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Technical Report

Development of High-performance Fine Powder Spherical Filler Product Technology
(Fine Powder Alumina Filler, High-performance Silica Filler)

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Abstract

The Micron Div. of Nippon Steel Chemical & Material Co., Ltd., in which the division's predecessor was led by Micron Co., Ltd. (a joint venture between the former Nippon Steel Corporation and the former Harima Refractories Co., Ltd.), has been promoting the spherical filler business since 1985, based on the world's first successful development of flame-fused spherical fillers. As a pioneer in the spherical filler business, the Micron Div. of Nippon Steel Chemical & Material provides high-performance spherical fillers suitable for semiconductor encapsulants, casting materials, etc. This paper introduces the product features of the current general-purpose product line-up and the relevant applications, by classified mesh. With the rapid evolution and development of semiconductor devices, the spherical filler properties for semiconductor encapsulants are now required to have new functions such as high thermal conductivity and low dielectric properties for high frequencies, in addition to the conventional key properties of high density filling and high flow properties. A basic thermal management approach was investigated to address the high thermal conductivity properties in the relevant customer requirements. From the verification of the basic approach to the high thermal conductivity and high functionality of the fine spherical alumina filler AX1M developed by the Micron Div. of Nippon Steel Chemical & Material, this paper presents the development guidelines for further high functionality. In addition, as an effort to develop high-performance silica products, we focused on the thermal conductivity and thermal expansion coefficient of quartz to convert spherical amorphous silica to quartz, organized the effects of the Ca addition amount and heat treatment temperature on the phase transition ratio to quartz and cristobalite, and reported in this paper that the quartz ratio can be increased under limited conditions.

1. Introduction

In recent years, the development of high-functionality product technologies for semiconductor device encapsulants has advanced significantly. Fillers are added to improve physical properties and functions and reduce costs and these materials serve as the key to various composite materials. In addition to the original properties that fillers are required to have (conventional encapsulants' protection of semiconductor device environments and adjustment of ex-

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pansion dimensions), they are now required to have high flow properties for ultra-narrow gaps as well as higher thermal conductivity and properties to deal with high frequencies as the speed of semiconductor devices is becoming ultra high and their performance is advancing. High-performance fine powder spherical fillers (fine powder alumina filler, high-performance silica filler) are materials that realize such higher functionality. This paper describes in detail the development of product technologies for the high-performance fine powder spherical fillers (fine powder alumina filler, high-performance silica filler). This paper also focuses on the Micron Div. of Nippon Steel Chemical & Material Co., Ltd., that was the first in the world to develop the original spherical products and that is now searching for new ways to develop higher-performance spherical fillers in line with the development guidelines.

As silica fillers, which are added to semiconductor sealing resin, crushed silica fillers had been used from the advent of semiconductors to 1985. The main function of such crushed silica fillers was to reduce the difference between the coefficient of thermal expansion (CTE) of the semiconductor silicon chips and that of the sealing resin so as to improve the dimension accuracy of the semiconductor devices. In addition to such improvement, adding crushed silica reduced the usage of expensive resin and thereby also served as a cost reduction material. However, around 1985 in the early stage of the development, when crushed silica was added to resin and kneaded, silica could be charged to resin at approximately 50% at the maximum. Meanwhile, the flame-fused spherical silica fillers developed by Micron Co., Ltd. achieved a high filling factor at approximately 70 to 80% even at that time, and the technology was regarded as an innovative breakthrough. Thanks to various improvements in the quality of spherical filler products since then, the filling factor has reached 90% or so recently. Spherical filler products are exhibiting the most important function as a main element for improving the material physical properties of resin compositions containing added fillers.

With regard to the application as a semiconductor encapsulant material, which is a conventional main application, the main required property of fillers was to mitigate the stress generated from the difference in the thermal expansion between the semiconductor chips and the sealing resin (dimension accuracy improvement). However, in recent years, as chips started having higher functionality and becoming denser, heat generated from the chips themselves has become a problem, revealing heat management as the most important task. In addition, the communication frequencies of semiconductor chips, etc., for smartphones must be higher so as to transmit large-capacity information and thereby filler materials are required to have new functions to deal with high frequencies. The Micron Div. of Nippon Steel Chemical & Material is earnestly promoting various projects to meet those new requirements and this paper describes part of such projects.

2. Fillers Manufactured by the Micron Div. (Former Micron) of Nippon Steel Chemical & Material

In 1978, Nippon Steel Corporation studied, in cooperation with the former Harima Refractories Co., Ltd., hot repairing (by thermal-spraying and building raw materials of refractories) of eroded sections of furnaces (e.g., coke ovens, converters, and ladles) at the works. In the joint research, the research and development group of Harima Refractories found that the flying particles were spherical in shape during thermal spraying. This discovery served as a trigger to start spherical filler development. The spherical filler was named micro bead and companies began to create new filler product technologies. In 1980, based on the aforementioned discovery, the Nippon Steel group started developing micro beads (patent applied for the spherical ceramics particle manufacturing method (December 1980)).[1–4)]

In 1982, a large experimental plant (5 t/month) was installed and the group started experiments to make spherical silica, alumina, zircon, mullite, and spinel, etc. In parallel with the experiments, the group supplied prototype spherical fillers to customers in order to determine how they would be applied. As a result, spherical silica fine particles were more excellent as fillers for resin encapsulants for semiconductor integrated circuits because they were spherical and thereby usable, compared with high-purity crushed silica stone products and crushed molten quartz products, which had been used until then. With regard to resin encapsulants used at that time, the resin accounted for approximately 70% and the filler accounted for approximately 30%. We proposed to sealing resin manufacturers that using spherical fillers would bring various advantages, such as cost reduction thanks to the improved filling factor, higher working efficiency due to enhanced flowability, higher quality, and reduction of wear of dies. Nippon Steel and the former Harima Refractories jointly applied for a total of six patents on the manufacturing methods and applications.[5–11)]

In 1985, Micron was established as a pioneer of the new material business of the Nippon Steel group through joint investment by Nippon Steel and Harima Refractories (current Krosaki Harima Corporation) for the purpose of manufacturing and selling spherical silica and alumina fine particles. The current Micron Div. of Nippon Steel Chemical & Material was set up based on that Micron. In the sector of semiconductor encapsulant materials, which is the main application of flame-fused spherical fillers, Nippon Steel Chemical & Material is valued highly as the world's first spherical silica filler manufacturer. The company has advanced with these manufacturing technologies and sales records as its business base and nowadays it supplies silica and alumina spherical fine particles to many sectors around the world.

2.1 Processes to manufacture spherical filler products and their characteristics

Figure 1 illustrates the processes to manufacture spherical silica fillers. A silica raw material (crushed high-purity silica stones) is separately put into a spraying burner. Silica melted in the high-temperature area becomes spherical due to a physical phenomenon that

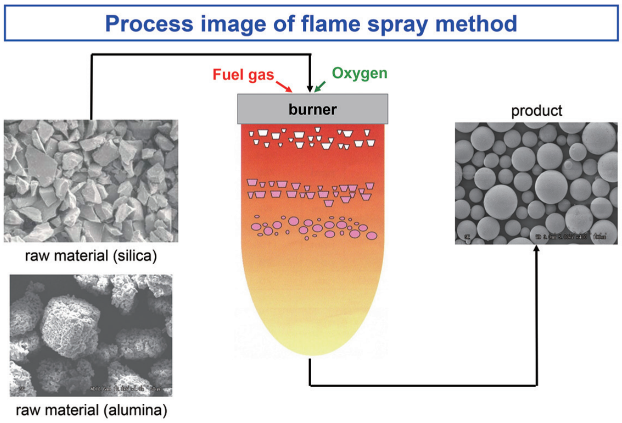


Fig. 1 Overview diagram of the flame spray process

works to minimize the surface area of liquid and then solidifies in the low-temperature area, becoming spherical silica particles. The obtained spherical silica particles are turned into products through a classification process involving cyclones and meshes.

The aforementioned spheroidization achieves a higher filling property and higher flowability (refer to **Fig. 2**). As an application for semiconductor encapsulants, the improved filling property has made it possible to manufacture high-functionality encapsulants with high strength, high thermal conductivity, and low thermal expansion, and such properties cannot be achieved with crushed silica. We provide products in various particle size distributions to supply products having optimum particle size distributions so as to exhibit these functions more effectively.

2.2 Spherical filler product groups (silica and alumina fillers) manufactured by the Micron Div.

Table 1 lists the typical (silica and alumina) products offered by the Micron Div. of Nippon Steel Chemical & Material. Quartz ore crushed using a ball mill into a designated size is used as a raw material for spherical silica fillers and there is the particle size distribution of the obtained product exhibits a certain degree of spread.

For spherical silica fillers, such distributions are effectively used to improve the filling property. Meanwhile, the existence of fillers in sizes equal to or larger than a certain size may pose a problem when such fillers are charged. Accordingly, a classification process involving meshes and cyclones is added to provide user-friendly spherical fillers classified by meshing that are suitable for the users' applications and purposes (hereinafter, meshing is referred to as "top cutting").

The spherical silica product lineup of the Micron Div. of Nippon Steel Chemical & Material is outlined below focusing on the top-cut sizes.

2.3 Spherical silica product lineup according to top-cut sizes

1) 75-*µ*m cut grade (**Table 2**)

General-purpose spherical silica filler products (spherical silica product group). They are used for cast materials and resin composite products for which the dimensions must be accurate. The company offers various types of products according to the purpose and cost by adjusting the raw materials and melting conditions.

2) 53- and 45-*µ*m cut grades (**Table 3**)

Spherical silica product groups used for general-purpose semiconductor devices and in-vehicle semiconductor devices that must be highly reliable and durable.

3) 32- and 20-*µ*m cut grades (**Table 4**)

Product groups suitable for encapsulants to be used for mold underfill. They are used for highly densely packed semiconductor devices, such as ball grid array (BGA) packages and chip scale packages (CSPs), contributing to downsizing of the devices. These grades manufactured by the Micron Div. of Nippon Steel Chemical & Material feature the removal of rough particles larger than a designated size while the particle diameters of whole particles are retained as large, which achieves both the flowability and property for filling narrow sections as their designs.

2.4 Characteristics of the alumina filler products of the Micron Div.

Regarding the alumina filler products of the Micron Div. of Nip-

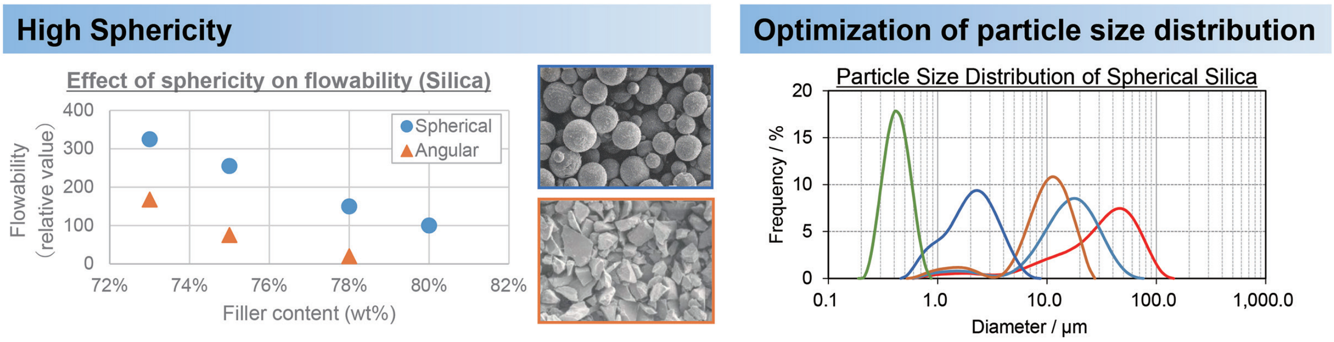


Fig. 2 Improvement of filler filling ratio and flowability by spheroidization of silica filler and examples of particle size distribution of spherical silica filler (The five lines in the figure show the particle size distribution of typical spherical silica filler products in the fine to large diameter range.)

Table 1 Spherical filler product lineup (silica & alumina) of the Micron Div. of Nippon Steel Chemical & Material Co., Ltd.

Silica

Product	D50	S.S.A	Roundness	Na+	Cl−	SiO_2	Mesh
name	*µ*m	m^2/g	-	ppm	ppm	%	*µ*m
S140	28	1.7	0.90	0.3	0.2	99.9	72
S210	28	1.8	0.92	0.3	0.2	99.9	72
S3030	26	2.2	0.94	0.2	0.3	99.9	75
S430	20	3.0	0.93	0.2	0.2	99.9	72
SC70	17	1.0	0.97	0.3	0.1	99.9	50
SP60	2	7.6	0.98	0.8	0.1	99.0	-

Alumina

Product	D50	S.S.A	EC	Na+	Cl−	Al_2O_3	Mesh
name	*µ*m	m^2/g	*µ*S/cm	ppm	ppm	%	*µ*m
AZ2-75	3	1.3	7	4	8.0	99.9	75
AZ4-75	5	0.6	6	3	1.5	99.9	75
AZ10-75	11	0.3	4	3	1.0	99.9	75
AZ35-125	37	0.2	5	6	0.4	99.9	125
AZ75-150	75	0.2	10	10	0.5	99.9	150
AX1M	1	3.2	77	170	10.0	99.9	-

D50: Particle size corresponding to 50% cumulative frequency in the particle size distribution.

S.S.A: specific surface area

pon Steel Chemical & Material, the lineup satisfies various purposes through combinations of wide-ranging particle diameters from D50 = 1 μm (hereinafter, "φ1 μm") to φ150 μm and top-cut sizes (**Table 5**). As a typical application, the products are used for thermal conductive fillers, such as heat dissipation sheets, heat dissipation grease, and heat dissipation adhesives (they are called thermal interface materials (TIMs)), by drawing on their excellent thermal conductivity.

Figure 3 below shows the AY series, general products of the Micron Div. of Nippon Steel Chemical & Material.

Large amounts of AY75-150 and AY35-125, which are large-diameter fillers included in the aforementioned AY series, are charged into TIMs as fillers that play a key role in thermal conduction. AY75-150, in particular, is often used for heat dissipation sheets and the product is contributing to the enhancement of the thermal conductivity of heat dissipation sheets thanks to its large particle diameter.

Table 2 Product specifications for typical 75 μm cut products

Item	Unit	S140	S210	S3030	S430	S4070	S4060P
D50	μm	27.9	28.8	26.2	20.1	28.4	19.9
Wet sieve							
75 μm on	%	0.0	0.0	0.0	0.0	0.0	0.0
Specific surface area	m^2/g	1.7	1.8	2.2	3.0	2.3	3.3
Roundness (Range)	-	0.90 (45–75 μm)	0.92 (45–75 μm)	0.94 (45–75 μm)	0.93 (45–75 μm)	0.94 (45–75 μm)	0.94 (45–75 μm)
Extract impurities							
Na+	ppm	0.3	0.3	0.2	0.2	0.2	0.2
Cl−	ppm	0.2	0.2	0.3	0.2	0.1	0.1
Flowability (Q-value)	mL/s	0.40	0.53	0.75	0.76	0.82	0.93

Table 3 Product specifications for typical 53 μm cut products and typical 45 μm cut products

		53 μm-cut	53 μm-cut	53 μm-cut	45 μm-cut
Item	Unit	ST3050-50	S3030-50	S4140-53P	S4140-45P
D50	μm	9.7	19.6	16.9	14.3
Wet sieve					
53 μm on	%	0.0	0.0	0.0	-
45 μm on	%	-	-	-	0.0
Specific surface area	m^2/g	2.9	3.4	3.5	3.8
Roundness (Range)	-	0.96 (10–53 μm)	0.95 (10–53 μm)	0.97 (10–53 μm)	0.97 (10–45 μm)
Extract impurities					
Na+	ppm	0.1	0.1	0.1	0.1
Cl−	ppm	0.4	0.4	0.1	0.1
Flowability (Q-value)	mL/s	0.53	0.65	0.80	0.72

Table 4 Product specifications for typical 32 μm cut products and typical 20 μm cut products

		32 μm-cut	20 μm-cut	20 μm-cut	20 μm-cut
Item	Unit	ST7011-3	ST3050-20	ST7011-2	ST7030-20
D50	μm	12.3	8.5	9.6	7.5
Wet sieve					
32 μm on	%	0.0	-	-	-
20 μm on	%	-	0.1	0.0	0.0
Specific surface area	m^2/g	3.3	2.8	3.5	3.0
Roundness (Range)	-	0.98 (10–32 μm)	0.97 (10–20 μm)	0.99 (10–20 μm)	0.97 (10–20 μm)
Extract impurities					
Na+	ppm	0.1	0.1	0.1	0.1
Cl−	ppm	0.1	0.1	0.2	0.1
Flowability (Q-value)	mL/s	0.54	0.37	0.42	0.37

Table 5 Characteristics of spherical alumina filler

Grade		AY series					AZ series				
Product name		AY2-75	AY4-75	AY10-75	AY35-125	AY75-150	AZ2-75	AZ4-75	AZ10-75	AZ35-125	AZ75-150
Particle size (D50)	μm	2.5	4.5	10.5	37.0	75.0	2.5	5.5	10.5	37.0	75.0
Specific surface area	m^2/g	1.3	0.6	0.3	0.2	0.2	1.3	0.6	0.3	0.2	0.2
Electric conductivity	μS/cm	35	12	30	20	50	7	6	4	5	10
Free Na+	ppm	80	30	50	30	80	4	3	3	6	10
Free Cl−	ppm	13.5	1.5	0.8	0.5	0.5	8.0	1.5	1.0	0.4	0.5
Al_2O_3	wt%	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Sieving size	μm	75			125	150	75			125	150

* The data mentioned above are not the specifications, but the typical value.

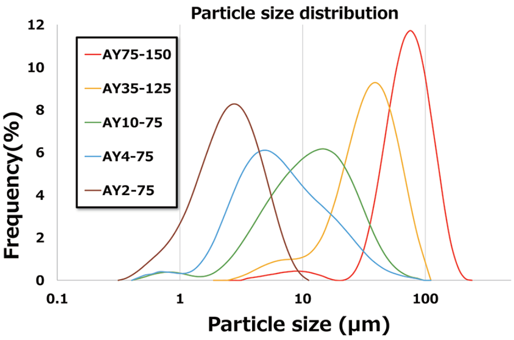


Fig. 3 Particle size distribution of spherical alumina filler (AY series)

Meanwhile, small-diameter fillers AY10-75, AY4-75, and AY2-75 are used as fillers for liquid TIMs, such as heat dissipation grease and heat dissipation adhesives, when they are used alone. The small-diameter fillers are also mixed with the aforementioned large-diameter fillers and the mixtures are charged into various types of TIMs. Mixed small particles fill clearance between the large particles, which improves the filling factor and which can in turn improve the thermal conductivity.

Combining particles as described above is generally carried out and TIM users often have knowledge acquired on their own. The Micron Div. of Nippon Steel Chemical & Material also proposes combination products that the company has verified and developed on its own to users who do not have such knowledge.

In addition to the aforementioned general products, the Micron Div. of Nippon Steel Chemical & Material provides the AZ series for which the amount of Na ions on the surface has been controlled. The raw material of alumina is aluminum hydroxide purified with the Bayer process and it contains a large amount of Na ions originating in the process. It is said that Na ions have an adverse effect on the resin to be used in TIMs (e.g., curing defects). To resolve such problems, the amount of Na ions on the surface has been reduced through a Na ion reduction process for the AZ series.

The AZ series are mainly used for applications that require high reliability and they are mainly used as fillers for in-vehicle heat dissipation sheets.

In addition, the Micron Div. of Nippon Steel Chemical & Material customizes products via various types of top cutting. Characteristic products are as follows: 20-μm cut products called low top-cut products for which rough particles were removed using meshes and 10-μm cut products for which rough particles were removed at high accuracy using an air classifier. **Figure 4** shows the example particle size distributions of the low top-cut products.

These products are used for applications for which contamination with rough particles is not allowed (e.g., films). In addition, in recent years, because the products release generated heat efficiently, they are used as fillers for bond line thickness (BLT) materials for which the thickness can be reduced. Any existing rough particles hinder compression and thereby customers regard the low top-cut products for which rough particles were removed by the high-accuracy classification technology of the Micron Div. of Nippon Steel Chemical & Material as suitable.

Although the alumina fillers of the Micron Div. of Nippon Steel Chemical & Material are used as fillers for TIMs as described above, the usage as fillers for semiconductor encapsulants is also increasing. In recent years, increased integration of IC chips has increased the caloric value and thereby encapsulants using conventional silica particles cannot secure sufficient heat dissipation. The technology for combining particles is combined with the Na ion reduction and rough particle cutting technologies so as to develop and supply filler products for encapsulants.

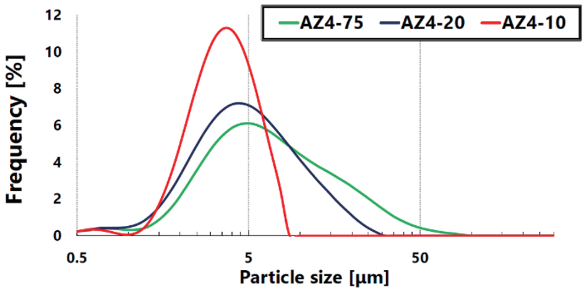


Fig. 4 Particle size distribution of spherical alumina filler in low top cut products

2.5 Expansion of the application area of spherical fillers

There is no doubt that high-performance spherical fillers that the Micron Div. of Nippon Steel Chemical & Material commercialized in 1985 as a pioneer of the spherical filler business have been greatly contributing to improvement of the functionality in the application for semiconductor encapsulants. In recent years, the division has been changing course so as to develop higher-performance fillers. Specifically, the application of silica fillers to high frequencies is expanding by making the most of the low dielectric property, and the application of spherical alumina fillers is expanding by drawing on their high filling property and high thermal conductivity in uses for in-vehicle devices and EVs for which high reliability is demanded (**Fig. 5**). To further improve the functionality more quickly in such uses, the Micron Div. of Nippon Steel Chemical & Material is eagerly developing and improving product technologies (top cutting and bottom cutting) to more quickly create high-quality fine powder fillers and products with particle size distributions that exert the required properties.

3. Fine Powder Alumina Fillers

3.1 Fine powder alumina filler AX1M

In recent years, heat management of semiconductors and their surrounding devices – heat dissipation measures, in particular – has become increasingly important. The main cause is the necessity for large-capacity high-speed processing in high-speed communication devices (e.g., the use of 5G for smart phones) and also in driving support systems and automatic driving in the automotive sector. In addition, electric vehicles (EVs) are being actively promoted to prevent global warming, which is rapidly increasing the demand for EV batteries and power semiconductors. With the expansion of more highly packed semiconductor devices used in those sectors, the caloric value and heat generation density are increasing, which is increasing the risk of damage, etc., due to thermal runaway, thermal degradation, and thermal stress. Accordingly, heat management is regarded as the most important technical task.

Heat dissipation fillers that are used in heat management and that autonomously exert functions are as follows: 1) Low-soda alumina, 2) spherical, round, and polyhedral alumina, 3) aluminum nitride, 4) boron nitride, and 5) carbon fiber, etc. Fillers with high thermal conductivity tend to be expensive. As a material for heat dissipation fillers, the cost and performance of spherical alumina are best balanced and thereby spherical alumina is regarded as playing

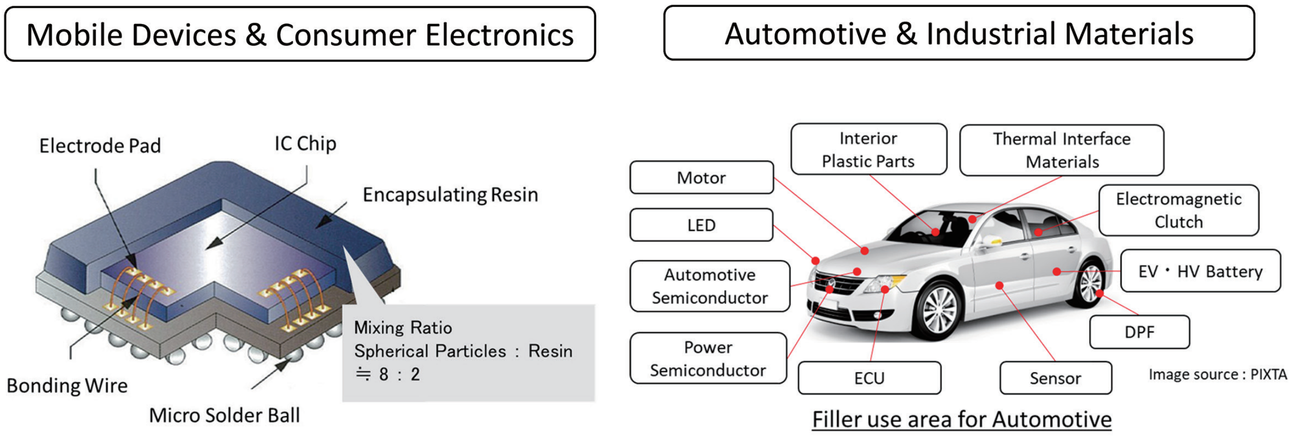


Fig. 5 Application areas of the spherical filler

the leading role in heat management. As shown in **Fig. 6**, the Micron Div. of Nippon Steel Chemical & Material manufactures spherical alumina filler products in wide-ranging sizes from φ1 μm to φ150 μm. Especially, φ1-μm minute-diameter alumina fillers and φ150-μm large-diameter alumina fillers are proprietary products of the Micron Div. of Nippon Steel Chemical & Material.

In heat management, spherical alumina, in particular, are essential heat dissipation fillers as a TIM in a wide variety of uses, such as in-vehicle devices (e.g., ECUs (Electronic Control Unit)) and base stations. The Micron Div. of Nippon Steel Chemical & Material has developed, based on spherical alumina, φ1-μm-class fine powder aluminum fillers (AX1M) that can further enhance the heat dissipation property in heat management. This paper describes in detail the properties of this material and discusses the functions of fine powder fillers when higher thermal conductivity is achieved.

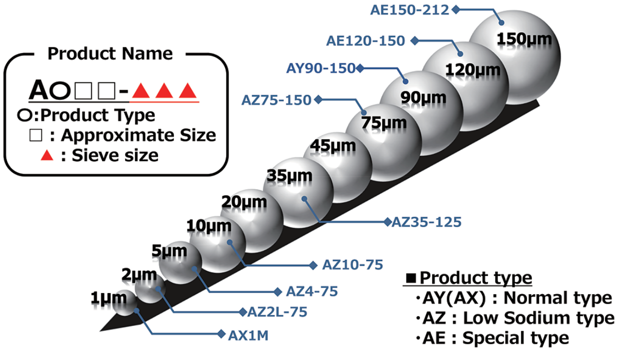


Fig. 6 Particle size lineup in spherical alumina filler

3.2 Consideration of approaches to increase the thermal conductivity of kneaded mixtures of fillers and resin

Possible approaches to increase the thermal conductivity of resin compositions, which are kneaded mixtures of fillers and resin such as heat dissipation sheets, heat dissipation gap fillers, heat dissipation grease, and sealing resin, are as follows:

1) Increase the thermal conductivity of resin to be used for resin compositions.
2) Increase the thermal conductivity of filler materials to be used for resin compositions.
3) Optimize the particle size distributions of filler materials to be used for resin compositions to improve the filling property.

It is widely known that, in these cases, multimodal distributions of filler size distributions improve the filling property, which can improve the thermal conductivity. The Micron Div. of Nippon Steel Chemical & Material also supplies multimodal distribution fillers that are manufactured by mixing multiple types of fillers based on customer requests as all-in-one products.

Takezawa, et al.[12, 13] achieved very high conductivity of 20 W/m K by applying the aforementioned approaches to heat dissipation sheets. Based on this research, this paper verifies the direction of the alumina filler development by the Micron Div. of Nippon Steel Chemical & Material.

Analysis of the patents[14–16] revealed that Takezawa, et al. developed the sheets having high-thermal conductivity of 10 W/m K and 20 W/m K through the following processes. The high thermal conductivity is mainly achieved by the utilization of newly developed resin for which self-organizing mesogenic groups were introduced into epoxy resin and that dramatically enhanced the thermal conductivity up to 0.45 W/m K (the thermal conductivity of general epoxy resin is 0.21 W/m K). By using epoxy resin with a mesogen skeleton as the base, various improvements were made and the addition of fillers was arranged to develop high-thermal conductivity resin sheets. **Figure 7** illustrates the mechanism to utilize the high functionality of fine powder fillers.

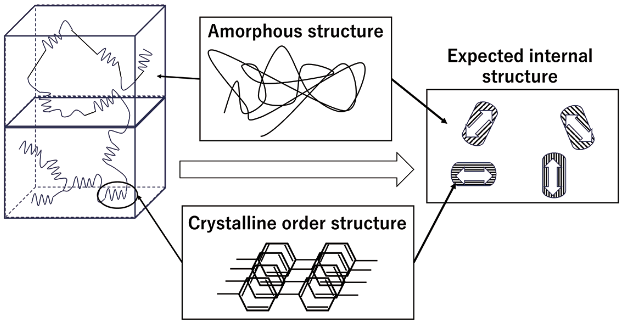


Fig. 7 Mechanism of high functionality of fine powder filler (High functionality is achieved by submicron spherical filler in the mesogen skeleton & sea-island structure of high thermal conductivity epoxy resin.)

Takezawa, et al. also tried to optimize filler material types to be added, filler size distributions, and filler mixing ratio. As the base, the matrix resin was epoxy resin having a mesogen skeleton and submicron α-alumina (φ0.4 μm → φ0.15 μm) was used to achieve 10 W/m K as an alumina material. In addition, the main thermal conduction filler type in the base above was changed from α-alumina to boron nitride having higher thermal conductivity than α-alumina to achieve 20 W/m K. Accordingly, such high thermal conductivity may have been achieved by combining the following three factors: 1) thermal conductivity of epoxy resin increased by introducing a mesogen skeleton, 2) thermal conductivity of the filler material increased by changing the main thermal conduction filler material type, and 3) optimization of the particle size distribution by the utilization of submicron alumina.

Based on this mechanism analysis, the Micron Div. of Nippon Steel Chemical & Material, which provides a wide variety of spherical alumina products, selected fine powder spherical alumina filler products as targets of the development of product technologies with spherical alumina as its core because such products will be in greater demand. Meanwhile, such high-thermal conductivity epoxy resin and boron nitride are very expensive and we thought this would be a problem. Accordingly, in the alumina filler product development, low-priced, easy-to-use alumina filler products were also selected as the development targets. Under these concepts, we promoted the development to commercialize high-performance fine powder alumina filler AX1M and maximize the manifestation of the functions.

3.3 Alumina filler AX1M of the Micron Div. of Nippon Steel Chemical & Material

Under the aforementioned concepts, the Micron Div. of Nippon Steel Chemical & Material started developing φ1-μm products aiming to halve the diameter of φ2-μm products, which used to be the minimum size products for alumina fillers. The target size of the AX1M developed was smaller than φ2 μm and it was difficult to stably mass-produce φ2-μm products in the flame-fused process. Accordingly, to achieve φ1 μm, the company established new technologies for the special pre-treatment of raw materials to be put in and for a separate charging process during charging into flames.

Figure 8 shows the scanning electron microscope (SEM) image of the AX1M developed and the results of measurements with electron backscatter diffraction (EBSD). Because the crystal grain size is φ1 μm, an AX1M crystal consists of a single crystal grain or a few crystal grains. When viewing the mechanism of the manifestation of the excellent thermal conduction property of AX1M, the influence of grain boundary thermal phonon dispersion is smaller because AX1M has fewer grain boundaries and this reasonably leads to the manifestation of the excellent thermal conduction property. We will actively utilize this characteristic.

In addition to the excellent thermal conduction property thanks to decreased grain boundary dispersion, AX1M fillers exert completely different functions compared with the conventional φ2-μm products as a result of downsizing to φ1 μm. As an example, **Fig. 9** shows the viscosity characteristics of a resin composition consisting of φ10-μm and φ2-μm products as well as those of a resin composition consisting of φ10-μm and φ1-μm products. Adding AX1M dramatically improves the viscosity characteristics. **Figure 10** presents a photo showing AX1M dropping from a spoon as a visible example.

Then, we investigated the relationship between the usage amount of AX1M and the viscosity because we considered this would be the

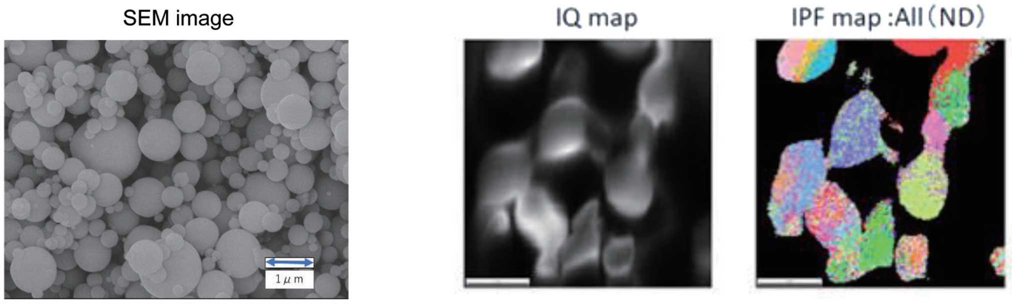


Fig. 8 SEM image of AX1M and cross-sectional EBSD results
AX1M crystals consist of a single grain or two grains.

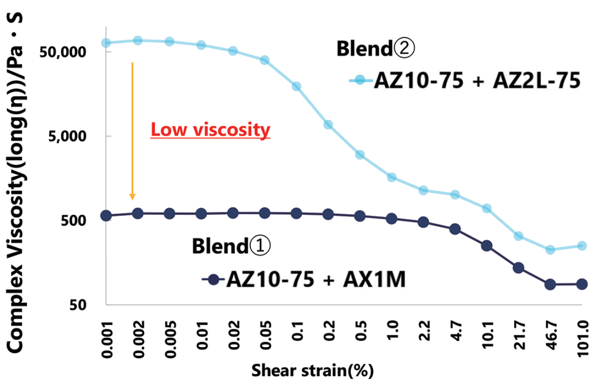


Fig. 9 Viscosity characteristics of resin compositions with fine spherical alumina filler AX1M

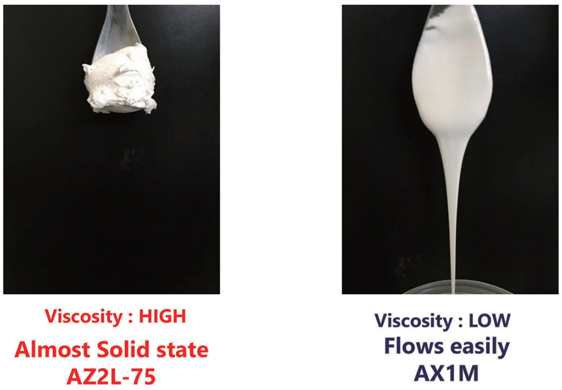


Fig. 10 Change in resin flowability with the addition of fine spherical alumina filler AX1M

most important from the perspective of cost. **Figure 11** shows at which addition level the viscosity starts decreasing due to the addition of AX1M. The experimental data shows that adding AX1M from 3% to 5% or so exerts excellent low-viscosity. This has made it possible to propose such excellent low-viscosity that is obtained by adding a very small amount of AX1M as a new filler function. Figure 11 also shows the results of measurements of flowability (viscosity) when AX1M was added and when the shearing strain conditions were changed. For the measurements, mixtures of spherical alumina particles were mixed with epoxy resin and a rheometer was used to measure the viscosity of the obtained resin compositions. In the measurements, the shearing strain was set to 0.1% (Shear 0.1%) and 10% (Shear 10%). Under these two measurement conditions, the rotational viscosity was measured. These results clearly show that under wide shearing strain conditions, the added AX1M works to exert low-viscosity characteristics.

In addition, **Fig. 12** shows the results of the thermal conductivity simulation of the AX1M developed. The thermal conductivity when the *φ*2-*μ*m fine powder alumina filler is used is 7.2 W/m K while when *φ*1-*μ*m AX1M is used, the thermal conductivity is remarkably higher at 8.7 W/m K. We will actively release information on the possibility of *φ*1-*μ*m spherical alumina filler AX1M contributing to the manifestation of the excellent thermal conduction property, in addition to the fact that it exerts excellent flowability and low-viscosity characteristics. We will also develop new applications of the fine powder alumina fillers.

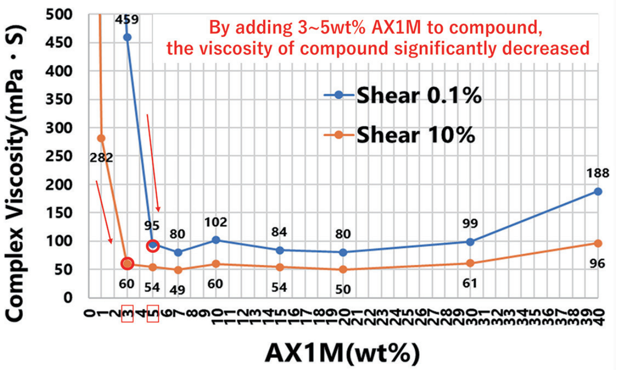


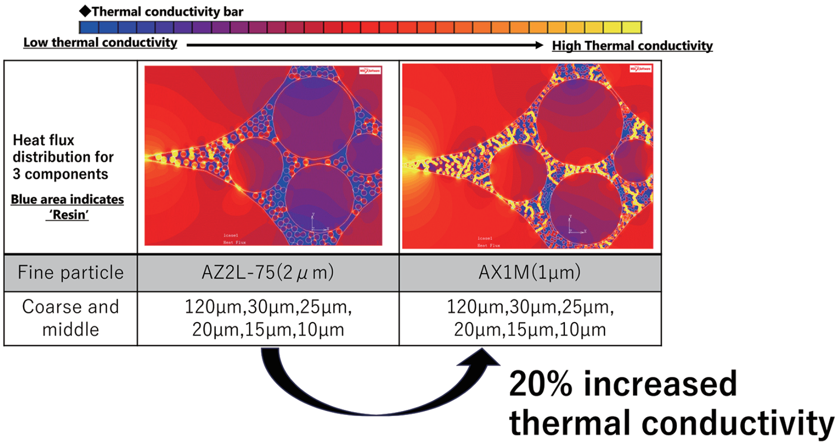
Fig. 11 Effect of the amount of fine spherical alumina filler AX1M added on the viscosity of resin compositions

4. High-performance Silica Fillers

4.1 Crystal structure and physical properties of silica

Silica has been used as fillers for semiconductor encapsulants because it is highly reliable. Silica is often used because the spheroidicity of silica that was manufactured with the flame spraying method is high, in particular, and increasing the filling factor of silica fillers can realize high-functionality encapsulants. Although spherical silica manufactured with the flame spraying method is amorphous, there are many types of silica crystal structure, such as quartz, tridymite, and cristobalite (phases stabilized at normal pressure) and coesite, etc. (phases stabilized at high pressure),[17] and according to the equilibrium diagram, quartz is regarded as a phase stabilized at normal temperature and normal pressure.[18, 19] However, during the crystallization of amorphous silica, cristobalite forms at high temperatures. It has also been reported that when alkali metals are added, quartz, tridymite, and cristobalite form depending on the heat treatment temperature, the components of the alkali metals, and the added amount.[20] Meanwhile, when amorphous silica crystallizes as a result of the addition of alkali metals, the particles sinter and soften even at low temperatures and it is difficult for amorphous silica to crystallize while maintaining the spherical form. In addition, alkali metals cause IC wires to erode and thereby it is not favorable to use such metals in encapsulants. Accordingly, we focused on Ca as an element that would work to accelerate crystallization and that would not easily combine with Si among the alkaline earth metals. **Table 6** lists the crystal structure of silica and its properties.

The thermal conductivity and thermal expansion ratio of crystalline silica are higher than those of amorphous silica and thereby crystalline silica can be used to improve the heat dissipation property and to control thermal expansion in applications where alumina fillers cannot be used. However, phase transition occurs at 220°C in the case of cristobalite and there is concern that thermal expansion will occur at reflow temperature during the implementation to semiconductors, so cristobalite is not favorable. Meanwhile, the phase transition temperature of quartz is sufficiently high at 570°C and thereby there is no concern of phase transition at operating temperature. Accordingly, we studied the development of spherical quartz particles through heat treatment of amorphous spherical silica particles manufactured with the flame spraying method.



Fine particle	AZ2L-75(2μm)	AX1M(1μm)
Coarse and middle	120μm,30μm,25μm, 20μm,15μm,10μm	120μm,30μm,25μm, 20μm,15μm,10μm

Fig. 12 Simulation of thermal conductivity of fine spherical alumina filler AX1M

Table 6 Silica crystal system and physical properties

Property	Quartz	Cristobalite	Amorphous silica
Crystal system [Low/High]	Trigonal/Hexagonal	Tetragonal/Cubic	–
Phase transition temperatures (°C) [Low↔High]	570	220	–
Density (g/cm^3)	2.65	2.33	2.21
Thermal conductivity (W/mK) [Horizontal/Vertical]	10.7/6.2	10	1.38
Thermal expansion coefficient (ppm) [Horizontal/Vertical]	8.0/13.4	20–34	0.52

4.2 Quartz phase forming conditions (impurities and heat treatment), experimental procedure, and consideration of quartz crystallization

Spherical amorphous silica particles for which D50 was 2.2 μm were manufactured with the flame spraying method and they included 0.8 mass%Al_2O_3 as impurities. Silica particles were mixed with Ca(OH) as a calcium source, added in amounts equivalent to 0.2–4.0 mass% as CaO. Then, the mixed powder of 30 g was put into a melting pot and an electric furnace was used to heat the powder in the air. The heating rate and cooling rate was set to 10°C/min and the holding time was 60 minutes. The heat-treated mixed powder was carried out X-ray diffraction (XRD) to measure the crystal phases.

The amorphous silica containing CaO of 1.1 mass% was heat-treated at each temperature from 1180 to 1250°C and cooled at room temperature. **Figure 13** shows the XRD patterns measured after the cooling.

The crystal phases formed as a result of the addition of Ca and heat treatment were quartz and cristobalite. Through heat treatment at 1180°C, a small amount of quartz formed and at 1200 to 1220°C, a large amount of quartz were obtained. In addition, cristobalite formed through heat treatment at 1200°C or higher and the higher the heat treatment temperature was, the more cristobalite formed.

From the XRD patterns, the mass of each crystal was quantified through Rietveld analysis. Firstly, **Fig. 14** shows the formed amounts of quartz organized by CaO contents and heat treatment temperatures.

When the added amount was 0.2 mass%CaO, no formed quartz was observed while for 0.5 mass%CaO, the ratio of quartz formed through heat treatment at 1250°C was 20% or more. For 1.1 mass%CaO, the ratios of quartz formed through heat treatment at 1200 to 1220°C were 80% or more. For 2.0 to 4.0 mass%CaO, the ratios of quartz formed through heat treatment at 1200 to 1220°C were 60% or more; however, the amount of formed quartz was smaller than that under the addition condition of 1.1 mass%CaO. The higher the amount of the added CaO, the sharper the peak of the amount of formed quartz. It was found that, in order to obtain a larger amount of quartz, the addition of CaO must be increased; however, excessive addition significantly narrows the appropriate heat treatment temperature range.

Secondly, **Fig. 15** shows the amounts of formed cristobalite organized by CaO contents and heat treatment temperatures.

At addition levels of 0.2 mass%CaO and 0.5 mass%CaO, the formation of cristobalite could not be detected within the measurement error range even after heat treatment at 1300°C. For 1.1 mass%CaO, the amount of cristobalite increased as the heat treatment temperature increased at 1200°C or higher. For 2.0 to 4.0 mass%CaO, the amount of cristobalite increased as the heat treatment temperature increased at 1200°C or higher as is the case with 1.1 mass%CaO, and the increased amount of cristobalite was larger

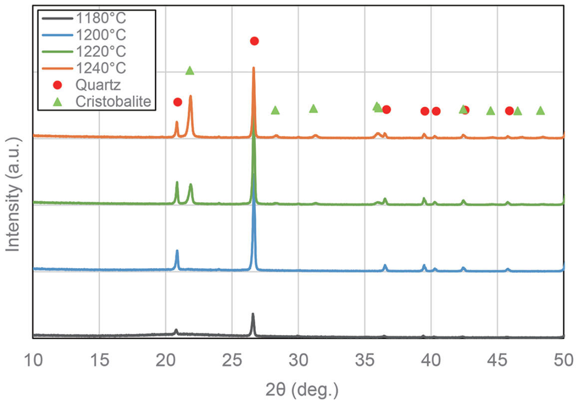


Fig. 13 Crystallization of silica at each heat treatment temperature

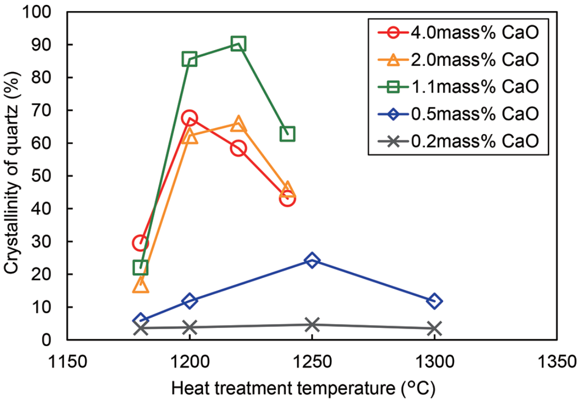


Fig. 14 Effect of heat treatment temperature for crystallization on the crystallinity of quartz

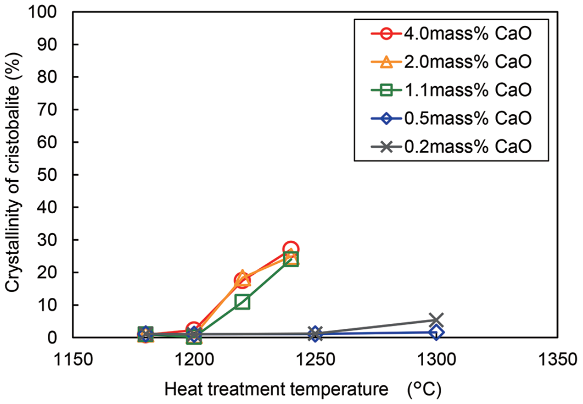


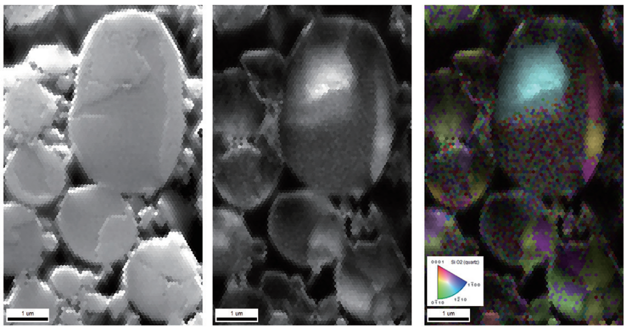
Fig. 15 Effect of heat treatment temperature for crystallization on the crystallinity of cristobalite

than the amount of cristobalite for the 1.1 mass%CaO silica. These results show that containing more Ca than necessary encourages the formation of cristobalite. In addition, for the silica to which 2.0 mass% or higher CaO was added, the amount of quartz became smaller through heat treatment at 1220°C to 1240°C (Fig. 14) while the amount of cristobalite became larger. These results show that phase transition from quartz to cristobalite may also have occurred. In addition, the phase transition from quartz to cristobalite may increase as the amount of added Ca increases. These results clarify that to obtain a large amount of quartz, the addition of Ca in an appropriate amount and heat treatment are required.

4.3 Crystal structure of quartz phases

We carried out EBSD analysis to understand changes in the crystal structure from amorphous silica to quartz. EBSD can visualize crystal structure by determining and mapping crystal structure by reading and analyzing patterns produced by electron diffraction using a detector installed on an SEM. However, because silica is non-conductive, charge-up easily occurs and the crystal structure tends to change by the influence of beams, which makes measurement difficult. Considering these problems, this analysis was performed by paying attention to control of the applied voltage and current values within the range where patterns could be read. **Figure 16** shows the EBSD analysis results of the cross sections of 1.1 mass%CaO particles for which the quartz crystal ratio is 86%.

The SEM image shows height differences in the cross sections of the particles and the bright section in the Image Quality (IQ) map is protruding. The bright section in the IQ map means that the Kikuchi pattern of EBSD is clear and thereby means the particle is crystalline, i.e., quartz. The hardness of quartz is slightly higher than that of amorphous silica and thereby the protrusion of the quartz may have been formed because it wore less during polishing. Figure 16 also shows the IQ + IPF map where the IQ and inverse pole figure (IPF) maps were overlapped. The IQ + IPF map shows that the crystal orientation is the same for each particle and most particles are single crystal quartz. However, large particles tend to have quartz and amorphous silica sections. These results show that for quartz particles produced by this manufacturing method, when amorphous sections of silica crystallize to quartz, crystallization starts from sections that are in contact with the added Ca and the quartz ratio may increase as the crystals grow. In addition, compared to the quartz ratio measured with XRD, the ratio of particles analyzed as quartz with EBSD is lower and this is because the crystal structure was destroyed by the electron beam irradiation during EBSD measurements, as mentioned earlier. The sections that could be analyzed this time may be part of quartz that was not destroyed by the electron beam irradiation.



(a) SEM image (b) IQ map (c) IQ + IPF map

Fig. 16 EBSD analysis of silica with 1.1 mass%CaO heat-treated at 1200°C

5. Conclusion

5.1 Conclusion for fine powder spherical alumina filler AX1M

The Micron Div. of Nippon Steel Chemical & Material started, based on the world's first successful development of flame-fused spherical fillers, the spherical filler business in 1985 as a pioneer of spherical filler manufacturing. The division offers high-performance spherical fillers for semiconductor encapsulants and cast materials. In addition to conventional properties that fillers must have, such as high density filling and high flow properties, in recent years, newly demanded properties (e.g., high heat dissipation property) have been revealed. To satisfy such requests, the division developed fine powder spherical alumina filler AX1M ($\varphi 1\ \mu$m) and clarified its excellent filler properties. As the next step toward higher functionality, the division will mass-produce submicron-level fine powder alumina fillers via the flame-fused process. Using the flame-fused process can greatly reduce the material cost. The division will energetically develop product technologies so as to expand new application areas, in addition to the existing application areas.

5.2 Conclusion for high-performance spherical silica fillers

With regard to highly reliable silica filler products that have been used for semiconductor encapsulant fillers for an extended period of time, the division worked to develop spherical quartz from conventional spherical amorphous silica so as to achieve higher functionality (thermal conductivity and thermal expansion ratio). The influence of the amount of added Ca and heat treatment temperature on the quartz and cristobalite ratios was investigated and the fact that the quartz ratio can be increased under limited conditions was clarified. By using the physical properties of various silica crystal systems, such as quartz and cristobalite, we aim to develop products that meet new, wide-ranging functional requirements.

References

1) Japanese patent: Japanese Examined Patent Publication 61-035145
2) Japanese patent: Japanese Examined Patent Publication 60-026505/JP1411034
3) Japanese patent: Japanese Examined Patent Publication 60-026505/JP1411034
4) Japanese patent: JP1640189
5) Japanese patent: JP1853603
6) Japanese patent: JP2122565
7) Japanese patent: JP2029247
8) Japanese patent: JP5116968
9) Japanese patent: JP5506883
10) Japanese patent: JP5036984
11) Japanese patent: JP5085050
12) Takezawa, Y.: Journal of the Society of Rubber Science and Technology, Japan. 81 (3), 33–38 (2008)
13) Takezawa, Y.: Pulverization. (55), 32–37 (2012)
14) Japanese patent: JP5573842
15) Japanese patent: JP6222209
16) Japanese patent: JP5928477
17) Nukui, A.: Ceramics. 20 (4), 266 (1985)
18) Hirano, S. et al.: Ceramics. 14 (3), 279 (1979)
19) Kiriyama, R.: Ceramics. 15 (11), 881 (1980)
20) Fujino, S.: New Glass. 20 (1), 19 (2005)

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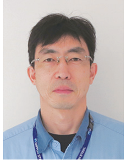

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