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Preparation process of functional particles: III. Preparation of composite particles by rapid expansion of supercritical fluid solutions and release behavior

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기능성 미분말의 제조공정에 관한 연구: III. 초임계 분출법에 의한 복합분체의 합성과 용출특성

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Abstract The Rapid Expansion of Supercritical fluid Solutions (RESS) process was applied to particles coating. Microcapsules prepared by spray drying were used as the core particles, and two kinds of paraffin were used as the coating materials. Supercritical CO_2 solutions of paraffin were expanded through the short nozzle into the bed that was fluidized by air. Extraction temperature and pressure were varied at 50~120℃, 150~200 kg/cm^2, respectively. The thickness of theoritical coating layer was measured, and precipitate coating layer on surface was analyzed by using SEM, FT-IR. The release behaviors of Mg^{2+} ions were inspected by atomic absorbance spectrophtometer.

요 약 초임계 분출법을 이용하여 입자의 코팅을 행하였다. 핵입자로는 분무건조법으로 제조된 Microcapsule을 사용하였으며, 코팅 물질로는 녹는 점이 다른 두 종류의 파라핀을 사용하였다. 파라핀이 녹아 있는 초임계 CO_2 용액은 공기에 의해 유동중인 유동층 내부로 작은 직경의 노즐을 통해 분출된다. 이 때 추출조의 온도와 압력은 각각 50~120℃, 150~200 kg/cm^{2}으로 변화시켰다. 이론적인 코팅 두께를 계산하였으며, 코팅층의 분석은 SEM과 FT-IR을 사용하였다. Mg^{2+} ion의 용출특성은 원자흡광광도계를 사용하여 조사하였다.

1. Introduction

A new process utilizing the rapid expansion of supercritical fluid solutions (RESS) is described for the production of fine powders and thin films. In generally, a supercritical fluid is defined as a substance above its critical temperature and critical pressure, where it remains in a single fluid phase regardless of the applied pressure. Supercritical fluids have higher thermal diffusivities than liquids and higher densities than gases. Solute powder changes due to density changes can be obtained by depressurization. So several researchers have also experimented that fine particles and thin films can be synthesized by RESS process.

In this study, the authors applied this method to particle coating using a fluidized bed. The RESS through short nozzle can be considered to be adiabatic expansion. So pressure decrease extremely and solubility of coating materials (solute) increase highly. Then the solute (coating materials) can be precipitated on the surface of core particles in fludizing [1-5].

2. Experimental procedures

Magnesium Hydroxide Carbonate (MHC) Micro-

Table 1
Experimental conditions

Run No.	Coating materials	Extraction temperature (℃)	Extraction pressure (kg/cm^2)	Coating time (min)	CO_2 flow rate (l/min)
1	Paraffin①	80	150	180	6.31
2	Paraffin①	50	150	180	2.25
3	Paraffin②	120	150	90	3.94
4	Paraffin②	120	200	90	12.17

Prarffin ①: melting point 48~50℃.
Paraffin ②: melting point 70~72℃.

capsules (MC, mean particle size 49 μm, density 1.8 g/cm^2), prepared by spray drying, were used as the core particles. The coating material was two kind of paraffin (melting point 48~50℃, 70~72℃, respectively), and a supercritical carbon dioxide (critical temperature 31℃, critical pressure 7.4 MPa) was used as a solvent.

Experimental apparatus showed in previous paper [6].

Experimental condition is shown in Table 1. 50 g of core particles were fluidized with air from blower. Liquefied carbon dioxide was charged to a high pressure pump, compressed up to 150~200 kg/cm^2, heated to 50, 80, 120℃ and delivered to the supercritical autoclave containin paraffin. After the extraction of paraffin at 100℃ for 90, 180 min, the supercritical carbon dioxide solutions of paraffin were expanded into the bed through the short nozzle. To increase the solubility of paraffin in supercritical CO_2, extraction was carried out above the melting point of paraffin. The nozzle was maintained at a temperature of 100℃ by a line heater. During expansion supercritical carbon dioxide was fed into the supercritical autoclave by high pressure pump. The flow rate of CO_2 was 6.31, 2.25, 3.94, 12.17 l/min, respectively.

At the end of the run, the CO_2 flow was stopped, the autoclave was depressurized and the paraffin was removed from the autoclave. Particle size distribution was determined by a laser diffraction particle size analizer (LDSA-1400A, Tohnichi Computer Applications, Japan). Surface morphologies prepared particles were observed by scanning electron microscope (SEM, JSM5410, Jeol Ltd., Tokyo, Japan). The qualitative analysis of coated particles was performed by FT-IR ("Protebe460": Nicolet Instrument Corporation, Madison, USA). The thickness of theoritical coating layer was measured. The released mass of Mg^{2+} ion was measured by atomic asorption spectrophtometer (AA, 170-50A: Hitachi, Ltd., Tokyo, Japan).

3. Results and discussion

The size distribution of MHC MC particles coated for No. 2, No. 4, compared to that of the non-coated core particles, is shown in Fig. 1. There is no significant difference in particle size distribution. This result indicates that no agglomeration takes place during coating in the bed. For conventional particle coating process which has a solvent atomization system, it is difficult to coat fine particles because the strong cohesive force leads to the formation of agglomerates. In contrast, in the RESS coating processing, the coating material is deposited on the surface of fluidized-bed particles without a liquid phase, so that it is possible for fine particle coating to avoid particle agglomeration.

This figure shows that the coated particles shift into smaller size than non-coating particles. This result was thought to indicat that coated particles break down during the fluidized-bed coating by collision with each other.

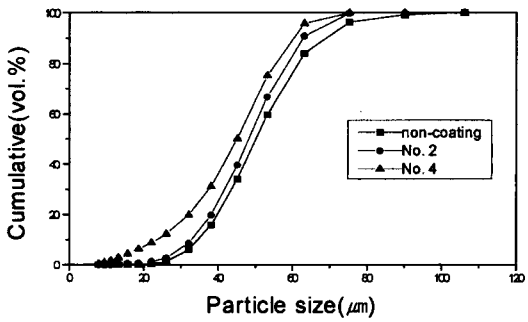

Fig. 1. Particle size distribution.

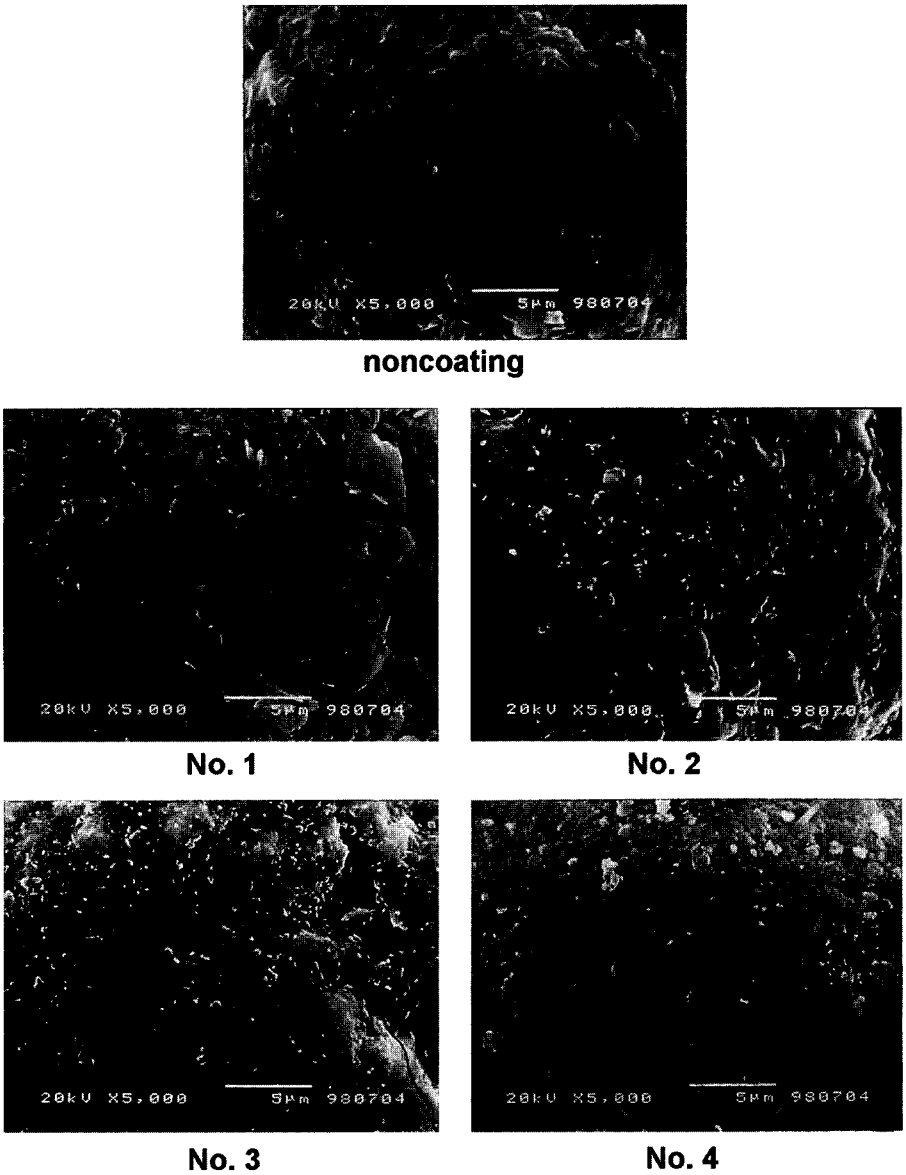

Fig. 2. SEM photographs. Reaction conditions are given in Table 1.

Figure 2 shows the surface morphology of each particle using SEM. The surface of coated MC has different morphologies from pure MC. Coated particles shows anything adhere to the surface. From this result, the authors thought that the adhered material is paraffin coating layer.

To inspect that coating process is complete, particle surface was investigated qualitative analysis using FT-IR. Figure 3 shows that result. As shown in this figure, coated particles show C-H band peaks in the vincinity of 2848 cm^{-1} and 2920 cm^{-1}. From this result, we confirmed that paraffin was coated on surface of core particles. And the peaks appear in 720~1350 cm^{-1} and 3700 cm^{-1} were CO_3^{-2} ion and OH^- ion band peaks, respectively. So microcapsule consist of $MgCO_3$ and $Mg(OH)_2$ types.

Figure 4 shows schematic illustration of paraffin coated MC. MC consists of core and shell which had tens or hundreds micropores. The most external layer is paraffin coating layer with thickness t [3]. Many researchers reported, the thickness of coating layer (t) increases as coating efficiency and coating

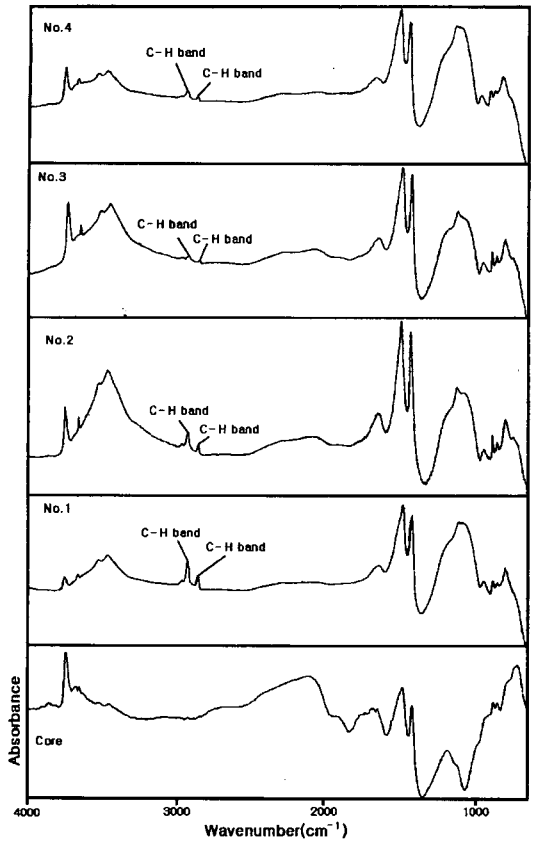

Fig. 3. Infrared spectra of microcapsules. Reaction conditions are given in Table 1.

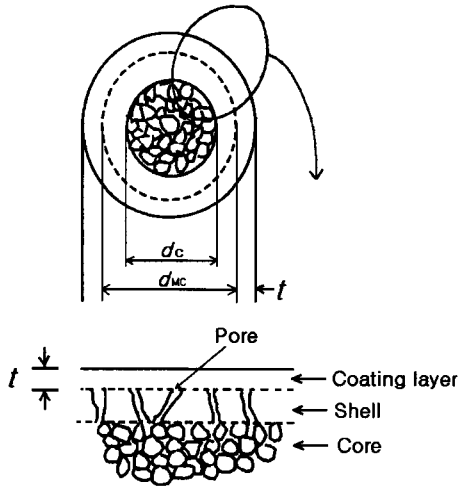

Fig. 4. Illustration of MC coated paraffin.

time increase [6-14]. In general, there are many formulas to calculate the theoritical coating layer (t), but in this study, the below formula [15] was used.

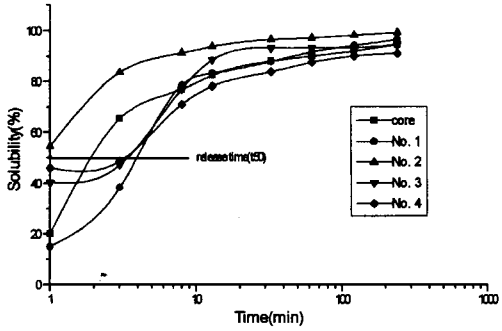

Fig. 5. The release behaviors of Mg^{2+} ion.

$$t = \frac{1000\,D_c\left[\sqrt[3]{\{1+(\rho_c/M_c)(M_p/\rho_p)\}}-1\right]}{2}$$

where, t: the thickness of paraffin coating layer (nm)

D_c: the core particle size (43.89 μm)
ρ_c: the density of core particle (1.8 g/cm^3)
M_c: the weight of core particles (50 g)
ρ_p: the density of paraffin (0.9 g/cm^3)
M_p: the weight of paraffin (g)

For convenience, M_p was calculated by the difference between the initial and the final paraffin weight. In cases of No. 1~4, the values of M_p were 2.033, 0.249, 0.023, 0.200 g, respectively. So thicknesses of coating layer were 592, 72, 10, 59 nm, respectively. From these results, as the quantity of dissolved paraffin increases, the coating layer thickness increases. However, we thought the thickness in practical could be different from the theoritical thickness, because the autoclave temperature and the pressure were varied to increase the solubility of paraffin. Eventually, as the supercritical CO_2 flow rate was altered, the fluidized state could be varied. Finally, we thought the coating layer thickness would affect the release behavior of Mg^{2+} ions.

Figure 5 show the result of release behavior of Mg^{2+} ion using atomic asorption spectrophotometer. This figure noted the releasing amount of Mg^{2+} ion with time. If the release time (t_{50}) is defined as the time releasing 50 % Mg^{2+} ion, for the case of No. 1, release time is longer than that of others, 4 min. Generally, release behaviors of coated particles are superior to non-coated praticle, except for No. 2. This result was though that in case of No. 2, solubility of paraffin was very low and particles break down by collision.

4. Conclusions

From these results, it is possible to coating on core surface by using the RESS process, and any no agglomeration takes place during coating. In case of No. 1, the thickness of theoritical coating layer was 592 mm, and the release time (t_{50}) was 4 min, so the release behavior was superior to others.

Acknowledgements

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