Review

Current Status of the Mechanofusion Process for Producing Composite Particles*

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1. Need for Composite Particles

This article reviews the current status and future prospects of the mechanofusion process as an approach to producing composite particles. This article places special emphasis on the process used for particle formation.

Composite particles have been studied as a way to allow each component to express its inherent functions. These particles are used mainly in cosmetics, foods, and medicines, and some have already found commercial applications. However, other applications have received scant attention. In the area of characteristics of single-phase industrial materials, including structural and functional materials have been fully developed, and many researchers are interested in composite materials in which dissimilar materials are combined or joined to realize new functions or to improve characteristics of known materials1-6. Powder mixing is a common way to develop composite powders; but the process is inevitably accompanied by segregation during manufacturing, when particles of different powder characteristics are mixed. This makes it difficult to secure a uniform composition, one of the essential prerequisites for improved composite characteristics. Segregation is particularly noted in composite systems, such as metal-ceramics, where the components differ greatly in their respective powder characteristics. On the other hand, composite particles are characterized by each particle being a composite of dissimilar materials. Recently, composite particles have been studied extensively in view of their potential for realizing ordered mixtures9 that consist of components of different particle size, shape, and density that are difficult to mix without causing segregation or to dissolve in each other by the ordinary method. The other potential advantages are improved spraying in the nozzles improved sprayed structures, when spraying is adopted to handle them.

In addition, CVD- or PVD-based hard facing and other surface modification techniques have recently been developed to a stage where particles can be coated directly.

A variety of techniques have been studied to realize composite particles, including mechanical methods (such as mechanical blending), moving beds, and CVD- or PVD-based approaches17). Of these, mechanofusion has been attracting special attention because of its potential for producing composite particles relatively easily and in large quantity10-16. Mechanofusion compresses mixed particles, and the resulting heat energy is used to coat the core particles with added particles (hereinafter referred to as “guest particles”) to form the composite particles. The process has been applied mainly to metal-ceramic systems and in some cases has been developed to a commercial stage. The process by which composite particles are formed, however, is not fully understood.

The authors have demonstrated that mechanofusion works well when producing metal-ceramic composite particles. The coating layer is sufficiently dense and adheres quickly to the nucleus particles17-18. For the composite particles to be commercially viable, the coating layers must have uniform thickness, and the joining characteristics of the heterogeneous interfaces must be improved, by efficiently removing gases remaining in the void spaces in the particles that constitute the coating layers. Finally particles sinterability must be high. It is therefore essential to produce composite particles that satisfy these requirements. The authors have been working to develop such composite particles.

This article discusses the characteristics of
composite-forming, with special emphasis on the effects of the properties of the core particles, mechanofusion duration and rotation speed on the changes in the coating layer phases, such as these by agglomeration, condensation and solidification, and on the proposed composite particle forming process based on our results to-date. This article also gives an overview on devices that adapt to different atmospheres, including vacuums.

2. Requirements of Composite Particles

For composite particles to produce high-performance and highly reliable composite materials, they must satisfy the following requirements.

1) The components must be compounded at a specific ratio.

2) The structure of the coating layer, which significantly affects the sintering characteristics of the composite, must be accurately controlled.

3) There must be no void spaces in the interfaces between the core particles (guest particles) and the coating layer, and between the host particles that constitute the coating layers. These spaces contain gases that may degrade mechanical and electrical properties of the composite material.

4) Composite forming must be done using an apparatus that is free of impurities. This is particularly important when producing composite particles that contain metal.

In addition to the above requirements, it is necessary to keep the composite highly pure during forming. Most high-performance composite materials require high purity.

3. How Mechanofusion Works

Figure 1 illustrates the basic stages of mechanofusion. A mechanofusion apparatus consists essentially of a rotary vessel that supplies the starting powders for the composite particles, and the semi-cylindrical inner pieces and the scrapers provided in the rotary vessel. The starting powder is forced outward towards the vessel walls, and when the vessel begins to rotate, the powder remains along the walls and rotates.

Providing a sufficiently narrow gap between the inner piece and the inner wall of the rotary vessel allows the particles passing through this gap to violently collide against each other, thereby generating enough heat energy to fuse the particles together. The fused and condensed particles are coated on and adhered to the core particles by the rotary motion of the nucleus particles and by strong compressive forces acting on them. (The rotary motion is generated by friction between the particles.) This is the current explanation on how composite particles form.

The types of particles and the processing conditions used in this study are summarized below:

Core particles;
- water-atomized stainless steel particles (SUS 316L) : 3.0 μm
- gas-atomized stainless steel particles (SUS 316L) : 35.0 μm
- gas-atomized Cu particles : 35.0 μm
- gas-atomized Pb-Sn particles : 35.0 μm

Coating layer particles (guest particles);
- PSZ (containing 3 mol% of Y₂O₃) : 0.3 μm
- α-Si₃N₄ : 0.3 μm
- Al₂O₃ particles : 0.3 μm

Processing conditions;
- rotating speed of the processing vessel : 250 to 1500 r.p.m
- processing time : 5 to 300 min
4. Basic Parameters Affecting Formation of the Composite Particles

As shown in Fig. 2, mechanofusion adheres mechanically fine particles to core particles to form composite particles. This process makes it relatively easy to produce composite particles. However, the structure of the coating layers produced widely vary depending on the rotation speed of the compounding vessel, treatment time, atmosphere, and other processing conditions. This means that these conditions can be modified to produce composite particles of varying structures. The important processing parameters are summarized below.

4.1 Effect of treatment time on composite forming

Figure 3 shows the effects of the mechanofusion treatment time on temperature at a depth of approximately 1 mm in from the inner surface for cases with and without water cooling. The rotation speed was set at 16.6 Hz.

Temperature varied with rotation speed. When not water-cooled, temperature attained the highest level approximately 5 min. after the apparatus was started at the above rotation speed. The measured temperature represents a rough average, and actual local temperature on the particle surfaces was significantly higher when taking into account the effects of thermal conduction. It was observed that the core particles of Pb-Sn and Pb were fused in a short time of approximately 5 min. Indicating that local temperature was fairly high. Significant water-cooling effects were noted, because little temperature rise was observed at the measurement point in the water-cooled case.

Figure 4 presents the composite particles changing in outer appearance with treatment time. As shown, morphologies of the guest particles attached to the core particles were represented at first by irregular agglomerates. These particles then interacted gradually over the core particles, and were condensed through a sintering-like phenomenon. They finally
Fig. 4 Morphological changes of the composite particles with time, SUS 316L/PSZ, Rotating speed 16.6 Hz, Ar atmosphere

Fig. 5 Magnified SEM images of the coating layer surfaces

Fig. 6 Cross-sectional structures of particles constituting the condensed phase (SUS316L/PSZ)

formed the solidified coating layers covering the entire surfaces of core particles. Figure 5 presents the magnified SEM photographs of the coating layer surfaces, showing the conditions of the guest particles changing with time. Figure 6 presents the optical microscopic photographs of the composite particle cross-sections, showing that the condensed phase was partly formed in the coating layers. These results indicated that the changed phases by agglomeration, condensation, and solidification started not from the coating layer surfaces or the interfaces with the core particles, but from unspecified points within the coating layers, and from there propagated throughout the layers.

Fig. 7 Compositional analysis of composite particle cross-sections (Si-Kα analyzed line of SUS/Si₃N₄)

Figure 7 presents photographs produced by line- and surface-analysis with the aid of Si-Kα-rays for the cross-sections of the SUS/Si₃N₄-base composite particles. As shown, solid coating layers were formed in this system. X-ray diffraction analysis also indicated that the composite system became amorphous as treatment time increased.

4.2 Effect of rotation speed on composite forming

Increasing the rotation speed increases the particles’ kinetic energy producing more heat by particle-particle bombardment and compression. This naturally accelerates fusion. Figure 8 shows the morphological changes of the composite particles treated for 1.8 ks in a rotary vessel which was cooled with water to control fusion. No fusion was observed in the samples rotated at 8.3 Hz or less, and the particles remained dispersed. Irregular agglomeration was observed sporadically in the samples ro-
tated at 16.6 Hz, indicating that weak agglomeration started between the guest particles at this rotation speed. However, SEM images did not clearly indicate interparticle condensation. The solidified phase was apparently formed at 26.6 Hz, though the system was cooled with water.

4.3 Effect of the compounding ratio

Mechanofusion can potentially handle a wide range of compounding ratios, from 0 wt% to 100 wt%, though the conditions differ to some extent depending on specific gravity of the guest particles. A typical example is shown in Fig. 9. However, some guest particles were found to be agglomerated with each other when their proportion exceeded 50 wt%. It is therefore necessary to develop compounding techniques further to handle agglomerated particles in such cases. Removing the agglomerated particles would be one approach.

4.4 Effect of materials

Mechanofusion has been shown to work well with metal-ceramic and metal-metal composite systems, though success has not been achieved with ceramic-ceramic systems. It should be noted, however, that the coating layer conditions varied depending on the way the particles interacted. Figure 10 shows sample results for core particles of different hardnesses (a) SUS/Si₃N₄, (b) Cu/Si₃N₄, and (c) Pb-Sn/Si₃N₄. The coating layers solidified quickly on hard core particles, but remained lightly agglomerated and did not solidify when the core particles were soft. This is suggested by Fig. 11, which shows particle cross-sections. The extent of agglomeration of the coating layer over the core particle of Pb-Sn was too weak to permit a
Table 1 summarizes how composite conditions vary with treatment time using different combinations of core and guest materials for cases with and without water cooling. Coating layers varied significantly depending on the hardness of the core particles. It was also found that fusion was efficiently controlled when the vessel was cooled with water. These results indicate that the coating layer of the composite particles can be greatly modified by selecting the right combination of rotation speed, treatment time, and treatment temperature.

Mechanofusion also works for producing metal-metal composite particles. Figure 12 shows an Fe/Cu composite particle as one example.

4. 5 Composite forming

Based on our current understanding, composite forming consists of the following steps:

(1) First, a strong shear stress created in front of the inner piece acts on the agglomerated guest particles to divide them into monodispersed of smaller agglomerated particles.

(2) The strong compressive and impact forces created in a narrow space between the inner piece and the rotary vessel force the guest particles to adhere to the core particle surfaces by mechanochemical reactions at the interfaces. These reactions include the embedding of guest particles into the core particle surfaces (Fig. 13) and the resulting deformation of the core particle surfaces (Fig. 14).

(3) The heat energy generated by the collision of particles against each other increases the temperature of the minute surfaces of the guest particles. This, coupled with the compressive force acting on the particles, causes reagglomeration of the particles. At the same time, friction between the particles causes the core particles to rotate, rolling the reagglomerated particles onto them.
crates, spreading throughout the agglomerated guest particles through plastic deformation.

(5) The solidified layer propagates throughout the coating layer to form a shell encasing each of the core particles.

5. Mechanofusion Apparatus Working under a Vacuum

The authors have developed a new apparatus capable of satisfying the requirements described in Section 2 to produce composite particles suited for the development of new materials. This apparatus is characterized by its ability to adapt to different processing atmospheres, including vacuums. Figure 16 shows the apparatus.

The main mechanofusion devices for forming composite particles such as the rotating chamber and the powder feeder, are encased in a sealed vessel. The processing atmosphere — whether a vacuum, inert gas, or reducing gas — can be selected at will. The powder supply rate can be also freely controlled for both the core and guest particles.

Figure 17 shows the change in the pressure
Fig. 17 Desorption of the absorbed gases during mechanofusion

of the sealed vessel with time, where the vessel containing the mixed powders was evacuated to $5 \times 10^{-5}$ Torr to remove the residual gases between the particles. Mechanofusion was then started. The vacuum became sharply lower immediately after the treatment started because of desorption of the gases adsorbed on the particle surfaces. The newly developed apparatus allows you to remove the gases remaining in the interfaces between the nucleus particle and coating layer and between the guest particles that constitute the coating layer. When used in a vacuum, it also allows you to remove gases adsorbed on the particles that are desorbed as mechanofusion proceeds. Furthermore, if the atmosphere is switched to a reducing gas, the apparatus forms composite particles by compounding the nucleus and guest particles while keeping intact the new surfaces formed on the particle surfaces. Other processing atmospheres can be used as needed.

Operating under a vacuum greatly reduces the turbulence of the processing atmosphere by changing the gas flow within the processing vessel from one governed by viscous flow to a flow that is nearly molecular.

This makes it relatively easy to coat the core particles with guest particles. Figure 18 gives SEM images of composite particles surfaces prepared in varying processing atmospheres. As can be seen from the results, the newly developed apparatus produces very pure, adhesive composite particles and will be useful for producing new materials.

The authors are now assessing sintering properties. Our results will be presented separately.

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