Characterization of metal powder suspension to improve the functionality of cemented carbides
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Characterization of metal powder suspension to improve the functionality of cemented carbides

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Abstract

Cemented carbide is produced by sintering a mixture of metal carbides and binder. Both materials are formed into granulated powders via suspension with the object of a uniform product and an easy handling. And the granule was sintered to produce final products. In addition to excellent toughness and wear, accurate and minute figuration is required for commercial products. The method to produce the granulated powders significantly affects those properties rather than latter processes, because the interaction between materials plays a notable role for the particle agglomeration in a suspension. Because of sedimentation of materials, however, the agglomeration in a suspension had ever been difficult to evaluate, and those operating conditions were decided semi-empirically. In this study, the extent of particle agglomeration was evaluated by the measurement of viscosity; further the relationship between the particle interaction and the properties of granules was investigated. As a result, suspensions with a small addition of surfactant showed almost constant particle and provided similar granules. However, much more addition than critical resulted in the decrease of the particle interaction and strength of granulated powder.

Keywords: Cemented carbide, suspension rheology, surfactant, agglomeration, granulated powder

1. Introduction

Cemented carbide is a kind of alloys and produced by the sintering of hard metal carbide particles combining with some kinds of binder. Most of the cemented carbides consist of Tungsten carbide (WC) as a main material and Cobalt (Co) as a binder. And for the property control of the final products, various kinds of metal carbide, e.g. TiC, TaC, VC are used as sub materials. Because the cemented carbides show an excellent toughness at a high temperature and a superior wear, they mainly utilize in the field of cutting, grinding, and moulding of metal products. For example, when mining a tunnel, the cutting blades to crush rocks are made of the cemented carbide, and the metal mould for punching out aluminium cans or metal coins are also made of the cemented carbide. The effect of Co content on the wear of cemented carbide [(1)] and the improvement of wear or toughness by the addition of hard materials like Alumina [(2)] or by the spattering of diamond have been investigated. In addition to toughness and wear resistance, various characteristics including small defects, high density and strong connection between material particles are required in order to produce the product with intended properties.

In the process of cemented carbide production, a handling of fine material powders and a nonuniformity of materials in a final product are serious problems. For the improvement in productivity, the cemented carbide is generally produced by the following 3 steps. (1) The preparation of a suspension consisting of material powders, solvent, and additives. (2) The spray drying of the suspension to produce granulated powders. (3) The sintering of the moulded granulated powders. The flowability and homogeneity of granule will directly affect the productivity and the property of final products. The physical property of granule can be influenced by the dispersed state of material particles in a suspension and the operating condition of spray drying. Some researchers are investigated the granule produced in a spray drying [(3)], and some models for granule production process have been proposed [(4, 5)]. In this study, we investigated the extent of material particle agglomeration in a suspension and the effect of the surfactant on agglomeration, further referred to the correlation of characteristics between suspension and final product.

Thus far, in our research group the comparative study between the rheological characteristics and particle agglomeration has been conducted focusing on the viscosity decrease or the agglomeration break-up according to the increase in a shear rate [(6, 7)]. In the viscosity measurement of the suspension containing fine metal particles, we may encounter inevitable problems. That is, the sedimentation of particle prevents keeping the suspension uniform; and the particle agglomeration sometimes results in a blockade of the measurement section. Thus, for example a helical flow viscometer was invented to minimize the effect of sedimentation [(8)]. In this work, we prepared a vertical capillary tube viscometer with a large inner tube diameter, which may provide considerably valuable results if the flow velocity in a tube is much larger than that of particle settlement. Further by applying these data to our proposed model, which can estimate the particle interaction and the extent of agglomeration in a suspension, the effect of the surfactant concentration on the particle agglomeration was evaluated. And the granules were produced by using a lab-scale spray dryer from suspension; the characteristics of which was controlled by the addition of surfactant and then the evaluation of the properties including shape and size was conducted.

2. Experiments and Materials

2.1. Materials

The suspension used in this study consisted of some kinds of metal powders, ethanol and some additives. Material powders are composed of Tungsten Carbide (WC), Titan Carbide (TiC), Tantalum Carbide (TaC), and Co as a binder. The weight fraction of Cobalt into the total amount of metal carbides was adjusted to 8wt%, and the solid volume fraction of the suspension was 0.11. Diameters and specific densities of mixed material powders were ranging from 0.2 to 7μm and 7 to 15, respectively.

The suspensions containing a certain non ionic surfactant with the concentration from 0 to 1.0wt% into the total amount of metal carbides were prepared by means of a stirred type ball mill. At first, the mixture of materials without surfactant was mixed for a certain time. The mixing time was fixed for each suspension in this process, because the metal powders are crashed and the mixing time influences the particle size in a suspension. And then the mixture was stirred for another one hour following the addition of surfactant. Just before the viscosity measurement, the cylindrical container in which suspension was stored rotated on a mill pot rotator to keep a uniform dispersion.

2.2. Experimental setup

For the purpose to evaluate particle agglomeration, we conducted the measurement of apparent viscosities and corresponding shear rate by using the capillary tube type viscometer (Fig.1). In this equipment, when the velocity of suspension in the vertically installed capillary tube was enough larger than the terminated settling velocity of dispersed metal particles, the suspension will flows in a homogeneous state because the effect of sedimentation can be neglected. As shown in the figure, the capillary viscometer consists of the cylindrical vessel and stainless-steel tube, which is connected at the bottom of the vessel via a cock. The cylindrical vessel has a diameter of 12cm and inner height of 12cm, and the test fluid was stored in it and stirred by a mixer. Three vertical tubes, which have constant inner diameter D of 5mm and different length L of 0.50, 0.75, and 1.00m, were used. And the vertical tube was connected at the cock beneath the bottom of vessel, and the length from the bottom of the vessel to the entrance of the tube L_0 was 0.13m. The inner figuration of this section was almost circle and the equivalent diameter will be approximately 5mm, thus the substantial length of the tube where fluid flows will be (L + L_0).

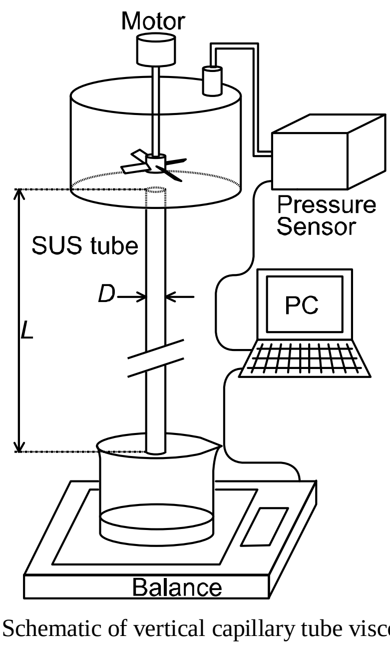

Fig.1 Schematic of vertical capillary tube viscometer

Kwon and Pallerla [9] also analyzed the rheological characteristics of Newtonian fluid by using tank-tube viscometer. In their study, the shear stress applied at the inner surface of the tube was nearly constant since the pressure across the tube was only due to the height difference between the liquid surface in the tank and the outlet of the tube. However, for non-Newtonian suspensions, the shear stresses and corresponding shear rates are necessary to evaluate the state of particle dispersion, which is influenced by the magnitude of shear. In the field of a polymer rheometory, the capillary viscometer was sometimes operated with the control of the pressure exerted on a test fluid. Thus, in this viscometer, the test fluid was effluent from the pressurized vessel through the tube, and the total amount of the outflow from the tube was weighed by using an electrical balance. In this study, it is difficult to repeat measurement several times because the evaporation of dispersing solvent during the measurement may change the solid volume fraction. However, various pressure drop conditions must be required for the evaluation of Non-Newtonian fluid. For that reason, the vessel was closed when the fluid flows in a tube to make the inner pressure of a vessel fall down according to the outflow from the vessel, and the flow rate in a tube and the inner pressure in a vessel were measured at the same time.

The experiment was conducted as the following procedure. The test fluid is pored into the vessel and stirred; following the cock beneath the vessel is closed. The inner pressure of the vessel is increased up to a certain value by using air compressor, and then the vessel was closed. A container is placed just below the outlet of the tube and onto the electrical balance. The cock is opened to effluent the test fluid after stopping the mixer and tearing the balance. The weight of the outflow and the inner pressure of the vessel are recorded simultaneously by using a data acquisition system. The initial pressure and fluid volume should be decided carefully, because they primarily affect the range of shear stress we can measure.

3. Data analysis

From the experimental results of the inner pressure and outflow weight, the relationship between the pressure drop across the tube and the flow rate in the tube can be calculated. The pressure drop will be estimated by reducing the ambient pressure, which is measured before and after the measurement, and the pressure drop caused by the height difference between the liquid surface in a vessel and the outlet of the outlet. For Newtonian fluid, the viscosity can be easily obtained from Hagen-Poiseuille equation. For non-Newtonian, however, the viscosity changes with respect to shear rate, and then the rheological characteristics was evaluated by introducing the following Rabinowitsch analysis [10].

If the flow assumed as a steady, laminar and fully developed flow with no slip at the tube wall, the volumetric flow rate Q can be expressed by

$$\frac{Q\sigma_R^3}{\left(\pi D^2/4\right)\left(D/2\right)} = \int_0^{\sigma_R} \sigma_{rz}^2 \left(-\frac{dV_z}{dr}\right) d\sigma_{rz} \qquad [1]$$

where σ_R is the shear stress at the tube wall. Taking the derivative of this equation with respect to σ_R , the shear rate at the wall is written in the following form:

$$-\dot{\gamma}_R = -\frac{dV_z}{dr} = \frac{3}{4}\left(\frac{8V}{D}\right) + \frac{1}{4}\left(\frac{8V}{D}\right)\frac{d\ln\left(8V/D\right)}{d\ln\sigma_R} \qquad [2]$$

,where V is average flow rate in the tube. Defining $n'=d\ln\sigma R/d\ln(8V/D)$, equation [2] can be written as

$$-\dot{\gamma}_R = \frac{3n'+1}{4n'}\left(\frac{8V}{D}\right) \qquad [3]$$

Hence, the non-Newtonian viscosity at the wall shear rate is defined by

$$\eta(\dot{\gamma}_R) = -\frac{\sigma_R}{\dot{\gamma}_R} = \left(\frac{D\Delta P}{4L}\right) \Big/ \frac{3n'+1}{4n'}\left(\frac{8V}{D}\right) \qquad [4]$$

In this experimental set up, when flowing in the tube fluid experiences the sudden compression and expansion at the inlet and outlet of the tube, and the configuration change at the cock. Although the pressure drop due to these configuration changes must not be neglected, these effects must be constant when flowing at the same flow rate for each tube with different length. Thus, the pressure drop at a certain flow rate estimated from Fig.2 (a) is plotted against the effective tube length (L+L_0) (Fig.2 (b)). And it is found that the slop of the plot in Fig.2(b) is the pressure drop per unit length $\Delta P/L$, then the shear stress at the tube wall σ_R (=$D\Delta P/4L$) can be calculated. The intercept of the plot shown in Fig.2 (b) represents the pressure drop caused by the configuration changes in the flow path. However, in some cases, that could be ignored because it was much smaller than that across the tube.

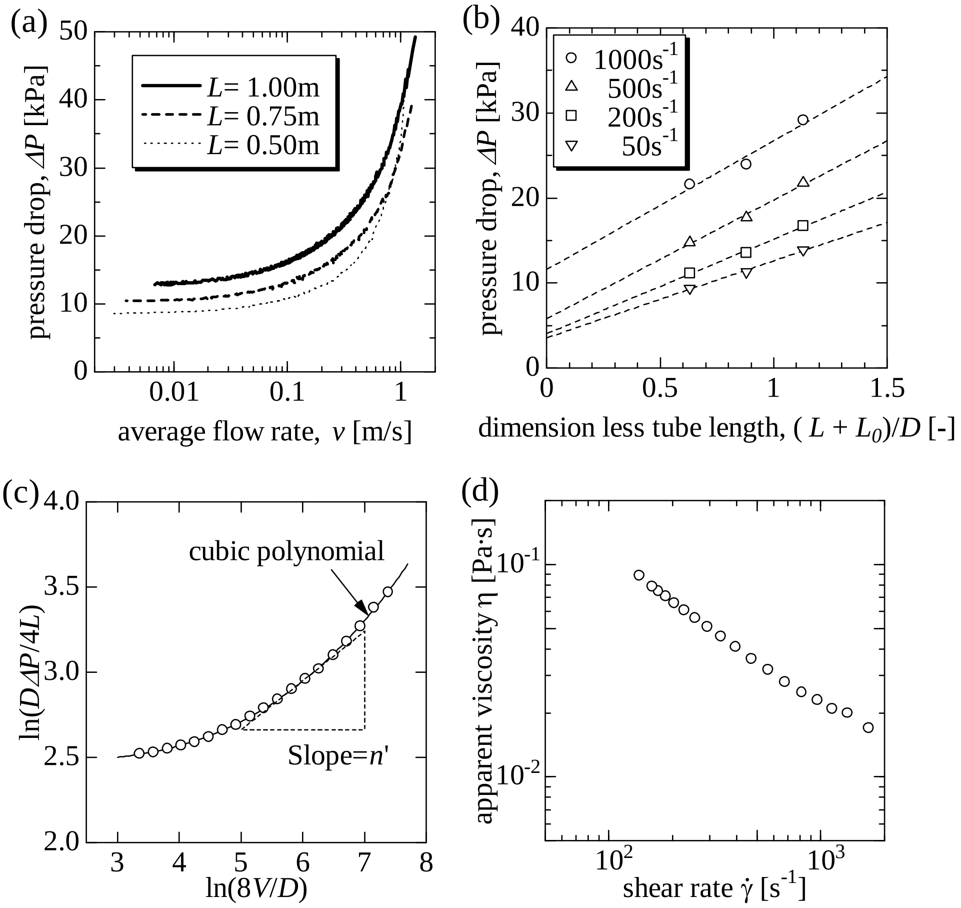

Fig.2 procedure for pressure drop calculation

In many cases, the parameter *n'*, which is the slope of the log-log plot between the shear stress σ_R and apparent shear rate 8V/D, is a constant. In this study, nevertheless, the slope was not constant as shown in Fig.2 (c) but the plot was well correlated by a cubic curve. Thus, the slope *n'* was calculated mathematically by the use of coefficients of the approximated curve to estimate apparent shear rate. Thus, As a result, apparent viscosity calculated from Eq.[4] as shown in Fig.2 (d).

4. Results and Discussions

4.1. Verification of vertical capillary tube viscometer

In advance of the rheological evaluation of suspensions, the confirmation of the accuracy and validity of the vertical capillary tube viscometer was conducted. We prepared 50, 70wt% starch aqueous solutions as Newtonian fluid and 0.2, 0.4 wt% Xthantan gum aqueous solutions as Non-Newtonian. And the viscosity measurements were performed for those fluids by using both vertical capillary tube and cone-plate type rheometers, and the results are shown in Fig.3.

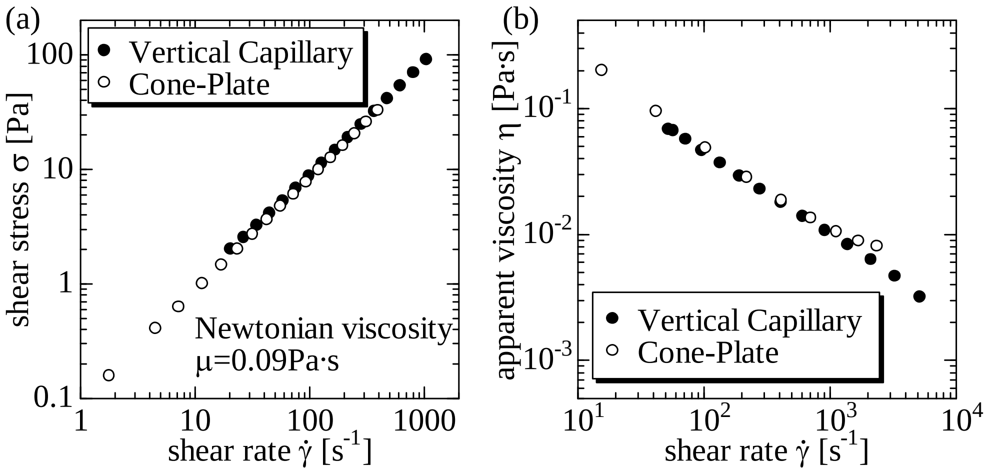

Fig.3 Rheological comparisons between results of vertical capillary tube and cone plate rheometer
(a) 70wt% aqueous starch solution (b) 0.4wt% Xthantan gum aqueous solution

For Newtonian fluid the relationship between shear stress and shear rate shows good agreement, and for Non-Newtonian fluid the difference in apparent viscosity is scarcely observed. However, it is obvious that the range of shear rate for a vertical capillary is higher than that for a cone-plate rheometer. In a vertical capillary tube, the suspension may be not homogeneous and the effect of sedimentation will not be neglected when flowing slowly. This is why vertical capillary type viscometer is difficult to apply in a low shear rate region with good accuracy. Further, the accuracy will depend on the shear stress influenced by the pressure drop across the tube.

With the reference to those results, the lower limit will be determined by sedimentation, and the effective shear rate is roughly more than $10 s^{-1}$. On the other hand, the upper limit of the effective shear rate range will depend on Reynolds number, which must be below 2.1×10^3 for laminar flow. Since Reynolds number and apparent shear rate will be calculated from tentative apparent viscosity, we have to repeat the viscosity calculation in practice to decide the appropriate shear rate range.

4.2. Viscosity evaluation of metal powder suspension

In order to evaluate the particle agglomeration in a suspension, the apparent viscosities and corresponding shear rates with various surfactant concentrations are measured and shown in Fig.4. When the surfactant concentration is less than 0.2wt%, there cannot be observed the difference among suspensions. On the contrary, apparent viscosity of the suspension containing surfactant more than 0.5wt% was reduced by the addition of surfactant. In a high shear rate region of about $2000s^{-1}$, however, each suspension has almost the same viscosity regardless of surfactant concentration.

The reduction in viscosity by the addition of surfactant is not so large and 50% or less, but the result must have a good accuracy. This is because each suspension showed good reproducibility in an effluent experiment for each concentration and the viscosities were estimated by the combination of experimental results of three tubes. Thus, the rheological behavior must be clearly changed by the addition of enough large amount of surfactant. Approximate linear correlation of the suspensions of 0.2wt% or less in Fig.4 suggests that the particle agglomerate will be broken up by the increase in shear rate in a whole shear rate range investigated. Meanwhile, when the concentration is 0.5wt% or more, the slope of the plot in Fig.4 is reduced as the shear rate increases. It suggests that the particle interaction is reduced by the addition of surfactant and the particle agglomeration reached a critical or complete dispersed state with more moderate shear intensity condition. As a result, it is found that the surfactant used in this study is effective to encourage particle dispersion of the suspension investigated when the concentration is appropriate, but that effect will not be noticeable in a high shear rate region because particles are dispersed well. Therefore, the viscosity measurement with various shear rates must be indispensable to evaluate the effectiveness of surfactant.

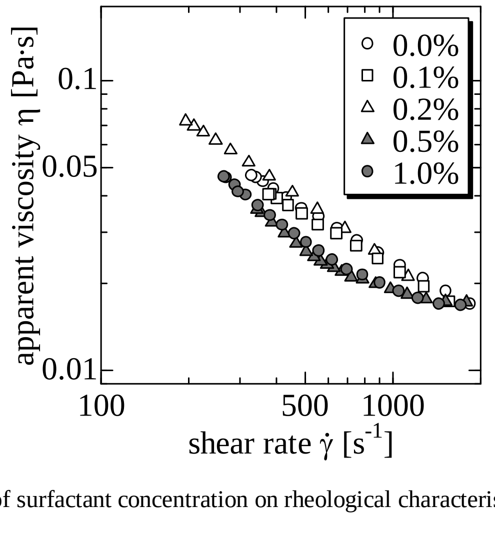

Fig.4 Dependency of surfactant concentration on rheological characteristics of suspension

4.3. Property and appearance of granule of metal powders

Granulated powders were produced by means of a rotational disk type spray dryer from suspensions used for viscosity measurement. And the observation of external appearance and the measurement of size and bulk density were conducted for each granule. The pictures of granules observed by SEM are shown in Fig.5. The outline of granule is almost spherical for each concentration, but an obvious difference in a surface could be noticed. The granule produced from suspensions including the surfactant less than 0.2wt% has rough surface, and it may be consisted from agglomerates of material particles or covered by those agglomerates. On the contrary, the surface of granules from suspensions of 0.5 and 1.0wt% was smooth but had some defects or fracture. Although the cause of the surface difference has not been made clear at present and the toughness of the granule needs to evaluate, the defect indicates the fragility of granules and then the weakness of particle interaction in a granule. Therefore, a good dispersion of raw material particles and a loose packing of agglomerate with weak interaction in a suspension with a high surfactant concentration will affect the surface of granules.

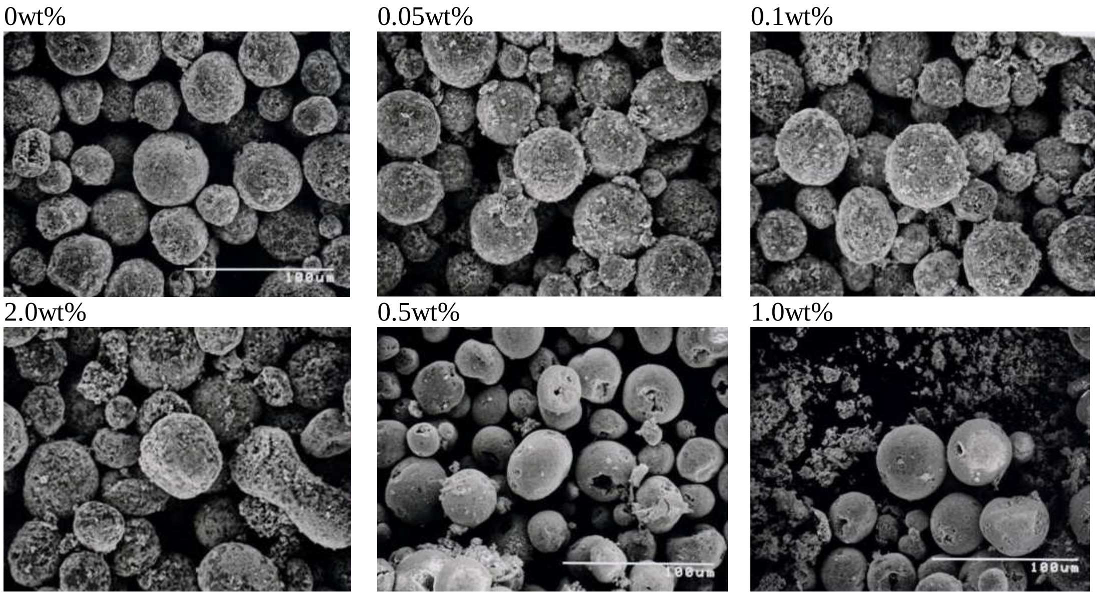

Fig.5 External appearance of granulated powders with different surfactant concentrations

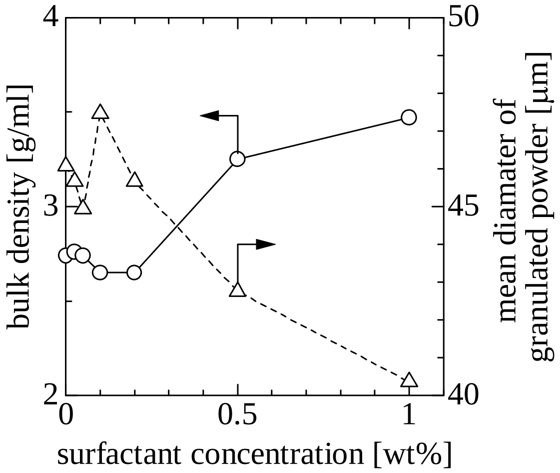

Fig.6 Dependency of surfactant concentration on properties of granulated powder

In Fig.6, both the bulk density and mean granule size are plotted against the surfactant concentration. Both are approximately constant at the concentration less than 0.2wt%, but at higher concentration the size of granulated powder fell down and bulk density became large. The increase of bulk density can be explained by the decrease in void between granules accompanied with the reduction in a granule size. It is sure that the surfactant concentration more than the critical must affect the formation process of granules. And more, the coincidence of critical concentrations for the rheological behavior and granule property supposes the inseparable relationship between the suspension and granule.

4.4. Evaluation of particle interaction by thixotropy model and that correlation with granule

The inter-particle bonding energy F_0 was calculated by applying the experimental viscosity data to the thixotropy model proposed by Usui [6] to evaluate the particle interaction in a suspension, and then the dependency of the energy to the granule size was elucidated. The inter-particle bonding energy is defined as the energy required when an adjacent two particles in agglomerate are separated to divide the agglomerate into two under a uniform shear rate flow. The specific process to estimate the inter-particle bonding energy can be seen in ref (6). Fig.7 shows the dependency of the inter-particle bonding energy on the granule size. The granule became small as the interaction between particles in a suspension became weak by a sufficient addition of surfactant, though the variation is large for small F_0.

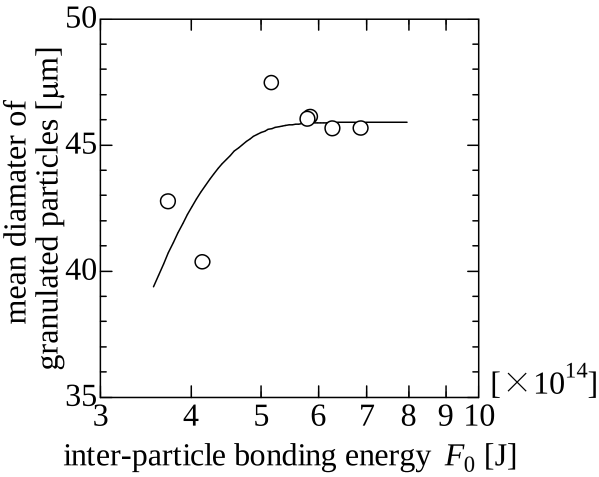

Fig.7 Relationship between granulated particle size and particle interaction

In a commercial production of cemented carbide, the concentration of surfactant is adjusted to approximately 0.1 or 0.2 wt% for the composition of raw materials investigated, but that condition may be decided semi-empirically. Although the granule produced from the suspension contains 0.1wt% surfactant shows a little larger size, the condition where the dependency of surfactant concentration is good agreement with that of commercial production. Thus, the efficiency and critical concentration of surfactant into suspensions with various compositions can be evaluated by the rheological evaluation, though the property difference among granules less than critical have not been clarified yet.

5. Concluding Remarks

In this study, the role of surfactant in a suspension and a granulation process was investigated because a kind and concentration of a surfactant may have been chosen almost experimentally for each raw material and composition.

By mean of a vertical capillary tube viscometer, which is able to apply to the suspension containing metal particles, the rheological and agglomerative behavior of suspension was researched. Further, the application to thixotropy model can elucidate particle interaction quantitatively. The small amount of surfactant addition will not affect the extent of agglomeration in a suspension. On the other hand, the interaction was reduced when the concentration of surfactant is more than critical. Further, the difference of agglomeration in a suspension significantly influenced the appearance and size of granulated powder produced by spray drying of each suspension. That is to say, the granule from too much dispersed suspension is a little small, smooth but probably breakable, however, a suitably agglomerated suspension could produce a granule with rough surface but may have good toughness.

From the experimental results of this research, the detailed function of surfactant when less than critical in the process to produce a granule from a suspension have not been clarified. Nevertheless, the effectiveness of surfactant with high concentration suggest a slightly but significant role to the property of granule even if the concentration is lower than critical. In the future work, the efficiency of a small surfactant addition for various combinations of material and surfactant should be investigated

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