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Mechanism of particle coating granulation with RESS process in a fluidized bed

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Abstract

In this study, the rapid expansion of supercritical fluid solution (RESS) process was employed for the coating granulation of fine particles in a fluidized bed and its mechanism was examined. The rapid expansion of the supercritical solution causes very high supersaturating ratio of solute in the spraying flow, forming a large number of superfine nuclei. The superfine nuclei deposited on the surface of the particles form a thin film. It was found that the fine particles were all covered with the thin film. This coating mechanism has been confirmed by SEM inspection. The granules with fine particles adhered were circulated through the spraying region and were covered with the binder or coating material (solute) in the region in the form of a film, resulting in the fine particles being cumulatively coated on core particles layer by layer. The temperature at the nozzle inlet was found to be an important factor affecting the coating granulation process.

Keywords: Granulation; Fines; RESS process; Fluidized beds

1. Introduction

Particle coating granulation has been applied in various fields, including pharmaceuticals, food processing and fertilizers. There are distinctive advantages in controlling the release, particle modification and particle uniformity. A fluidized-bed coater equipped with a spray nozzle, such as Wurster coater, is commonly used for particle coating granulation. Conventional coating granulation in fluidized beds is by atomizing droplets of binder and/or coating material solution through the nozzle into a particle bed, which is fluidized with hot gas. The droplets collide with particles and cause the agglomeration of particles by virtue of liquid bridges. Rapid evaporation of solvent takes place because of the excellent heat and mass transfer in fluidized beds, causing bonding by solid bridges and/or coating. However, the large droplets in the bed lead to excessive size enlargement of granules and/or bed defluidization. Uncontrollable enlargement of granule size often takes place especially for fine particles because of relatively large adhesion forces among particles [1,2].

Recently, the rapid expansion of supercritical fluid solution (RESS) process has been employed for particle coating granulation in fluidized beds [3,4]. The deposition of binder by rapid expansion of supercritical CO_2 solution incorporated fine silica particles into the layers around core particles. A stable coating granulation was achieved without excess agglomeration due to the absence of liquid droplets in the bed. In this paper, the coating granulation mechanism by RESS process is experimentally studied.

2. Experimental

The particle coating granulation with RESS process in a fluidized bed consists of extraction, expansion and fluidization. The experimental system is schematically shown in Fig. 1. A high-pressure pump charged the liquefied CO_2 to an extraction column, in which the paraffin pieces were put. To increase the solubility of paraffin in supercritical CO_2 (SC-CO_2), the extraction was run above the melting temperature of paraffin. A magnetic stirrer agitated the melted paraffin in the column to improve the solvating of

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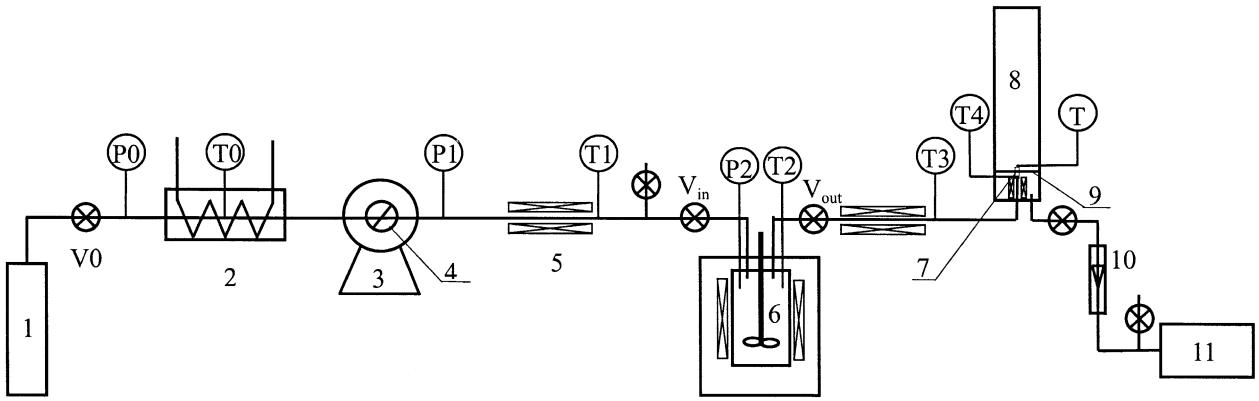

Fig. 1. Experimental system (1) CO_2 bomb; (2) cooler; (3) pump; (4) CO_2 flow rate; (5) heater; (6) extraction column; (7) nozzle; (8) fluidized bed; (9) distributor.

the paraffin in SC-CO_2. A stainless steel nozzle was located at the center of the gas distributor in the fluidized bed. After extraction, the SC-CO_2 solution of paraffin was expanded into the fluidized bed through the nozzle. Liquefied CO_2 was fed into the extraction column at a constant flow rate to keep the pressure constant in the column during the coating granulation process. The core particles and fine particles were employed to simulate the drug carrier and drug in pharmaceuticals. The core particles carry the drug of fine particles to the human body and dispersed in it. The releasing control of the fine particles is determined by the surface coating on the fine particles. The core particles and fine particles were mixed and fluidized before the rapid expansion of the supercritical fluid solution. After the expansion started, 20 g of fine particles were fed into the fluidized bed at intervals of 20 min. Samples were taken from the fluidized bed every 10 min. The experimental parameters are listed in Table 1.

Table 1
Experimental parameters

Materials	solvent	CO_2; $P_c = 74$ kg/cm^2; $T_c = 31$°C
	binder or coating material	paraffin C_nH_{2n+2} $n = 20 \sim 35$; 30 g; $T_m = 48 \sim 50$°C
	fine particle	spherical SiO_2; $d = 1$ μm; $\rho = 2200$ kg/m^3
	core particle	glass beads (GB); $d = 130$ μm; $\rho = 2500$ kg/m^3
Extraction	vessel	cylinder; 1500 ml
	condition	$P = 20$ MP$_a$; $T_2 = 95$°C
	extraction time	60 min
Expansion	nozzle	$d = 0.1$ mm; $L = 15$ mm, $T_4 = 95$°C
	CO_2 flow rate	50 ml/min (liquid)
	spraying time	60 min
Fluidization	bed	cylinder ϕ50 mm; $H = 1500$ mm
	distributor	hole ϕ4 mm + 74 μm sieve; open rate 51%
	initial hold-up in bed	GB 200 g + fine particles 20 g
	gas velocity	0.71, 1.41 m/s

In order to clarify the mechanism of particle coating granulation process by using the RESS process, the temperature at the nozzle outlet in the expansion process was measured with pure CO_2. The experimental apparatus is shown in Fig. 2. A K-type thermocouple with diameter of 0.3 mm was mounted above the center of the nozzle at a height of 1.5 mm. A transparent acrylic resin tube of 10 mm ID and 200 mm length was centrally mounted surrounding the nozzle to prevent the nozzle being influenced by moisture freezing from the convection of ambient air when spraying. The pure CO_2 was introduced into the extraction column up to pressure of 25 MPa, the feeding of CO_2 was stopped and then SC-CO_2 fluid was released through the nozzle for rapid expansion. The temperature change at the nozzle outlet and the pressure in the column were recorded. The temperature condition near the nozzle outlet with pure CO_2 can be considered roughly the same as the rapid expansion of supercritical solution of binder or coating material in the coating granulation process due to the low concentration of paraffin in the SC-CO_2 ($\sim 0.2\%$) [5].

An SEM (Hitachi, S-900) was used to analyze the morphology of granules and fine particles. The electronic beam in the SEM instrument was employed to heat the

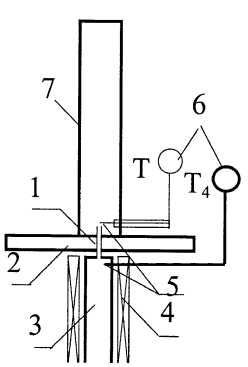

Fig. 2. Experimental apparatus for studying rapid expansion process of pure SC-CO_2. (1) Nozzle ($d = 0.1$ mm); (2) support flange; (3) feed line ($d = 2$ mm); (4) controlled heating; (5) temperature sensor; (6) temperature meter; (7) protecting tube.

local surface of the fine particles on the granules to check the surface film. When the electron accelerating voltage is constant in SEM, the higher the magnification is, the higher the intensity of the electronic beam on the scanning area is. The kinetic energy of the high density electrons penetrated through the surface of paraffin disperses in the paraffin, which makes the temperature of the scanning area increase. The intensity of the electronic beam on a certain area can be increased by focusing on a smaller area on the particle surface at a large magnification. The temperature at the scanning area increased due to the heating of electronic beam focusing at high intensity. The scanning area was about 200×200 nm.

Samples were taken from the fluidized bed in the coating granulation process at every 10 min. The samples were heated in an electric furnace at 450°C for 3 h to thoroughly vaporize the paraffin coated on the fine and core particle surface. The residual particles were weighed and the coating fine particles were washed off with water through a filter. After drying and weighing the residual core particles, the average coating mass was determined.

3. Results and discussion

3.1. Rapid expansion process of SC-CO_2

The rapid expansion of the supercritical fluid through a nozzle causes a large temperature drop. In this research the lowest temperature at the nozzle outlet was -80°C. The outlet temperature was affected by the temperature and pressure at the nozzle inlet. The higher inlet temperature results in higher outlet temperature for a certain inlet pressure. Experiments were carried out at inlet temperatures of 70°C, 95°C and 140°C. It was observed that at an inlet temperature of 70°C and when the inlet pressure is above 15 MPa, the temperature at the nozzle outlet was lower than the freezing point of CO_2, thus forming solid carbon dioxide at the nozzle outlet. In this condition, the nozzle is easily clogged.

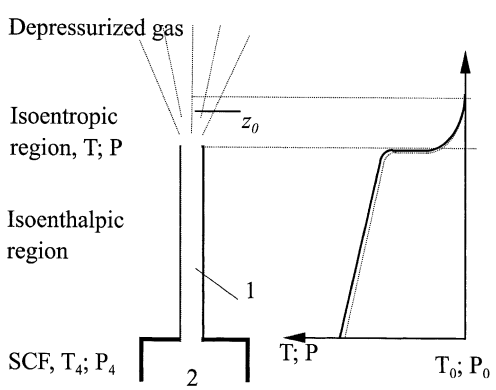

Fig. 3. The schematic diagram of the rapid expansion process through the nozzle. (1) Nozzle; (2) feed line.

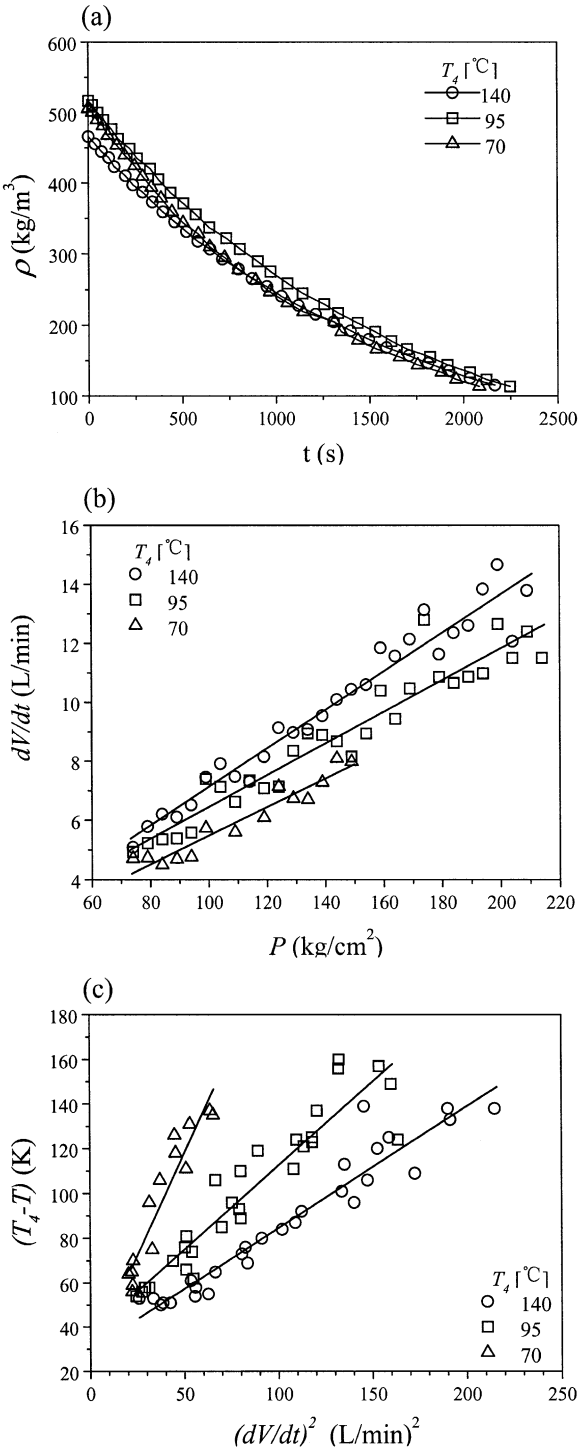

Fig. 4. The rapid expansion profile of the pure SC-CO_2 fluid through a nozzle.

In the rapid expansion, the density of SC-CO_2 in the column can be calculated from the pressure and temperature conditions in the extraction column [6]. The mass flow rate of CO_2 discharged from the column, dm/dt, can be given as:

$$\frac{dm}{dt} = V_0 \left.\frac{d\rho}{dt}\right|_{\text{column}} \quad (1)$$

where V_0 is the volume of the extraction column and ρ is the density of SC-CO_2 in the column. The state of RESS process in the vicinity of the nozzle can be illustrated schematically as Fig. 3. The volume flow rate of CO_2 efflux at the nozzle outlet can be calculated from the measured temperature (see Figs. 2 and 3) according to:

$$\left.\frac{dV}{dt}\right|_{z_0} = \left.\frac{d\rho}{dt}\frac{V_0}{\rho(P_0,T)}\right|_{z_0} \quad (2)$$

where dV/dt is the volume flow rate of CO_2 gas, z_0 is the position of the temperature sensor at the nozzle outlet, and $\rho(P_0, T)$ is the CO_2 density at point z_0.

The experimental results are shown in Fig. 4. It can be seen that the density in the column decreases exponentially with release time. The volume flow rate dV/dt at the nozzle outlet increases linearly with the pressure drop through the nozzle. The temperature drop through the nozzle was found to have a linear relationship with $(dV/dt)^2$.

The RESS process in the vicinity of the nozzle consists of an isoenthalpic region along the nozzle and an isoentropic region at the nozzle outlet [7,8]. For a steady state of expansion, the energy balance at the nozzle outlet in the expansion process can be written as:

$$\Delta H + \frac{1}{2}u^2 = Q - W \quad (3)$$

where ΔH is the enthalpy change in the expansion process, u is the gas velocity at the nozzle outlet in the spraying flow, Q is the heat exchange in the expansion process and W is the work extracted from the system.

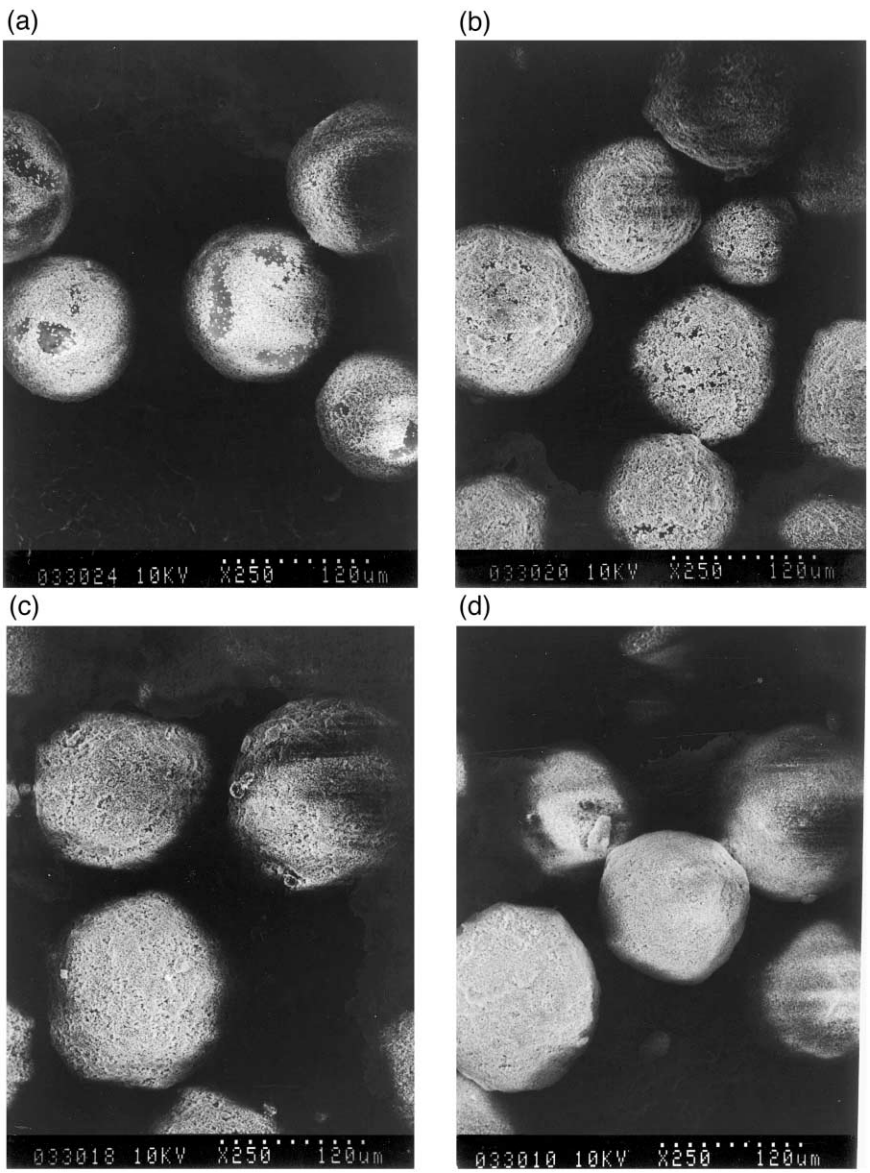

Fig. 5. The morphology change of granules during coating granulation (fluidization gas velocity: 0.71 m/s). (a) $t = 0$ min; (b) $t = 10$ min; (c) $t = 30$ min; (d) $t = 60$ min.

Substituting $H = U + PV$ and $\Delta U = \int_T^{T+\Delta T} C_v dT = \bar{C}_v \Delta T$ into Eq. (3) gives:

$$\bar{C}_v \Delta T + \Delta(PV) + \frac{1}{2}u^2 = Q - W \quad (4)$$

where $\bar{C}_v$ is the average heat capacity of the gas at constant volume in the expansion process. The superficial gas velocity, u, is proportional to the volume flow rate at the z_0 point. The rapid expansion of supercritical fluid can be considered as an adiabatic process because of high flow rate at the nozzle outlet. Thus, Q can be assumed negligible. The work, W, includes the work of gas expansion $\int_{V_1}^{V_2} P dV$ and the work consumption W_f in the adiabatic process due to the friction and fluid viscosity. Thus, W can be expressed by:

$$W = \int_{V_1}^{V_2} P dV + W_f = \frac{\Delta PV}{1-\gamma} + W_f \quad (5)$$

where $\gamma = C_p/C_v$ for the gas. In the expansion process, the gas compressibility changed from 0.4 ~ 0.7 to 1 in the experimental conditions. For simplifying the analysis of the expansion process, assume $\bar{Z}$ is the average compressibility of the gas in the expansion process at a certain temperature and pre-expansion pressure. In the experimental conditions, $\bar{Z}$ is estimated at the range of 0.73 ~ 0.86, 0.78 ~ 0.90 and 0.85 ~ 0.93 along with the pre-expansion pressure in the expansion process at the inlet temperature of 70°C, 95°C and 140°C, respectively [9]. In the qualitative analysis, a constant $\bar{Z}$ is roughly taken at certain inlet temperature. Therefore, the substitution of $PV = \bar{Z}RT$ into Eq. (4) gives:

$$\Delta T = -\left(\frac{dV}{dt}\right)^2 \Big/ \left[2A^2\left(\bar{C}_v + \frac{2-\gamma}{1-\gamma}\bar{Z}R\right)\right] - W_f \Big/ \left(\bar{C}_v + \frac{2-\gamma}{1-\gamma}\bar{Z}R\right) \quad (6)$$

where A is the section area of spraying flow at point z_0. Eq. (6) indicates that the temperature drop, ΔT, is basically linear with $(dV/dt)^2$. This temperature drop results from internal energy transfer to kinetic energy and energy dissipation in the rapid expansion process. The experimental results in Fig. 3(c) are qualitatively consistent with the above analysis.

The rapid temperature drop at the nozzle outlet leads to the phase transition of CO_2 from SCF to gas/liquid/solid phases at different temperatures and pressures of the nozzle inlet. This causes the high supersaturation ratio of solute to form the fine nuclei in the spraying flow. At lower outlet temperature, the deposition of finer solute nuclei occurs, which can form a homogeneous coating film on the particle surface [10]. However, if the temperature of the nozzle outlet is below the melting point of CO_2, the formation of large solid CO_2 particles (dry ice) results in the agglomeration of the solute nuclei after the evaporation of solid CO_2 in the bed. Hence, in the coating granulation process, the temperature of the nozzle inlet was controlled at 95°C to maintain the temperature of the nozzle outlet at about −30°C.

3.2. Coating granulation process

The morphology change of the granules during the coating granulation process is shown in Fig. 5. It was observed that before coating granulation, each of the core particles was covered by a thin layer of fine particles in the fluidized bed. This is probably due to the attractive force of the static electricity produced by the collision and friction between core particles and fine particles. The fine particles were observed to be uniformly coated on the surface of core particles in the coating granulation process. The coating of fine particles on core particles gradually increased with time. The coating mass per unit core particle mass (C_w) vs. coating time is shown in Fig. 6. There existed errors in some experimental points such as at the coating time of 20 and 40 min, which might result from the unthorough washing and filtering. Some fine particles might remain on the core particle surface and absorb more moisture because of the large BET area, which resulted in the error of lower coating mass. The coating mass of fine particles was found to increase almost linearly with coating time. The rate of coating granulation decreased with the increase in fluidization gas velocity [3].

The surface of fine particles was checked using an SEM. The electronic beam at high intensity in the SEM was employed to focus on a certain area on the surface of a fine particle. The images taken at different time-intervals are shown in Fig. 7. It was observed that the paraffin on the surface melted and formed a droplet as a result of heating from the electronic beam focusing. The droplet became larger when the focusing time was longer, due to a greater depth of the paraffin film melting. Higher tempera-

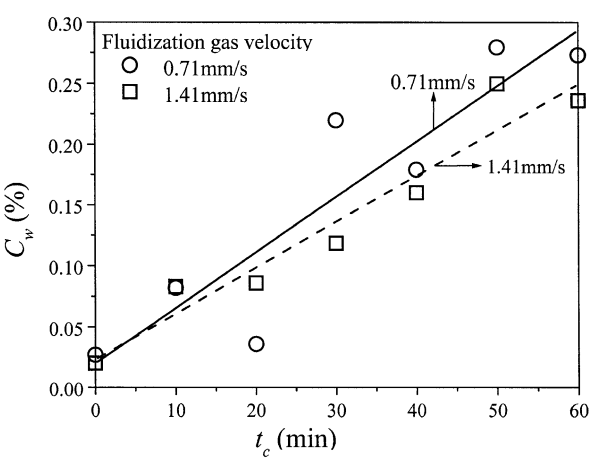

Fig. 6. Coating mass per unit core particle changes with coating granulation time.

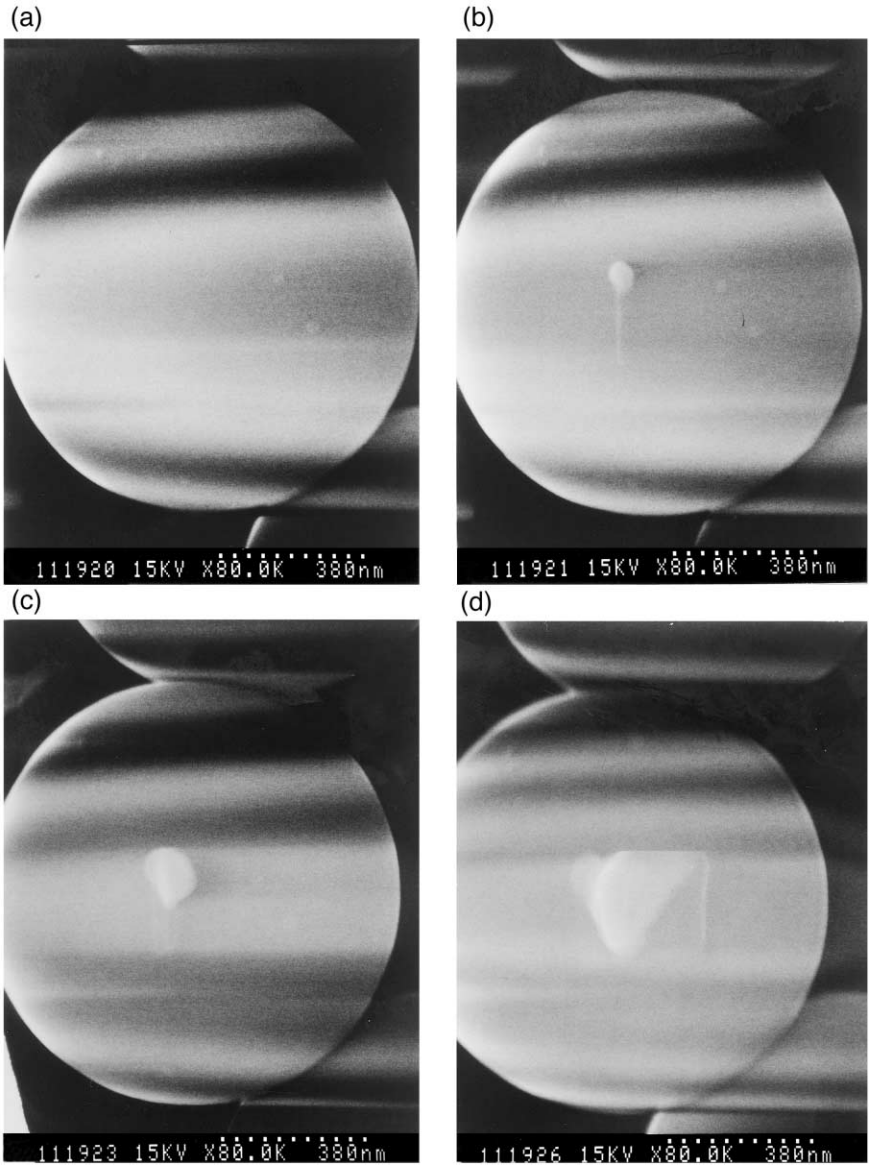

Fig. 7. The thin film coated on a fine particle surface is melted by the heating of the SEM electronic beam (scanning: 200 × 200 nm; $V = 15$ kV; ×20 K). (a) $t = 0$ min; (b) $t = 1$ min; (c) $t = 3$ min; (d) $t = 12$ min.

ture made the droplet disperse due to a reduction in surface tension when focusing for a longer time. By checking all the particles' surfaces, it was found that nearly every fine particle was covered by the thin film of paraffin. Simultaneous fine particle coating with paraffin takes place in the coating granulation process. The film thickness was estimated to be less than 40 nm from the coating mass on certain particles in this experiment. This implies that the size of nuclei was smaller than 40 nm. The average number of superfine nuclei in the spray flow was estimated at more than 5×10^{13}/s. In addition, solid bridges were observed to be formed at the contact points of the adjacent fine particles because of the deposition of the superfine nuclei as shown in Fig. 8.

The solubility of paraffin in SC-CO_2 strongly depends on temperature and pressure [5]. The rapid expansion of supercritical fluid solution causes a very high supersaturating ratio in the spraying flow. The strong pressure perturbation with high propagation speed in the spraying flow enables a rapid nucleation of solute in the fairly uniform nucleation environment, leading to the formation of superfine nuclei with a narrow size distribution [11]. The nucleation only occurs at 10^{-5} s, the time interval of rapid expansion of the SC-CO_2 solution [12]. The nuclei have almost no time for growth during the expansion process because of the abrupt change of SC-CO_2 directly to the gas phase. The low temperature condition at the nozzle outlet causes a rapid solidification of paraffin and the formation of finer nuclei. The superfine nuclei deposit on the surface of particles and granules forming a very thin film of binder or coating material. High strength turbulence in the spray flow and fast motion of particles in the

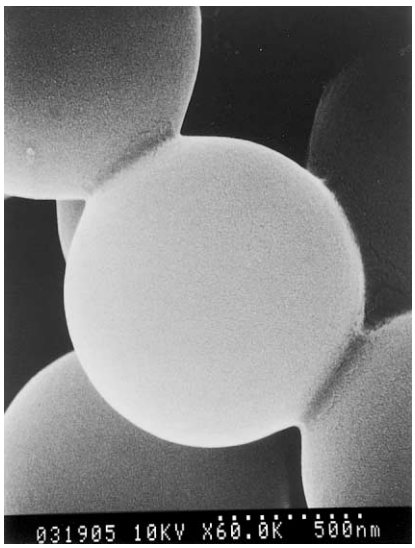

Fig. 8. Solid bridges formed at adjacent contact points between the fine particles on the surface of granules.

fluidized bed reduce the possibility of agglomeration in superfine nuclei.

When the rapid expansion began, the core particles coated with the thin layer of fine particles were covered by deposition of the superfine nuclei in the spray flow. The uniform deposition with high concentration of superfine nuclei caused the granules to be covered in the form of a film. The film covered granules adhered to other fine particles, and then were covered by the continuous deposition of the superfine nuclei again. The circulation of granules adhering to fine particles and then again being covered with thin films of binder or coating material made achievement of the coating granulation process cumulative, layer by layer, leading to the granule size enlargement.

4. Conclusions

A stable and uniform particle coating granulation was achieved with a RESS process in a fluidized bed. The rapid expansion of the SC-CO_2 solution of binder or coating materials forms a large number of superfine nuclei. The superfine nuclei transported by the turbulent flow collide with granules and fine particles, and deposit on the particle surface, forming a thin film covering on the granules and fine particles in the order of tens of nanometers. The circulation of granules adhering to the fine particles and the film covering of binder or coating material make the particle coating granulation cumulative layer by layer.

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