Applications of Comminution Techniques for the Surface Modification of Powder Materials

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(Received on April 1, 1993; accepted in final form on May 21, 1993)

This paper reviews a new method for surface modification to cover particle surface with fine particles mechanically in a dry phase by making use of comminution techniques.

First, the relation of comminution process with surface modification technology is discussed, and the advanced machines developed in Japan to treat core particles surface with fine particles based on grinding principles are introduced. Then, the details of the composite process of core/fine particles with these machines are explained.

In the second section, the effects of the controlling factors on the composite process such as mechanical actions, treating temperature and atmosphere are discussed.

The third section deals with the conditions of combinations of core/fine particles acceptable to this method, and it is demonstrated that this method has a great feasibility to fabricate composite particles by the combination of various kinds of core/fine particles. The scale-up of these machines is explained in the fourth section, and a typical example is introduced.

The last section summarizes the applications of the composite particles fabricated by this method to create various kinds of new materials, which include the application for surface modification technology. The applications of this method are shown to expand for other types of processing such as rounding particles and mixing different kinds of powder materials precisely. Furthermore, it is also explained that this method can fabricate composite particles inside which different kinds of components are dispersed.

KEY WORDS: surface modification; dry mechanical method; comminution; composite particle; composite process; particle rounding, mixing.

1. Introduction

Comminution process produces fine particles by giving feed materials the mechanical forces strong enough to destroy them. From a different point of view, the process is thought to be a useful method to act an effective force onto the surface of fine particles. In fact, this function has been applied for surface modification of particles.

For instance, in some operations, grinding aids or additives are mixed into powder materials for the purpose to improve the comminution performance such as the grinding rate. Some kinds of them are known to improve the flow properties of powders by modifying their surface,¹⁾ which is included in surface modification technology. **Table 1** shows the main grinding machines which have been applied for particle surface modification. It means that most kinds of fine grinding machines have a feasibility as surface modification machines.

Recently, many researches have concentrated on the technology to cover core particle surface with fine particles mechanically by the surface modification methods with grinding machines. Koishi²⁾ proposed a model to create composite particles with this technique as shown in **Fig. 1**. The processing has actually been conducted in both dry and wet phases^{4,5)} in the

experimental cases, but in the industrial scale, the dry phase processing has several advantages as compared with the wet phase one. For example, the dry phase processing is simpler, and doesn't have any residual solvent in the processed particles.

Table 1. Main grinding machines used for surface modification.

Type	Advanced machines for surface modification
Impactation-type Pin mill, disc mill centrifugal classifying type	Hybridization System ¹⁸⁾ (Nara Machinery Co.) KOSMOS ¹⁹⁾ (Kawasaki Heavy Industry Co.)
Attrition-type	Mechanofusion System ²⁰⁾ (Hosokawa Micron Corp.)
Ball mill rotation vibration planetary centrifugal fluidizing Agitated ball mill vessel-type	Mechanomill ²¹⁾ (Okada Seiko Co.)
Jet mill Mortar

Fig. 1. Surface modification model of core/fine particles.³⁾

Therefore, the four kinds of advanced machines for surface modification shown in Table 1 have been developed based on the mechanical principles in a dry phase making use of the machines shown in the left column.

The development of these machines were conducted in Japan, and the fundamental researches have just started lately. However, the applications have been actively advanced in diverse fields as explained afterwards, and are expected to spread out in the future. Therefore, this paper reviews the researches on this technique to provide readers useful information of the surface modification technique.

2. Composite Process in Core/Fine Particles Combination

Although each advanced machine for surface modification works on a different principle, all of them give mechanical actions to powder materials by the rotation of rotors or vessels. Here, it will be explained about the composite process where fine particles are fixed onto core particle surface by Mechanofusion System in Table 1 as an example.

Figure 2 shows the mechanical principle of this machine.^{6,7)} The main parts are a rotating chamber and an arm head fixed with a certain clearance against the inside wall of the chamber. The powder material compacted by the centrifugal force onto the inside wall of the chamber is compressed into the clearance and receives various kinds of forces, such as compression, attrition, and rolling. The processed powder is dispersed by the scraper. These actions are repeated during the chamber rotation to modify the core particle surface with fine particles.

Figure 3 shows the relationship between the rotation speed and the forces F_c , F_t acting on the arm head when glass beads ($100\text{ }\mu\text{m}$) are charged as brittle powder materials. F_c means the radial force and F_t means the tangential one. The forces of F_c and F_t increase as the

Fig. 2. Mechanical principle of surface modification machine.^{6,7)} (Mechanofusion System)

Fig. 3. The radial force F_c and the tangential one F_t exerting on the arm head.⁸⁾

rotation speed increases. When they reach a critical condition (*i.e.* breakage starting point), the size reduction of particles starts. At this point, particles of several micron were collected, but the glass beads which remained in the chamber didn't change their round shape but had the scratched surface. Therefore, over the breakage starting revolution, this machine has a function of surface grinding, which is effective to produce submicron particles.⁶⁾

On the other hand, in the case of modifying core particle surface with fine particles, the forces acting on particle surface are effectively used. For example, when a brittle material is used as core particle, it is necessary to treat them under the revolution of starting size reduction. This treating condition is applied for other kinds of materials. That is, in the case of resins as core particles, the mechanical conditions are needed to be kept under certain values which do not cause melting of the resin particles.

In discussing the composite process with the above method, it will be needed to analyze the relationship between the change of individual particle structure and

Fig. 4. Mixing process with high stirred shearing mixer (HSSM).⁹⁾ (Core particles: PMMA 50 μm , fines: magnetite black 0.17 μm)

Fig. 5. Mixing process during the treatment by Mechano-fusion System (AMS) of the powder treated 300 min with HSSM.⁹⁾

the local mechanical actions from the microscopic view. In fact, the authors are conducting this research with microscopic analyzers which include an image analyzer. However, as this trial has not been completed yet, the composite process from a macroscopic point of view will be explained.

In this modification technique, a small amount of fine particles are usually mixed with core particles. In a research,⁹⁾ the composite process was analyzed from the mixing operation as follows: Figure 4 shows the relationship between the lightness (mixing index) of the processed powder and the mixing time of a high stirred shearing mixer (HSSM). Here, the PMMA (50 μm) was used as core particles, and magnetite black (0.17 μm) as fine particles respectively. In all conditions of fines concentration, the lightness decreases as the processing time increases in a gentle curve to the direction of the lightness of fine particles itself. When the powder mixed

Fig. 6. Model of composite process with core/fine particles.¹⁰⁾

for 300 min by HSSM is processed by the apparatus shown in Fig. 2, the lightness decreases in a sharp curve as the time increases in all cases as shown in Fig. 5. It means the mixing is more advanced with this modification machine.

Furthermore, the composite process during the mixing will be discussed based on a model as follows: Figure 6 shows the model of composite process proposed from a series of experimental results with glass beads (core particle) and titanium dioxides (fine particles).¹⁰⁾ The figure shows the composite process is described with the following two steps:

The first (I) is a step of adhering of fine particles onto the core particle surface. As a result, the adhering rate of R (weight of fine particles fixed on the core particle surface/total weight of fine particles charged) increases and BET surface area, S_w of processed powder decreases as the processing time increases. In the second step (II), the adhering of fine particles onto core particle surface is saturated, and S_w value decreases with time increasing. It means the compacting step of fine particles on the core particle surface.

This composite process can be applied to change the compacting condition of fine particles layer fixed on the core particle surface. For example, Fig. 7 shows the TEM pictures of section areas of PMMA particles (12 μm) covered with fine particles of titanium dioxide (15 nm). Comparing Figs. 7(a) with 7(b), it is found that the compacting status changes drastically with the processing time.

The discussion similar to Fig. 6 is also seen in other reports. For example, Tanno *et al.*¹¹⁾ discussed the qualitative model similar to that demonstrated in Fig. 6 with the SEM pictures of processed powder of SUS 316L (3 μm)/PSZ (0.3 μm) and SUS 304L (35 μm)/ Si_3N_4 (0.3 μm) by Mechano-fusion System. Kaga *et al.*¹²⁾ also discussed the same model as that in Fig. 6 from the electron microscopic analysis of the Cu (30 μm)/ $\alpha\text{-Al}_2\text{O}_3$ (0.5 μm) composite particles treated by Mechano-fusion System. On the other hand, Koishi *et al.*¹³⁾ made the similar discussion as that shown in Fig. 6 from the experimental results of processing Lactose granules (core)/carnauba wax by Mechanomill. These results show that the model proposed in Fig. 6 has reasonable generality.

This model suggests that fine particles are partly

Fig. 7.
TEM pictures of PMMA particles covered with TiO_2 .¹⁰⁾
(a) short time processing
(b) long time processing

Fig. 8. Change of $\text{Ti}2p$ binding energy with processing time.¹⁵⁾
(Soda-lime glass beads covered with TiO_2)

embedded into the core particle when the core particles tend to deform more easily than fine particles. These phenomena are found out in the case of soft core particles such as metals and resins. For example, Fig. 5 shows that the lightness of the processed powder increases again after a certain processing time, which means a part of fine particles are embedded into PMMA core particles.⁹⁾ Furthermore, Senna *et al.*¹⁴⁾ reported the same phenomena as above explained by the microscopic analysis of the cross section of the composite particle of PMMA (100 μm) covered with titanium dioxide (15 nm). These results show that a composite particle which has fine particles inside the core particle can be fabricated by this method. It will be explained in Sec. 6.4 in detail.

The above discussion was conducted from the viewpoint of the composite structure. However, it should be also mentioned to the interaction between the different kinds of particles. Senna *et al.*¹⁴⁾ has already pointed out that an interaction occurred in this kind of composite particles, and it depended on the combination of core/fine particles. One example is shown in Fig. 7. In this case,

although a part of TiO_2 particles are embedded into PMMA surface, a chemical interaction is not found out. On the other hand, in the composite particle of soda-lime glass beads covered with titanium oxides, the following type of interaction is found: **Figure 8**, which was obtained by authors,¹⁵⁾ shows the change of $\text{Ti}2p$ binding energy measured by XPS analyzer with the processing time of Mechanofusion System. From Fig. 8, it is seen that the peak value of the binding energy shifts to a lower value as the processing time increases. Besides, the X-ray analysis indicated the crystal structure of the processed bulk powder had few change.¹⁵⁾ These results suggest that the interaction of interface between different kinds of particles can be emphasized by increasing the processing time without the change of bulk crystal structure of particles.¹⁵⁾

3. The Factors Controlling the Composite Process

The factors which affect the composite process are mechanical stress, temperature and atmosphere. The effects of these factors will be discussed in detail.

(1) Mechanical Actions

The main mechanical actions of the advanced machines in Table 1 are the rotation of rotors and the motion of air stream in Hybridization System and KOSMOS, and the rotation of chambers in Mechanofusion System and Mechanomill. Strictly speaking, the relationship between the stresses acting on individual particles and the local composite process should be discussed. However, it is almost impossible to analyze them. Here, the discussion will be focused on the effect of rotation speed of the chamber of Mechanofusion System on composite process.

As the force acting on the bulk material generally increases with rotation speed as shown in Fig. 3, the stresses acting on the particle surface should increase corresponding to the rotation speed. **Figure 9** shows the relationship between the flowability of processed powder and the rotation speed of Mechanofusion chamber. Here,

Fig. 9. Relationship between discharge rate F through a screen of composite particles and rotation speed N . (core: corn starch $6.9\ \mu\text{m}$, fines: silica particles $16\ \text{nm}$, fines weight fraction 0.01)¹⁶⁾

corn starch ($6.9\ \mu\text{m}$) was used as core particles, and silica ($16\ \text{nm}$) as fine particles, respectively. The weight fraction of fine particles was 0.01 , and the processing time was set at $300\ \text{sec}$. The flowability was obtained by measuring a discharging rate F [kg/s] of bulk material flowing through the screen of $74\ \mu\text{m}$ mesh size. Figure 9 shows that the flowability improves as the rotation speed increases and makes worse drastically at the rotation speed of $33.3\ \text{s}^{-1}$. Terashita *et al.*¹⁶⁾ reported that the embedding of fine silica into corn starch particles caused the decrease of the discharging rate at a higher rotation speed.

However, the effect of the rotation speed on composite process depends on the combination of core/fine particles. **Figure 10(a)** shows a model of composite process of titanium dioxide fine particles fixed onto brittle glass beads. The model was expressed by the change of adhering rate R with the processing time t as shown in Fig. 6. N_{CL} was defined as the maximum revolution which caused the pattern I phenomenon in Fig. 10(a), and N_{CU} was defined as the minimum one that caused the pattern II respectively. In this case, the composite process changes at the critical revolutions of N_{CL} and N_{CU} as follows:¹⁷⁾ The first pattern appears in the region of $N < N_{\text{CL}}$, where R increases with the increasing processing time in the same tendency as the curve in Fig. 6 as well as the fine particles layer on the core particle is compacted. In the second pattern, which appears in the region of $N > N_{\text{CU}}$, R increases with the time and decreases from a certain time when the detachment of fine particles from the core particle surface starts.

The revolutions N_{CU} and N_{CL} are correlated experimentally with the core particle size d_{p50} as shown Fig. 10(b), which is expressed by Eq. (1).

$$N_{\text{CU}}, N_{\text{CL}} \propto d_{p50}^{-1} \quad \dots\dots\dots (1)$$

where d_{p50}^{-1} means the specific surface area of core particles. It suggests that the force acting onto the core particle surface contributes to the composite phenomena. Besides, it explains that the effective mechanical action

Fig. 10. (a) Change of adhering rate with processing time. (b) Relationship between critical revolutions N_{CU} , N_{CL} and core particle size d_{p50} . (core: soda-lime glass beads, fines: titanium dioxide $15\ \text{nm}$, fines weight fraction 0.02)¹⁷⁾

is exerted into the powder materials at a lower revolution as the core particle size becomes larger.

(2) Treating Temperature

It is necessary to measure the local temperature at the particle surface from the microscopic viewpoint. As a method to measure it, the powder which changes its color corresponding to the temperature has been developed.¹⁸⁾ The results are reported that the temperature of particle surface is higher by one order than the ambient temperature inside Hybridization System in Table 1.¹⁸⁾ It is supposed that a fairly high temperature occurs on the particle surface in the actual processing.

However, from a practical viewpoint, stable processing is conducted by monitoring the temperature of machines and atmosphere. Thus, the advanced machines listed in Table 1 have a function to control the temperature with heater or cooler.¹⁸⁻²¹⁾ For instance, in case of treating resins as core particles, it is needed to process them under the temperature of their softening point.

There is a report of Tanno *et al.*²²⁾ which evaluated

Table 2. Effect of water-cooling of chamber on composite process.²²⁾

Processing time (ks)		0.3	0.6	1.8	3.6	7.2	10.8	18.0
Water-cooling	SUS 316L/PSZ	A	A	C	C	C	C	C+S
	SUS 316L/Si ₃ N ₄	A	A	C	C	C	C	C+S
Without water-cooling	SUS 316L/PSZ	A	C	S	S	S	S	S
	SUS 316L/Si ₃ N ₄	A	C	S	S	S	S	S
	Cu/Si ₃ N ₄	A	A	C	C	C	S	C+S

A: Agglomeration C: Coagulation S: Shell structure

experimentally the effect of temperature on the composite process. **Table 2** summarizes the results, which include the data of SUS 316L (5 μm) (core)/3Y-PSZ (0.3 μm) and SUS 316L (5 μm) (core)/Si₃N₄ (0.3 μm). The apparatus as shown in Fig. 2, which was put into a vacuum chamber, was used. The composite process in the case of cooling the rotating chamber was compared to the case without cooling by the analysis of the SEM picture of processed particles and the TEM picture of the cross section of the particles. The starting vacuum condition was set at about 4×10^{-3} Pa. Table 2 shows in the above both cases that the fine particles layer on the core particle surface is compacted like a shell structure (S) at 1.8 ks without cooling, but that the state of fine particles layer reaches near the shell structure (S) at longer time processing of 18 ks with cooling the chamber. These results prove that the temperature makes the positive effect on compacting ceramics particles layer on metal particle surface. However, it is difficult to generalize the temperature effect. For instance, the processing has to be carefully conducted for treating the powder materials which tend to change with temperature.

(3) Atmosphere

In the case of treating metal particles which have problems like oxidization in the air, it is necessary to process them in inert gases or vacuum conditions. When composite particles are processed with the machine as shown in Fig. 2 in vacuum conditions, some kinds of gases are generated from the powder materials to increase the residual pressure in the chamber at the starting, but the residual pressure decreases gradually as the processing time increases.¹²⁾ The atmosphere reaches down to 10^{-3} Pa in this type.²²⁾

The systematic research has been conducted by Kaga *et al.* concerning the effect of vacuum condition on the composite process. Cu (30 μm)/Al₂O₃ (0.5 μm)^{12,23,25)} and Al₂O₃ (45 μm)/Cu (0.2 μm)²⁴⁾ were selected as the combination of core/fine particles, and the apparatus as shown in Fig. 2 was used for processing them. **Figure 11** shows an example of the effect of vacuum conditions on the composite of Al₂O₃ fine particles (0.5 μm) fixing onto the surface of Cu (30 μm) core particles with the weight fraction of fine particles of 0.02. The BET specific surface area S_w was applied as the index to characterize the composite structure as explained in Fig. 6. In Fig. 11, S_w decreases as the ambient pressure decreases in the chamber. Furthermore, it is reported that the surface roughness of fine particles layer decreases with the decreasing ambient pressure from the analysis of SEM

Fig. 11. Effect of ambient gas pressure on composite process. (core: Cu particle 30 μm , fines: α -Al₂O₃ 0.5 μm , fines weight fraction 0.02)²⁵⁾

pictures of the processed particles.²⁵⁾

Consequently, fine particles layer on core particle surface is compacted more densely, as the ambient pressure is lower. As a trial to analyze the phenomena, the effect of the partial pressure of oxygen on the composite process has started to be studied.²⁶⁾

4. Combination of Core/Fine Particles

So far, the effects of factors on composite process have been discussed. Here, the conditions of combinations of core/fine particles acceptable to this method will be discussed.

Actually, the conditions have not yet been established. It is firstly because the microscopic mechanism for the composite process has not been made clear. Besides, it is the problem that a characterizing method for composite particles has not been established. Therefore, prior to strict discussions, the feasibility of the combination range for core/fine particles will be described from the examples which have been studied as application researches.

Table 3 summarizes the reports published on the applications mainly by the advanced machines for surface modification in Table 1. The following conditions on the combinations of core/fine particles will be pointed out from Table 3:

(1) It is possible to fabricate composite particles by the combination of various kinds of core/fine particles.

(2) The finer the particles to be fixed are compared with core particles, the better for making composite particles. In fact, the ratio of fine particle size to core

Table 3. Applications of composite particles.

Material	Core particle (μm)	Fine particle (μm)	Fines weight fraction (—)	Objectives	Ref.
Medicine	α -Lactose/aspirin granule (20–32 mesh)	Carnauba wax (15 μm)	0–0.042	Release control of aspirin	29)
	Potato starch (70 μm)	First layer: isoproterenol Hcl	0–0.05	Release control of isoproterenol Hcl	30)
	Starch	Second: Carnauba wax Indometasin	0.1 0.041	Acceleration of indometasin solution	31)
Cosmetics	Polyethylene (12 μm)	Pigment (1 μm)	0–0.16	New coloring of polyethylene by pigment coating onto its surface	27)
	Nylon sphere	Tatanium dioxide fine particle		Foundation material for face with well-spreading and covering from ultra-violet rays	32)
Toner	Resin (3–25 μm)	Pigment, charge control agent and others		New method to fabricate toners	27)
Electric conductible resins	PMMA (50 μm)	Ag (1 μm)	0.05–0.25	Forming a network structure of electric conductible path in bulk materials	33)
	PMMA (8 μm)	TiO ₂ treated by Ag (0.5 μm), etc.	0.4		34)
Metal/ceramics composite materials	Al-alloy powder (30–60 μm)	Y ₂ O ₃ (3.5 μm)		Fabricating interface layer between substrate and thermal spray layer	35)
	SUS 316L (3 μm)	3Y-PSZ (0.3 μm)	0–1	Fabricating sintered body with good uniformity of metal and ceramics components	36)
Thermal spray materials	Ti (10–44 μm)	Amorphous B (0.85 μm)	0–0.18	Thermal spray materials for plasma spraying in reduction of pressure or in the air	37)
	Ni (–350 mesh)	Al (3 μm)	0–0.2		38)
Filler	MgO (130 m ² /g)	Fatty acid		Surface reforming of MgO from hydrophilic to hydrophobic	39)
Ceramics filter	Al ₂ O ₃	ZrO ₂	0.06–0.16	Fabricating ceramics filter with alkalinity-resistance	40)
Solid lubricant	Inorganic powder	Polymer		Composite solid lubricant	41)
Electric contact materials	Ag–Ni alloy (210 μm)	Ni (1 μm)	0.1	Fabricating rivets in which the network structure of Ni is composed The rivets properties improved compared with them made of Ag–Ni alloy	42)
					43)

particle one is selected generally under 0.1.²⁷⁾

(3) The lower limit of core particle size is normally in μm order. However, there is a report which says the core particles down to 0.1 μm could be used.²⁷⁾

The above are general items. In the special cases, where a fine particle tends to deform easily compared to a core particle, the fine particle size could come up to the core particle size. One example is Cu particles (40 μm) covered with film-like Sn particles (10–30 μm).²⁸⁾

Fine particle fraction is an important condition as well as the particle size. The weight fraction of fine particles n is calculated by the following Eq. (2), on the condition that the fine particles are closely allocated onto core particle surface, and $d_p \gg d_a$.

$$n = \frac{1}{1 + \frac{\sqrt{3}}{2\pi} \cdot \frac{\rho_p}{\rho_a} \cdot \frac{d_p}{d_a}} \dots\dots\dots(2)$$

where d_p : core particle size
 d_a : fine particle size
 ρ_p : true density of core particles
 ρ_a : true density of fine particles.

Equation (2) is a guideline to determine the fine particle fraction. Actually the fraction is selected in a wide range as shown in Table 3.

Fig. 12.

Relationship between BET surface area S_w and energy consumption E of Mechanofusion System. (core: silica sand $26\ \mu\text{m}$, fines: titanium dioxide $15\ \text{nm}$, fines weight fraction 0.091)¹⁰⁾

5. Scale-up

In scale-up of the surface modification machine, it is necessary to determine the index to characterize composite particles, which depends on the purpose of use of the particles. Figure 12 is a simple case,¹⁰⁾ where BET specific surface area S_w was selected as a characterizing index of the composite particles. The machine as shown in Fig. 2 was used, and the chamber diameter D was changed in four sizes. Silica sand ($26\ \mu\text{m}$) was selected as core particles, and titanium dioxide ($15\ \text{nm}$) as fine particles respectively. The weight fraction of fine particles was 0.091 . Figure 12 shows that the BET surface area of the processed particles is correlated with the input energy per weight of the particles independent of the chamber size. This relation is applied for scale-up of the machine.

In the case the large type machine is used, some types have a pre-mixer prior to a modification machine. Hybridization System listed in Table 1 emphasizes that a pre-mixer should be used to fabricate an ordered mixture as shown in Fig. 1 before the modification process.¹⁸⁾ Therefore, it is found that a pre-mixing makes a positive effect on the composite process, and is an important method before modification processing to treat a large amount of particles effectively.

6. Applications

6.1. Applications of Composite Particles

The wide variety of application researches have been conducted to produce the composite particles in which the surface is covered with fine particles. Table 3 summarizes the researches published so far. Some cases, which are not open to the public, have been in the practical stage. References providing with the detailed information are listed. The applications include new materials of the future. For instance, the application field of metal-ceramics composite materials in Table 3 includes functionally gradient materials^{44,45)} for relaxing thermal stresses. The preliminary research to fabricate them with composite particles has started.¹¹⁾

This type of composite method have also a lot of feasibility for surface modification technology. One

 Fig. 13. Effect of TiO₂ content on angle of repose. (core: PMMA $7\ \mu\text{m}$, fines: TiO₂ fine particles)⁷⁾

 Fig. 14. Change in the water penetration rate of PMMA powder with TiO₂ content. (ϵ : porosity of powder bed)⁷⁾

example is a modification of PMMA particle surface with titanium oxide ($15\ \text{nm}$) with Mechanofusion System, which improves a flowability drastically.⁷⁾ Figure 13 shows the relationship between angle of repose of the

Fig. 15. Composite process model of superplastic core particle with SiC fine particles.⁴⁹⁾

processed powder and the weight fraction of titanium dioxide. In Fig. 13, the angle of repose decreases as the weight fraction of titanium dioxide increases, which means the flowability improves considerably with this method.

Another example is modification of hydrophobic PMMA particle surface with hydrophilic titanium dioxide (15 nm) with Mechanofusion System. Figure 14 shows wettability of the processed particle surface into water which was measured by a penetrating method of liquid into the powder bed.⁷⁾

From the slope of the penetrating weight squared of liquid against the measuring time in Fig. 14, a contact angle is calculated with Washburn equation.⁵¹⁾ The results show the contact angle decreases as the weight fraction of titanium dioxide increases. These examples mean this composite technique has a wide range of feasibility for surface modification technology.

6.2. Application for Rounding Particles

Each advanced machine in Table 1 has a function of rounding particles. In case of deformable materials such as resins or metals, particle rounding is achieved by deforming of particles or adhering of fine particles onto the large particle surface.

On the other hand, in the case of brittle materials, rounding is conducted by making use of the stress larger than comminution starting point as shown in Fig. 3. The projections of the particle surface are pared and generate fine particles. Then these generated fine particles fix onto the surface of large particles.

6.3. Application for Mixing

Figure 5 means that this composite technique is useful for dispersing a little amount of particles into bulk powder. This function is also applied for precise mixing of different kinds of powder materials. For example, the machine as shown in Fig. 2 has been applied for mixing powder materials for superconductive oxides, multi-component targets for thin films, and electric wires of Bi-based superconductive oxides.⁴⁶⁻⁴⁸⁾

6.4. Another Type of Composite Particles

This composite technique can fabricate composite particles inside which different kinds of components are dispersed. When core particles are more deformable compared to fine particles as shown in Figs. 4, 5 and 9, a portion of fine particles layer is embedded into core particles by the strong mechanical force. Consequently, in the case where the core particles have some roughness

on the surface and tend to have plastic deformation, fine particles can be aggressively dispersed into the core particles by making use of this technique.

As a special case, there are Satoh's papers^{49,50)} which reported the composite process of atomized powder of 2090Al-Li alloy (100–210 μm) with SiC fine particles (2 μm). The Al-Li particles are composed of fine grains, and cause superplasticity on certain conditions. The weight fraction of SiC was 0.06. The composite process in this case is described as follows: First, SiC particles fix onto the core particle surface, and then their embedding into the core particles starts by superplastic flow as shown in Figs. 15(b) and 15(c). As a result, the structure as shown in Fig. 15(d) is formed. The obtained particles are easy to be handled in compacting process, because SiC and metal components are not separated during the compacting process.⁵⁰⁾ This material will be applied for airplanes of the next generation.

This paper reviewed on the surface modification method to produce core/fine composite particles related with comminution. The authors hope this method will be also widely applied for metal processing fields.

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