality characteristics required of alumina for ceramics is the stability in linear shrinkage at the time of sintering.

We have established a method to clarify the target quality level of alumina by improving the measurement accuracy of pressed bulk density of ground powder, which density has good correlation with linear shrinkage. We also have developed a simple analysis method for calcination degree, thereby implementing a strict control of calcination degree. We thus have succeeded in meeting users' demand.

We hope this presentation will be of some help to you in producing alumina for ceramics.

References

1) S. Kazama, Y. Oda, "Current Alumina Powders for Ceramics," TAIKABUTSU 36 (11) (1984) 665-675

2) Y. Oda, S. Shibusawa, "Alumina Powders for Ceramics," FC Report 4 (9) (1986) 17-22

3) Y. Shibue et al., "Precipitation Process and Properties of Aluminum Trihydrate," Light Metals (1989) 27-32