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Prediction of degree of deformation and crystallization time of molten droplets in pastillation process

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Abstract

The direct solidification process of a melt into a particulate solid is studied to achieve the desired size and shape of the product and to predict the required crystallization time. For an example, a Bisacodyl melt is chosen. The role of the contact angle of the droplet is investigated as a function of Reynolds number, degree of subcooling and characteristic of used cooled surface (substrate). The static contact angle increases with increasing degree of surface roughness of the substrate. The contact angle, however, decreases with increasing Reynolds number and degree of subcooling. The phenomena of spreading and rebouncing of droplets are used in the discussion of the deformation process. By the model of Madejski the degree of deformation is found to be proportional to the Reynolds number to the power of 0.2. On the basis of a simple droplet solidification model and experimental data, a numerical study is presented. The equations allow to estimate the normalized deformation and crystallization times, which are proportional to the Reynolds number to the power of 1.23 and help the design of solidification processes.

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Keywords: Contact angle; Degree of deformation; Crystallization time; Direct solidification process

1. Introduction

Melt solidification is an important process to control the transition from the liquid into the solid phase in such a way that the products are obtained in an appropriate form for their transport, storage and subsequent use. This should be done by an economical process, employing the smallest and the simplest equipment possible. The transformation of a melt into a solid with a certain appearance and specific physical properties is an important operation in chemical and process industries. In most cases, the solidification is a crystallization without the aim of separation. Crystallization under defined process conditions influences properties of the solidified melt such as shape, size, crystalline structure, hardness and dust content. During the last couple of decades the large variety of different requirements for the final size and shape of a product has led to a considerable number of solidification processes (Mersmann, 1995).

The pastillation process is one of the solidification technologies to bring melts into dispersed solid form in high speed. In case of a pastille production, many droplets are positioned on a cooled surface. The pastillation of melts refers to the disintegration of the liquid directly into monosized individual volumes, which then solidify. In practice, this is done by generating drops of the melt, which then are positioned on a cooled surface. In depending on the size of the drops and the physical properties of the melt, the drops

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flatten to a certain extent. The physical properties of interest are its viscosity, surface tension and density. The process parameters are roughness of substrate, impacting velocity, degree of subcooling and crystallization behaviour. The solidified droplet, therefore, has the typical pastille-like shape. The disintegration of a liquid directly into individual volumes is especially interesting from the point of view of avoiding dust. Dust, typically generated by mechanical cutting and breaking processes, does not exist in case of a pastillation process (Buelau and Robens, 2000).

Especially, the direct solidification process is widely applied in pharmaceutical industry to produce crystalline formed medicine. The control of the shape of droplet is here the advantage. The release rate is one of the most important parameters in pharmaceutical industry. Compared to tablets, formed by amorphous materials, tablets formed by crystalline material function much easier as drugs with controlled release rate. Direct solidification has the additional advantage that it leads to an extremely high-pure product since it is a solvent-free process (Guirgis et al., 2001a,b).

Many researchers (Bennett and Poulikakos, 1994; Liu et al., 1995; Kang et al., 1995; Takahashi and Kuboi, 1996; Delplanque and Rangel, 1997; Rangel and Bian, 1997; Prunet-Foch et al., 1998; Wang et al., 2002) have been studying the deformation and solidification of melt drops, particularly in the field of metal alloys, painting and coating of materials which employ an atomizer. However, little work has been done to investigate the deformation process of fine chemicals and medicines as it impacts on the cooled surface, with a consideration of its crystallization time. Therefore, this study is divided into two parts. The first part contains, contact angle measurements which are related to spreading and rebouncing of drops. The result of such an investigation is an optimized drop size and shape. The second part is the estimation of the numerical deformation and the crystallization time.

After the contact is formed between a droplet and a solid surface, the liquid starts spreading and rebouncing (Martin, 1993; Zhang and Basaran, 1997; Mao et al., 1997). The kinetic energy of a liquid droplet is transformed into viscous energy dissipation and/or interfacial energy effects finally arresting the spreading droplet. The mentioned phenomena are studied for various operating conditions like initial diameter, density, impacting velocity, viscosity, degree of subcooling and the characteristic of the used cooling surface. Initial diameter, density, final impacting velocity and viscosity of the droplet are expressed through the Reynolds number.

Normalized deformation and crystallization times are introduced by the measure of Madejski's model (Madejski, 1976), a simple droplet solidification model (Hamarani et al., 1989) and experimental data. Madejski has developed a simple model for the motion and solidification of a droplet on a surface based on an energy balance. Madejski's equations are solved for one dimensional half-space heat conduction and solidification of superheated liquids. Madejski was able to produce analytical expressions for some special cases. Namely, the solidification is independent of the surface tension. He stated also that solidification does not contribute significantly to the termination of spreading of droplets. The model introduces the relationship between the degree of deformation and the Reynolds number.

The aim of this study is to investigate the contact angle of droplets as a function of Reynolds number, degree of subcooling and characteristic of the used substrates to control size and shape of the droplets. Moreover, the relationship between degree of deformation and Reynolds number is studied. Thus, the deformation and crystallization times are estimated.

2. Materials and methods

The schematic diagram of the experimental apparatus for the production of pastilles is shown in Fig. 1.

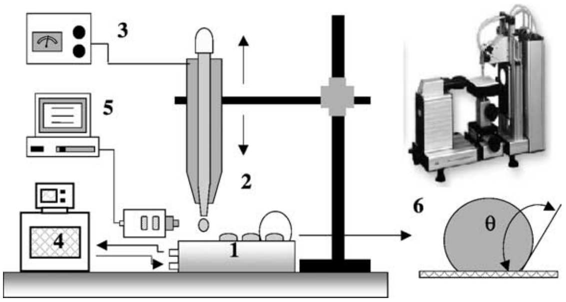

Fig. 1. Schematic diagram of experimental apparatus. (1) Crystallizer, (2) pipette with electric heater, (3) electric controller, (4) thermostatic bath, (5) high-speed camera, (6) drop shape analysis system and contact angle of droplet, θ.

Table 1
Experiment and numerical parameters of pastillation process

Component	Bisacodyl ($C_{22}H_{19}NO_4$)
Melting temperature of Bisacodyl	133 °C
Roughness of crystallizer surface (R_a)	0.15–3.1 μm
Dropping distance between surface and tip of pipette	5–50 mm
Degree of subcooling (ΔT)	113–143 K
Temperature of molten component	135–160 °C
Temperature of ambient air	25 °C
Density of Bisacodyl	1.2945 g/ml
Viscosity of molten Bisacodyl	1.60677–2.2163 mPa s
Final impacting velocity	0.17–1.85 m/s
Surface tension between air and molten Bisacodyl	0.020034 N/m
Thermal conductivity of stainless steel	15.7331–16.14536 W/m K
Latent heat of Bisacodyl	106.5 J/g

Reagent-grade powder of Bisacodyl (pharmaceutical-grade) was molten completely in a 300 ml crystallizer. The melt dropped through 1 ml pipette with an orifice diameter of 0.6 or 1 mm. The substrate was a cooled stainless steel surface (roughness of surface (R_a: average roughness), 0.15–0.31 μm) of a box-type crystallizer. The surface roughness is measured by means of Perthometer S2 (Mahr Federal Inc.) which takes the average deviation of the mean height of the entire surface within the sampling length. The space of the upper square and the height of the crystallizer were a 10 cm^2 and 20 mm, respectively. The atmospheric temperature was constant at 293 K. The pipette was set in a vertical position to the crystallizer and the orifice was positioned 5,10, 20, 30, 40 and 50 mm above the substrate, respectively. A sequence of pictures describing the impact process was taken by a high-speed camera. The focus of the camera was adjusted using the one-dimensional stage. Using the multiple exposure features, the drop impact velocities, v_o, the initial diameter, D_o and the phenomena of the droplet deformation upon impact could be precisely determined. Then the droplets were detached from the substrate. The static contact angle between droplet and substrate, θ, the diameter of droplet, D_t and the verticals height of droplet, x were measured by the drop shape analysis system (DAS 10 MK2 KRUESS). Experimental and numerical parameters are summarized in Table 1.

3. Results and discussion

3.1. Determination of drop shape after solidification

The shape of a drop depends besides on other operating conditions strongly on the contact angle between the droplets and the surface (stainless steel), because spreading and bouncing of drops is strongly influenced by the contact angle. Therefore, the operating conditions have been examined namely, initial diameter of drop, viscosity, degree of subcooling, final impacting velocity and characteristic of used surface.

Fig. 2(a) shows the general impact sequence of molten Bisacodyl droplets on the substrate at the conditions: final impacting velocity of 0.28 m/s, surface temperature of 10 °C and surface roughness of 0.23 μm. The camera is positioned at an angle 15°

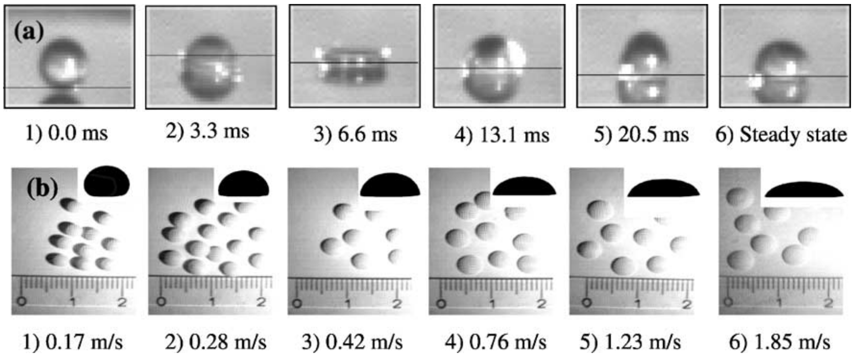

Fig. 2. (a) General deformation phenomena by elapsed time and (b) general shape and final diameter of droplets at various final impacting velocities.

below the horizontal in order to obtain clear images of the drop while spreading and rebouncing upon impact. The time of each image (ms), measured from the instant of first contact with the surface, is shown. The reflection of each droplet in the polished substrate can be seen in the photographs. At $t = 0$ ms, just before the impact, the drop is clearly spherical in shape. The impacting drop possesses big kinetic energy relative to surface and viscous energy. The drop deforms and spreads rapidly upon impact in the radial direction due to the rapid kinetic energy release at the point of impact. At $t = 6.6$ ms, the drop reaches its maximum spreading and is momentarily at a rest because of the depletion of kinetic energy. The initial impact energy of the drop is dissipated in overcoming viscous flow and in producing new surface area. The droplet moves back toward the center and rebounds upwards as a result of the interfacial tension. At $t = 20.5$ ms, the droplet reaches the maximum contraction. Here the kinetic energy is zero and the surface energy is maximum. At steady state, the droplet possesses a minimum energy that is equal to the static surface energy at the same time the droplet is rapidly solidified.

Fig. 2(b) shows that shape and final diameter of a droplet of various final impacting velocities after the droplets are solidified. The final impact velocities are measured by the high-speed camera. The final impact velocity is corresponding to the height of drop-off, which is varied ranging from 5 to 50 mm. At low velocities of 0.17 or 0.28 m/s, the drop has big static contact angles because the surface and viscous energy are dominant in the formation of the droplet. However, at high velocities of 1.23 or 1.85 m/s, the static contact angles are becoming small, because the kinetic energy is dominant in the formation of the droplet.

Fig. 3 shows the relationship between contact angle and viscosity of molten Bisacodyl for the following set of parameters: two pipette orifices (0.6 or 1 mm), velocity of 0.17 m/s, degree of subcooling of $\Delta t = 133$ K, and roughness of substrate of 0.23 μm. Moreover, it additionally shows the correlation between the viscosity of molten Bisacodyl and the temperature. The viscosity is decreased with increasing the operating temperature ranging from 135 to 160 °C. The viscosity is calculated by the method of van Velzen et al. (van Velzen et al., 1972). The deformation is represented by the static contact angle. It can be shown that contact angle increases with increasing viscosity of the molten Bisacodyl.

Fig. 4 shows that the relationship between the contact angle and the final impacting velocity on various

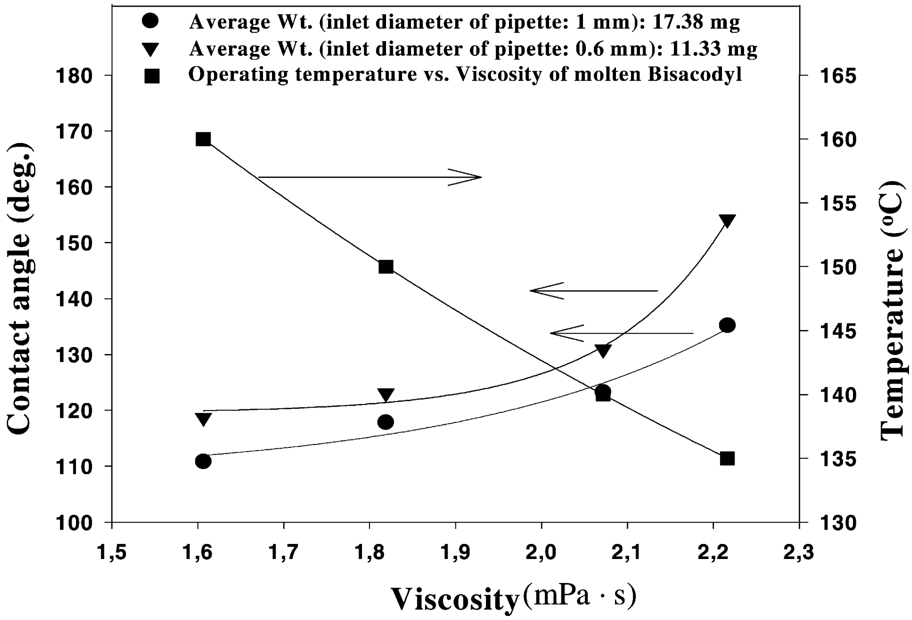

Fig. 3. Contact angle vs. viscosity of molten bisacodyl and operating temperature vs. molten bisacodyl viscosity.

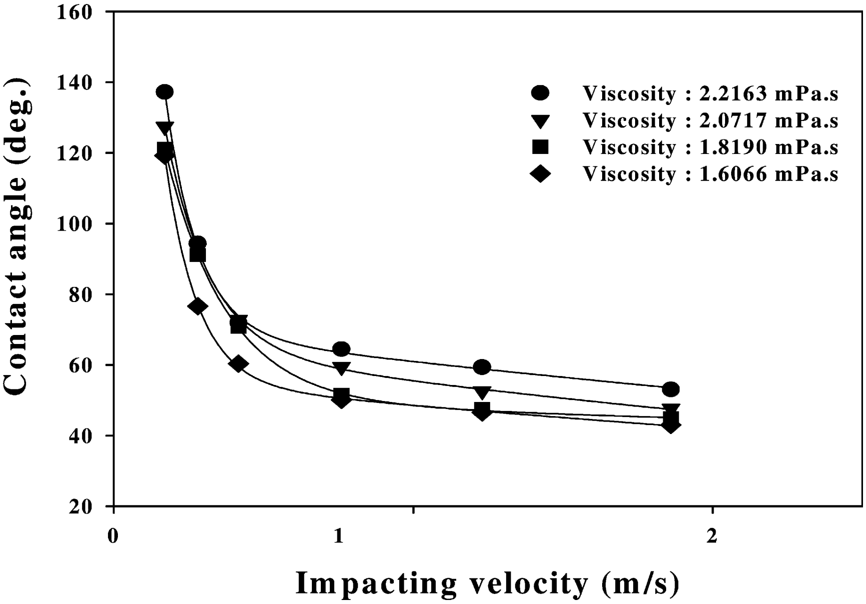

Fig. 4. Contact angle vs. velocity at various viscosities.

viscosities. The degree of contact angle is exponentially decreasing with increasing final impacting velocity. A larger contact angle of the droplet at the low impacting velocity is a result of the interfacial tension and viscous energy dominant for the formation of the shape of the droplet. On the other hand, a higher impacting velocity corresponds to a smaller contact angle. As expected, the kinetic energy decreases as the viscous energy does with the increase of the free surface area.

The contact angle of the droplet is directly a function of the Reynolds number according to Figs. 3 and 4 and the definition of Reynolds number.

$$\mathrm{Re} = \frac{\rho v_0 D_0}{\eta} \qquad (1)$$

Here is ρ the density, v_0 the impacting velocity, D_0 the initial diameter of droplet and η the viscosity. The correlation between the contact angle and the Reynolds number is shown in Fig. 5. Each point is based on measurement of all four parameters in Eq. (1). The Reynolds number has therefore a range between 200 and 3000. This figure enables a discussion of potential contact angles in formation of a droplet. Increasing the Reynolds number results in a smaller contact angle of the droplets. This is due to the fact that at high Reynolds numbers, the vertical height for the drop-off of droplets is much higher than at low Reynolds numbers. It means that the kinetic energy is dominant in the deformation of droplets. At low Reynolds numbers, there is a big contact angle because the viscous dissipation and the interfacial tension are dominant in the formation of the shape of the droplets.

Fig. 6 shows the characteristics of the used stainless steel substrates on the impact process at various final drop velocities. A 17.38 mg Bisacodyl droplet impacts on the surface with different types of roughnesses ranging from 0.15 to 0.31 μm. Under the same impact conditions, the contact angle of the droplet on the surface with 0.31 μm roughness is consistently larger than that on the surfaces with the two lower roughnesses. There are different effects affecting spreading and rebouncing after the impact of a drop. At drop impacts, the interfacial energy increases with increasing surface roughness. Then the surface area covered by the spreading becomes smaller due to the fact that the motion of droplet is restricted. Therefore, the droplet on the coarsest surface is rebouncing faster than drops on the other two surfaces. In all three cases, the droplet reaches equilibrium after its excess energy is completely dissipated. However, it takes much longer time

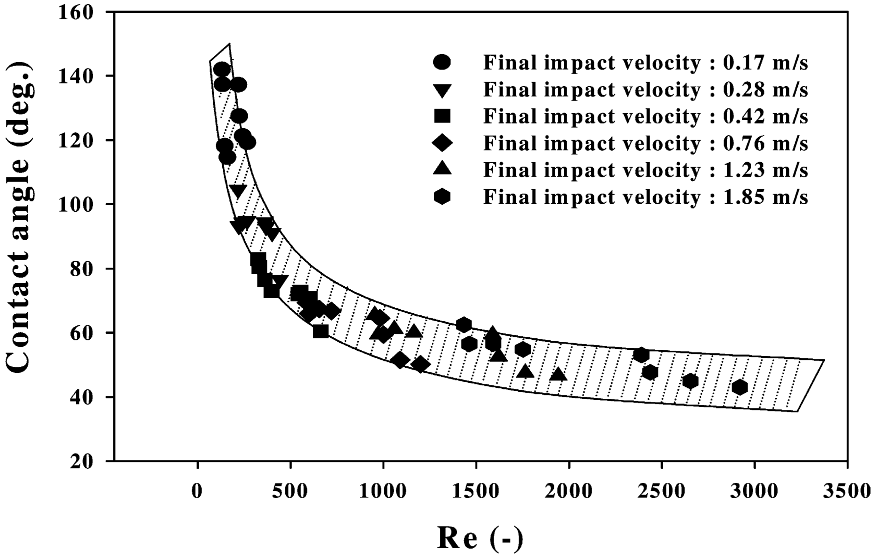

Fig. 5. Contact angle vs. Reynolds number.

to reach equilibrium on the roughest surface compared to the other two surfaces because of a much stronger rebouncing.

Fig. 7 shows a droplet impacting on the stainless steel substrate at four different degrees of subcooling. All other parameters are kept constant: final impacting velocity of 0.28 m/s, surface roughness of 0.23 μm and viscosity of 2.072 mPa s. The degree of subcooling is defined as difference between operating temperature of the cooled substrate and the melting temperature of Bisacodyl. After the droplet reaches steady state the contact angle in case of higher degrees of subcooling (143 or 133 K) are smaller than those of the lower degrees of subcooling (113 or 123 K). As expected the

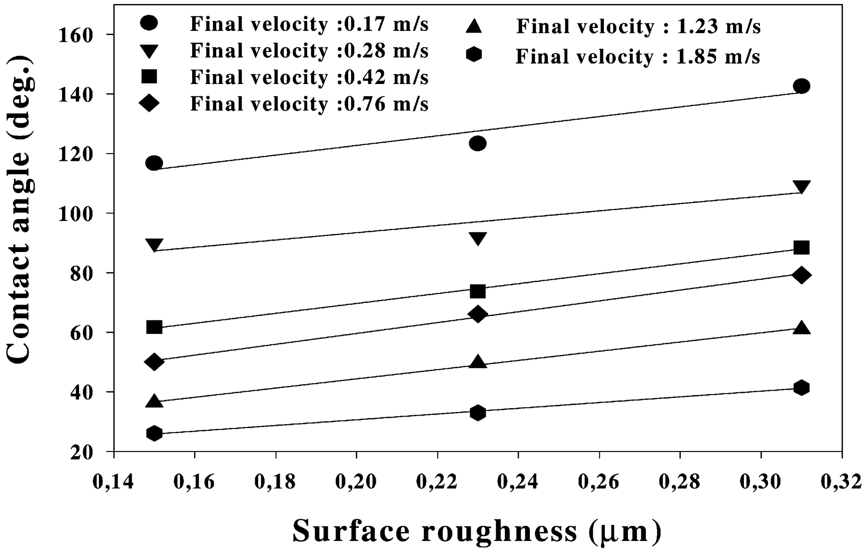

Fig. 6. Contact angle vs. degree of surface roughness at various velocities.

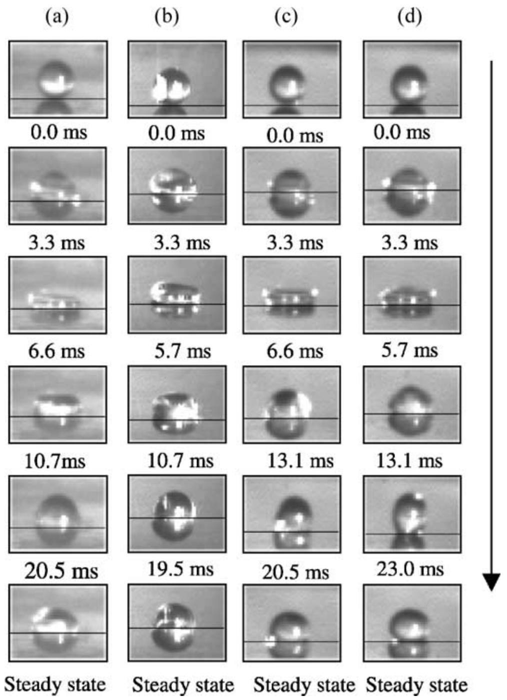

Fig. 7. Sequences of pictures of side views of droplets impacting on a medium rough cooled stainless steel surface at various degrees of subcooling ((a) $\Delta T = 143\,\text{K}$, (b) $\Delta T = 133\,\text{K}$, (c) $\Delta T = 123\,\text{K}$, (d) $\Delta T = 113\,\text{K}$).

degree of rebouncing at the lower degree of subcooling is much higher compared to that of a higher degree of subcooling. This is due to a lower value of interfacial tension between the molten droplet and the cooled substrate, while the droplet is rapidly solidified.

Fig. 8 shows the relationship between contact angle of the droplet and degree of subcooling for two different impacting velocities. The maximum contact angle of the droplet was 142° at the final impacting velocity of 0.17 m/s and the degree of subcooling of 113 K. The contact angle of the droplet is decreasing as the degree of subcooling is increasing.

As shown by Figs. 7 and 8, the contact angle of a droplet is found to be directly proportional to the degree of subcooling; it, however, is found to be inversely proportional to the Reynolds number and increasing degree of surface roughness.

3.2. *Determination of normalized deformation and crystallization time*

After impacting the molten Bisacodyl crystallizes when actual the temperature is below the melting point temperature of Bisacodyl. The rate of nucleation and crystal growth increases as the degree of subcooling is increased (for theory see Tamman (Tamman, 1922)).

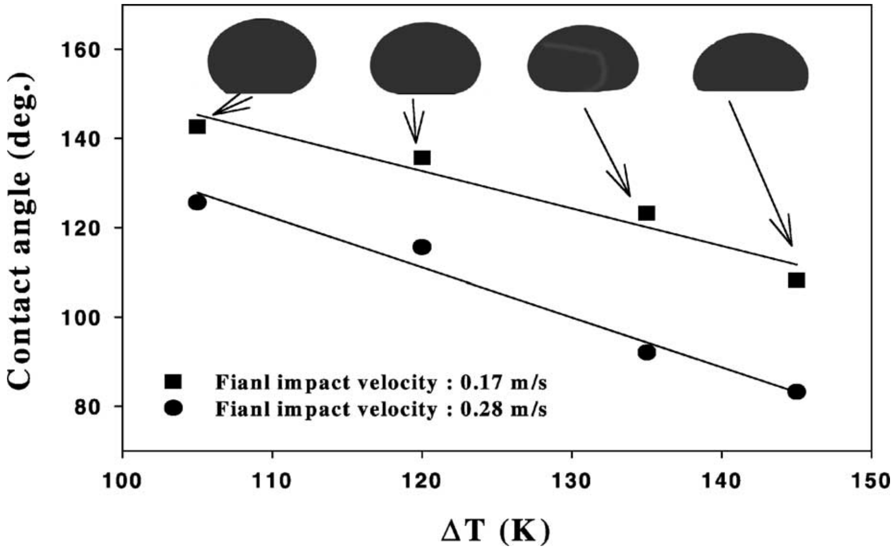

Fig. 8. Contact angle vs. degree of subcooling at two different impact velocities.

Nucleation and growth rate each pass through a different maximum concerning the under cooling. Thereafter, they fall back again to zero. Crystal growth rates in melts are primarily driven by heat transfer and are therefore simple to control. Here the deformation of a droplet (spreading and rebouncing) hardly influences on the crystallization kinetic. The molten Bisacodyl nucleates slightly below the melting temperature, T_m. The driving force is here the temperature difference between melting temperature, T_m and the cooled substrate at a temperature, T_{sub}. The approximation of the crystallization time, t_c is proportional to the square of the droplet thickness, x_s^2:

$$t_s \approx \frac{x_s^2}{T_m - T_{sub}} \tag{2}$$

The viscous energy dissipation and the changes in the surface tension (energy) are discussed in a variety of manners such as in the models of Jones (Jones, 1971), Collings et al. (Collings et al., 1990), Chandra and Avedisian (Chandra and Avedisian, 1991), Berg and Ulrich (Berg and Ulrich, 1997) and Madejski (Madejski, 1976). The most advanced treatment of the droplet deformation problem was presented by Madejski for the case of splat quenching. His model accounts for viscous energy dissipation, surface tension effects and simultaneous solidifying of the droplet. Madejski modelled the droplet kinetics as a spreading cylindrical cake, assuming that the flow is laminar and the advancement rate of the freezing in the splat is a heat transfer limited Stefan solidification problem (Carslaw and Jaeger, 1959). Madejski's treatment of the surface tension was analogous to that of Collings et al. (Collings et al., 1990) except that he considered only the surface tension between the liquid interface and vapour interface, excluding the introduction of the contact angle. Madejski expressed the viscous energy dissipation in terms of the shear stress invoked by the velocity gradient within the spreading droplet. Madejski's numerical analysis yielded the degree of deformation as a function of four parameters: Re, We $(=\rho v^2 D_o/\sigma)$, Pe $(=vD_o/a)$ and κ. Here We, Pe and κ are Péclet number, Weber number and dimensionless parameter, respectively. The κ introduced in Madejski's derivation reflects the degree at which the solidification arrests the flattening of the droplet. For the case in which κ is zero, the droplet flattens without solidification.

Madejski produced analytical expressions based on his analysis for some special cases. In the case in which the flattening of the droplet is arrested solely by viscous dissipation of energy within the splat, $\kappa = 0 = We^{-1}$, Madejski found that

$$\frac{D_t}{D_o} = 1.29(Re + 0.9517)^{0.2}. \tag{3}$$

Alternatively, for Re > 100, Eq. (3) can be approximated as

$$\frac{D_t}{D_o} = 1.29Re^{0.2}. \tag{4}$$

The degree of deformation is defined as the ratio of the final diameter of a droplet, D_t, to the initial diameter of a droplet, D_o. This is only a function of the Reynolds number. Hamarani et al. (Hamarani et al., 1989) obtained a similar equation from a numerical calculation with the SMAC (simplified Marker and Cell) algorithm:

$$\frac{D_t}{D_o} = 0.83Re^{0.2}. \tag{5}$$

Watanabe et al. (Watanabe et al., 1992), also calculated the relationship between degree of the deformation and the Reynolds number as follows:

$$\frac{D_t}{D_o} = 0.82Re^{0.2}. \tag{6}$$

As shown in the Madejski model not considering the surface tension, the degree of deformation of a droplet is only a function of the Reynolds number. The experimental results show the measured degree of the deformation (see Fig. 9). The relationship between the degree of deformation and the Reynolds number can be summarized in the form of the following equation calculated from the results by using a regression method:

$$\frac{D_t}{D_o} = 0.6Re^{0.2}. \tag{7}$$

In all equations, the degree of deformation is proportional to the 0.2 power of the Reynolds number. A high Reynolds number gives a fast deformation and a large diameter of the droplet.

From the simple model for droplet solidification (Watanabe et al., 1992), the normalized crystallization time can be calculated by the degree of the deformation. A cylindrical droplet is still molten impacting on

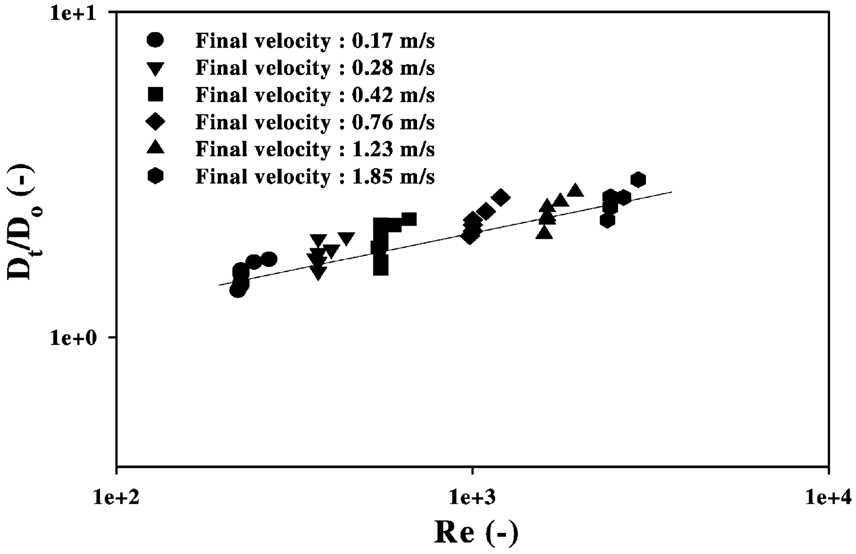

Fig. 9. Degree of deformation of a droplet D_t/D_o vs. Re number of the droplet at impact.

a substrate as illustrated in Fig. 10. The latent heat of crystallization at differential layers is conducted to the substrate through the solid layer with the height, x_s:

$$dE = \begin{cases} \rho_l \left(\dfrac{1}{4\pi D^2}\right) L\,dx \\ k_s \left(\dfrac{1}{4\pi D^2}\right) \left(\dfrac{T_{mp} - T_{sub}}{x_s}\right) dt. \end{cases} \tag{8}$$

Here the first and the second terms are the kinetic energy, E_k and the viscous energy, E_v, respectively. The latent heat transferred from the droplet to the cooled substrate and the crystallization time, t_c is derived from Eqs. (7) and (8), and can be expressed as follows:

Initial conditions: $x \to 0$, $E_k \to 0$ and $E_v \to 0$

$$E = 0.283 Re^{0.4} D_o^2 [k_s L \rho_l (T_{mp} - T_{sub}) t]^{0.5}. \tag{9}$$

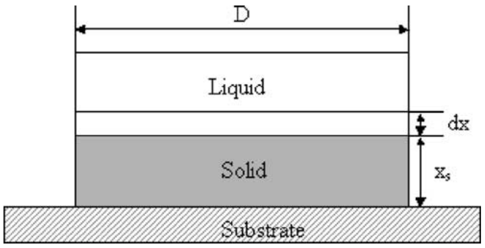

Fig. 10. Simple solidification model of droplet impacting.

Boundary conditions: $x \to D_t$, $E_k \to 0$ and $E_v \to 0$

$$t_c = \frac{0.36 \rho_l L Re^{0.4} D_o^2}{k_s (T_{mp} - T_{sub})}. \tag{10}$$

The deformation time, t_d is an input of experimental data. The dimensionless normalized deformation time, τ_d and crystallization time, τ_c are expressed as follows:

$$\tau_d = \frac{t_d v_o}{D_o}. \tag{11}$$

$$\tau_c = \frac{t_s v_o}{D_o}. \tag{12}$$

From Eqs. (11) and (12), the normalized deformation and crystallization times are numerically calculated. Fig. 11 shows that relationship between normalized deformation and crystallization times and the Reynolds number.

$$\tau_d = \frac{t_d v_o}{D_o} = 0.0372 Re^{1.23}. \tag{13}$$

$$\tau_c = \frac{t_s v_o}{D_o} = 0.924 Re^{1.23}. \tag{14}$$

The normalized deformation and crystallization times are found to be proportional to the Reynolds number of the same power of 1.23. The normalized

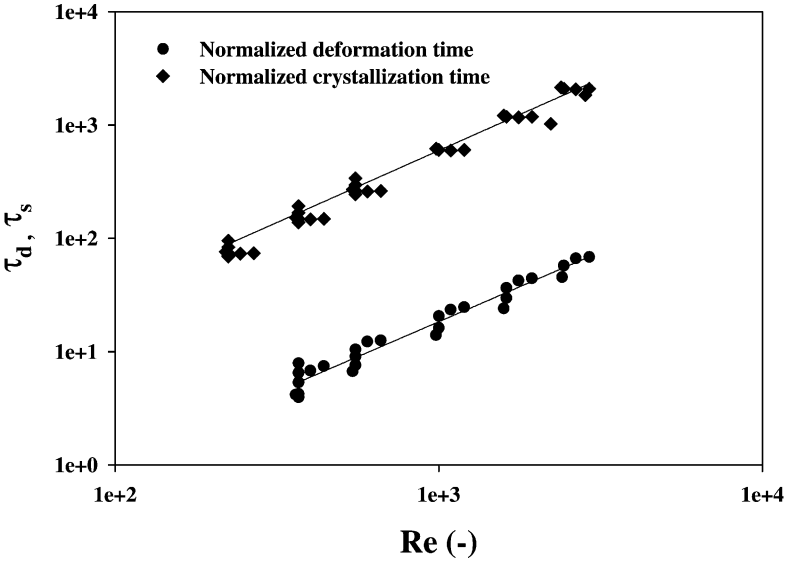

Fig. 11. The normalized deformation and crystallization time vs. Re number.

crystallization time is about 25 times higher than the normalized deformation time. It means that the required crystallization time should be estimated on the basis of that relation because the deformation time can easily be measured experimentally. The required crystallization time is however the important parameter for the design of the solidification technology since the crystallization time as kinetic value determines the size of an equipment.

4. Conclusion

The crystallization and deformation process of droplets on a cooled substrate is examined. The crystallization occurs immediately after the deformation. The static contract angles are measured. The role of the contact angle of the droplet on a substrate is investigated. The static contact angle increases with increasing degree of surface roughness. It, however, decreases with increasing Reynolds number and degree of subcooling. The phenomenon of spreading and rebouncing of droplets is observed and used to discuss the deformation process. From Madejski's model the degree of deformation was found to be proportional to the 0.2 power of the Reynolds number. Using a simple droplet solidification model and the achieved experimental data, a numerical study is undertaken to estimate the normalized deformation and crystallization time, which are found to be proportional to the Reynolds number to the power of 1.23. A prediction of the droplet deformation and crystallization times is possible by this procedure as showed above. On basis of the crystallization time drop solidification equipment can be designed.

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References

Bennett, T., Poulikakos, D., 1994. Heat transfer aspects of splat-quench solidification: modelling and experiment. J. Mater. Sci. 29, 2025–2039.

Berg, M., Ulrich, J., 1997. Experimental-based detection of the splash limits for the normal and oblique impact of molten metal particles on different surfaces. J. Mater. Synth. Process. 5, 45–49.

Buelau, H.C., Robens, A., 2000. Melt solidification and granulation technology. European Thematic Network, CRYSOPT, September.

Carslaw, H.S., Jaeger, J.C., 1959. Condition of Heat in Solids, 2nd ed. Clarendon Press, London, p. 283.

Chandra, S., Avedisian, C.T., 1991. On the collision of a droplet with a solid surface. In: Proceedings of the Royal Society of London, Series A, vol. 432, pp. 13–41.

Collings, E.W., Markwirth, A.J., Mccoy, J.K., Saunders, J.H., 1990. Splat-quench solidification of freely falling liquid-metal drops by impact on a planar substrate. J. Mater. Sci. 25, 3677–3682.

Delplanque, J.P., Rangel, R.H., 1997. An improved model for droplet solidification on a flat surface. J. Mater. Sci. 32, 1519–1530.

Guirgis, H., Broegmann, B., Sakr, A., 2001a. Hot melt technology—1st communication: effect of channelling agents. Part II: Tablet characteristics. Bunderverband der pharmazeutischen Industrie 63, 395–401.

Guirgis, H., Broegmann, B., Sakr, A., 2001b. Hot melt technology—2nd communication: effect of manufacturing method on tablet characteristics. Bunderverband der pharmazeutischen Industrie 63, 499–507.

Hamarani, H., Okada, T., Yoshida, T., 1989. Radio frequency and hybrid plasma spraying of ceramics, In: Proceedings of the ISPC-9, pp. 1527–1532.

Jones, H., 1971. Cooling freezing and substrate impact of droplets formed by rotary atomisation. J. Phys. D. Appl. Phys. 4, 1657–1660.

Kang, B., Waldvogel, J., Poulikakos, D., 1995. Remelting phenomena in the process of splat solidification. J. Mater. Sci. 39, 4912–4925.

Liu, W., Wang, G.X., Matthys, E.F., 1995. Thermal analysis and measurements for a molten metal drop impacting on a substrate: cooling, solidification and heat transfer coefficient. Int. J. Heat Transfer 38, 1387–1395.

Madejski, J., 1976. Solidification of droplet on a cold surface. Int. J. Heat Transfer 19, 1009–1013.

Mao, T., Kuhn, D.C.S., Tran, H., 1997. Spread and rebound of liquid droplets upon impact in flat surfaces. AIChE J. 43, 2169–2179.

Martin, R., 1993. Phenomena of liquid drop impact on solid and liquid surfaces. Fluid Dynamics Res. 12, 61–93.

Mersmann, A., 1995. Crystallization Technology Handbook. Marcel Decker, New York.

Prunet-Foch, B., Legay, F., Vignes-Adler, M., Delmotte, C., 1998. Impacting emulsion drop on a steel plate: influence of the solid substrate. J. Colloid Interface Sci. 199, 151–168.

Rangel, R.H., Bian, X., 1997. Metal-droplet deposition model including liquid deformation and substrate remelting. Int. J. Heat Transfer 40, 2549–2564.

Takahashi, S., Kuboi, O., 1996. Study on contact angles of Au, Ag, Cu, Sn, Al and Al alloys to SiC. J. Mater. Sci. 31, 1797–1802.

Tamman, G., 1922. Aggregatzustände. Die Zustandsänderung der Materie in Abhängigkeit von Druck und Temperature. Leopold Voss., Leipzig.