Deagglomeration and Coagulation of Particles in Liquid Metal Under Ultrasonic Treatment

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Ultrasonic processing in the cavitation mode is used to produce the composite materials based on the metal matrix and reinforcing particles of micro- and nano-sizes. In such a case, the deagglomeration of aggregates and the uniform distribution of particles are the expected effects. Although the particles can not only fragment in the acoustic field, they also can coagulate, coarsen and precipitate. In this paper, a theoretical study of processes of deagglomeration and coagulation of particles in the liquid metal under ultrasonic treatment is made. The influence of various parameters of ultrasound and dispersion medium on the dynamics of particles in the acoustic field is considered on the basis of the proposed mathematical model. The criterion of leading process (coagulation or deagglomeration) has been proposed. The calculated results are compared with the experimental ones known from the scientific literature.

Keywords: acoustic field; ultrasonic processing; metal melt; nanoparticles; acoustic coagulation; cavitation; acoustic deagglomeration.

1. Introduction

The development of composite materials based on the metal matrix and non-metallic nanoparticles is actively associated with new applications in industry. The use of nanoparticles in the composition of such materials assumes the technological stage of the introduction of particles into the liquid metal. In addition, the particles can be poorly wetted with the metal. Furthermore, nanoparticles are apt to agglomerate immediately after their formation, and then they exist as micro-sized aggregates. The nano-structured aggregates contain micro- and nanopores filled with air. The external influence must be used so that aggregates can disaggregate, and particles are uniformly distributed over the liquid volume. Ultrasonic treatment is often used for these purposes (Eskin, Eskin, 2014; Eskin et al., 2019; Kudryashova et al., 2019).

Ultrasonic processing is a well-known method for reducing the size of dispersed particles in the liquid fluid (Czyż, 2014; Wang et al., 2017). Ultrasonic processing is required to deagglomerate particles down to the nano-sizes due to the mechanical effect of ultrasonic cavitation. This phenomenon in metallurgy is applied to produce the composite materials containing micro- and nanoparticles.

Ultrasonic processing is used when particles are introduced into the liquid metal. According to numerous experimental studies (Chapter 9 in: Eskin, Eskin, 2014), it was shown that the treatment time is the main parameter determining the effectiveness of ultrasonic processing of the melt with particles. The time of ultrasonic processing, sufficient to achieve the effect (the improvement of the microstructure, mechanical and other properties of the casting), should be the greater, the smaller the size of particles introduced into the metal. The treatment time depends on power and frequency of oscillations, as well as on properties of the dispersion medium, in particular, the liquid viscosity, the surface tension and the wettability of the particle surface (Abramov et al., 2009; Tzanakis et al., 2016). The treatment time is also depend on melt temperature, input power and distance from the source of ultrasound (Tzanakis et al., 2017).

On the other hand, it is known that ultrasonic processing can not only deagglomerate the aggregate down
to original particles but also serve the coagulation and the growth of size aggregate under certain conditions (Sliwinski, 2001). In the term of creating a metal-particle composite material, the increase of particle size, and their gravitational deposition are undesirable effects. The aim of this study is to find the optimal conditions on time and intensity under ultrasonic treatment of metals with reinforcing particles.

2. Research objective

The effect of ultrasound on particles in the liquid metal can be qualitatively described as follows.

Firstly, ultrasound creates cavitation in the liquid which allows the liquid penetration into the pores of the agglomerate even with poor wettability of the surface (Kudryashova et al., 2016; 2017). This process takes some time which can be estimated from the problem solution of capillary penetration. The agglomerate is deagglomerated at the limit to the original nanoparticles when the pores are filled with liquid and a certain critical value of pressure is reached at the front of the wave.

Secondly, ultrasound facilitates the more intensive movement of particles and their collision which leads to coagulation and coarsening of aggregates. The characteristic time of particle agglomeration can also be estimated taking into account the parameters of the acoustic wave, the particle concentration, etc., based on the results of the classical study (Rozenberg, 1971). The growth of particle sizes can be described with the Smoluchowski model (Smoluchowski, 1916).

The criterion of the leading mechanism can be obtained by comparing the characteristic times of the fragmentation of agglomerates and of the particle agglomeration in the ultrasonic field. This determines whether fragmentation or coagulation prevail in this situation. If the values of the characteristic times are close, it is possible that one or the other process will prevail during ultrasonic treatment, and aggregates will either fragment or increase.

Before proceeding to the mathematical description of the problem, the following assumptions are made.

1) Agglomerates of particles are considered as they have a spherical shape. The sizes of agglomerates do not fit a certain distribution law $f(D)$.

2) The pores of nanostructured agglomerates are wetted with liquid for certain time $t_w$ by excess pressure during collapse of cavitation bubbles. Then the agglomerate is deagglomerated with a certain velocity $\frac{4D}{t} = v_f$.

3) Aggregates move in the liquid and collide with each other. Some of these collisions lead to the aggregation. The average time between collisions and aggregation is denoted by $t_c$.

3. Results and discussion

3.1. Fragmentation

Nanoparticles in the powder exist as micron and submicron-sized agglomerates because nanoparticles agglomerate immediately after their formation as a result of their developed surface. Such agglomerates contain nanopores and nanochannels.

The size of cavitation bubbles depends on the ultrasound frequency, the viscosity of the fluid and the surface tension (Rozenberg, 1971). Each agglomerate, placed or passing through the cavitation zone in the mode of the developed cavitation, is surrounded by pulsating and collapsing bubbles as the cavitation index (a ratio of the volume of bubbles to the volume of the cavitation area) tends to unity in such mode. Therefore, it can be assumed that at least one cavitation bubble will implose near the capillary entry at every moment in time, and it will create a pressure impulse contributing to the fact that the liquid fills the capillary. In this case, the pressure created by the collapse of cavitation bubbles $p_{ex}$ is proportional to the intensity of ultrasound.

By applying excessive pressure $p_{ex}$, the traverse speed of the meniscus in the capillary is estimated by the formula (Rol'dugin, 2011):

$$v_{cp} = \frac{R_{cp}^2 p}{8\eta l_{cp}},$$

where $R_{cp}$ is the capillary radius, $\eta$ is the dynamic viscosity of the liquid, $l_{cp}$ is the capillary length filled with liquid, and $p$ is the total pressure:

$$p = p_{ex} + \frac{2\sigma \cos \theta}{R_{cp}} = p_{ex} + p_l,$$

where $p_l$ is Laplace capillary pressure, $\theta$ is the wetting angle, and $\sigma$ is the surface tension.

When the surface of the particle substance is poorly wetted, Laplace pressure in Eq. (2) is negative, and it can reach large values for small capillary radii, therefore, it is necessary that the excess pressure exceeds Laplace pressure in order to achieve the effect of the fluid penetration into the pores.

If $p_{ex} > p_l$, the pore-capillary will be filled with liquid after some time. This time is derived by integrating Eq. (1):

$$t_w = \frac{4\eta l_{cp}^2}{R_{cp}^2 p}.$$  

The ratio $l_{cp}/R_{cp}$ can be estimated by determining the specific surface of powder $S_m$. In the case without pores, $S_m = 6/D\rho_p$, where $D$ is the agglomerate diameter, and $\rho_p$ is the true density of the substance. With $l_{cp}$ taken as equal to $k_{cp}D$ (i.e. the length of pores is proportional to the particle diameter), the specific surface of the powder is obtained as follows:
where \( k_p \) is the coefficient depending on the development of the pore system. Here the dimension factor is derived as follows:

\[
\frac{l_{cp}}{R_{cp}} = \frac{6k_p^2}{S_m D \rho_p - 6}.
\]

Typical values of the dimension factor are up to several hundred for nanoparticles according to rated values of powders of aluminium oxide, zirconium oxide and detonation-synthesized diamond presented in Table 1.

It is necessary to evaluate the pressure \( p_{ex} + |p_l| \) in order to calculate the time of melt penetration into the pores of particles. The values of excess pressure created in capillaries when cavitation bubbles implode in the aluminium melt under ultrasonic cavitation were estimated in (Tzanakis et al., 2014; 2015). Such pressure can achieve very high values – tens and hundreds of MPa, depending on the proximity of the imploding bubble to the capillary entry. On the other hand, the negative pressure \( p_l \) can reach values of the same order. According to the formula (1), it equals 80–160 MPa for \( R_{cp} = 10–20 \text{ nm} \) in the system of the nanoporous aggregate of hydrophobic aluminium oxide and liquid aluminium (wetting angle \( \theta = 152^\circ \) (Timoshkin, 2003), and surface tension \( \sigma = 0.9 \text{ N/m} \) (Hatch, 1984)).

Figure 1 shows the calculated dependences of Laplace pressure \( |p_l| \) and \( p_{ex} + p_l \) on the capillary radius at different values of excess pressure \( p_{ex} \). In practical conditions, when the excess pressure in the liquid can be tens of megapascals, it becomes possible that the melt penetrates into the capillaries of particles. Furthermore, the condition \( p_{ex} \gg p_l \) is met when relatively large pores filled \( (R_{cp} > 500–1000 \text{ nm}) \), Laplace pressure in Eq. (2) can be neglected. Laplace pressure takes into account for the calculation of total pressure, if there is a large number of nanopores in powder particles \( (R_{cp} = 10–500 \text{ nm}) \). In this case, the total pressure is about 1–100 Pa.

![Fig. 1. Dependence of Laplace pressure modulus \( |p_l| \) and total pressure \( p = p_{ex} + p_l \) in the pore on its radius.](image1)

![Fig. 2. Dependence of characteristic penetration time of the agglomerate on total pressure in the pore at different ratios of the scale factor \( l_{cp}/R_{cp} \).](image2)

The threshold intensity of deagglomeration is derived if the agglomerate of diameter \( D \) located on the front of the sound wave is considered and the forces acting on it are analyzed:

\[
I_t = 2W_l \left( \frac{\sigma_{stp}}{D \rho_l} \right)^2,
\]

where \( \sigma_{stp} \) is the tensile strength, \( f \) is the oscillations frequency, \( \rho_l \) is the fluid density, \( W_l = \rho c \) is the wave impedance, and \( c \) is the sound velocity in the liquid. It should be noted that the tensile strength of particle agglomerates is of an order of magnitude lower than one for a monolithic particle. Although aluminium oxide has high strength (about 500 MPa), agglomerates can be fragmented at hundreds of times smaller \( \sigma_{stp} \).
The minimum particle diameter, to which the agglomerate can be deagglomerated at a given level of the treatment intensity $I$, can be obtained from Eq. (6):

$$D_{\text{min}} = \frac{\sigma_{\text{stp}}}{f \rho_p} \sqrt{\frac{2W_l}{I}}. \quad (7)$$

For instance, the agglomerate can deagglomerate to a minimum value of $D_{\text{min}} \sim 2.5 \mu m$ at the intensity $I = 8 \text{ W/cm}^2$, the frequency $f = 15 \text{ kHz}$, and the tensile strength $\sigma_{\text{stp}} = 5 \text{ MPa}$.

Figure 3 shows the dependence of the threshold intensity of ultrasound at different frequencies on the particle diameter. The calculation is made for $\sigma_{\text{stp}} = 5 \text{ MPa}$.

The lower the frequency of ultrasonic oscillations and the smaller the size of agglomerates, the higher the intensity required for the deagglomeration.

### 3.2. Coagulation

The justification of the kernel form for the Smoluchowski coagulation equation is the important issue under mathematical simulation of ultrasonic coagulation. The number of particle agglomeration in the ultrasonic field is calculated in Rozenberg (1971) on the streaming model of particle convergence. The calculation is based on the assumption that particles agglomerate if the streamline, which arises nearly a particle and involves the next one, will pass at the distance equal to the particle diameter $d$. The total number of particle agglomeration per unit time $N$ is proportional to the cube of particle diameter $D^3$, the concentration $n_0$, and the amplitude square of vibration velocity for the medium $U_0^2$ (hence the energy of sound field), but inversely proportional to the kinematic viscosity of the medium $\nu$:

$$N = \frac{U_0^2 D^3 n_0 \rho_p \kappa_{\text{wrap}}}{\eta}, \quad (8)$$

where $\kappa_{\text{wrap}}$ is the wrap coefficient.

Suspended in melt, the particle is involved in oscillations under the influence of the sound field. Depending on properties of the medium, the size and the density of the particle, it can be moved by the medium better or worse, which is determined by the drag coefficient $k_{\text{drag}}$. This coefficient is the ratio of the amplitudes of the suspended particle velocity to that of the liquid-particle velocity. Considering that the Stokes force acts between the particle and the medium, the drag coefficient is expressed as follows:

$$k_{\text{drag}} = \frac{1}{\sqrt{1 + f^2 \tau^2}}, \quad (9)$$

where $\tau = \rho_p D^2 / 18 \eta$ is the particle relaxation time. Analysis of this expression shows that the oscillation amplitude of the particle is more different from the one of the medium, the larger the size and density of the particle, the higher the sound frequency and less the viscosity.

It can be considered that the particle is moved by the sound field, thereby the number of the particle agglomeration increases in $k_{\text{wrap}} = 1 - k_{\text{drag}}$ times. Then the Eq. (8) is expressed as follows:

$$N = \frac{U_0^2 D^3 n_0 \rho_p}{\eta} \left(1 - \frac{1}{\sqrt{1 + f^2 \tau^2}}\right). \quad (10)$$

The characteristic collision time $t_c$ is inversely proportional to the number of collisions per unit time:

$$t_c = \frac{\eta}{U_0^2 D^3 \rho_p n_0} (1 - \frac{1}{\sqrt{1 + f^2 \tau^2}})^{-1}. \quad (11)$$

The kinetic energy of the particle is proportional to the oscillations intensity

$$E_p = \frac{U_0^2 D^3 \rho}{12} \sim I.$$

The dependences of characteristic times of coagulation and wetting on the particle diameter and the oscillations frequency are shown in Fig. 4.
The higher the oscillations frequency, the less the time was needed for agglomeration and coagulation of particles. The wetting time in this model does not depend on the frequency of ultrasonic processing.

3.3. The criterion of fragmentation and coagulation

Depending on conditions under ultrasonic processing, either fragmentation of agglomerates to original particles or coagulation can occur. A ratio of characteristic times can serve as the criterion of the leading mechanism:

$$\frac{t_w}{t_w} = \frac{K_D}{3Pn_0 \rho^2_c \pi} \left(1 - \frac{1}{\sqrt{1 + f^2}}\right)^{-1}. \quad (12)$$

If $\text{CF} < 1$, particles will coagulate in the disperse system. Otherwise, agglomerates can be fragmented, if the additional condition $I > I_1$ is met, i.e., the intensity is greater than the threshold intensity determined by the Eq. (6) up to the minimum diameter determined by the Eq. (7).

In the example of calculation shown in Fig. 4, fragmentation is observed for particles with a diameter $D < 19-22$ μm determining by ultrasonic processing ($\text{CF} > 1$). Larger particles will not fragment under these conditions but only coagulate.

Even if fragmentation is the leading mechanism of disperse system evolution ($\text{CF} > 1$), it will not start immediately but after the time required to penetrate the pores of agglomerates with liquid. Particle coagulation will occur during ultrasonic processing of the melt in the first seconds (minutes). The coagulation dynamics is well described by the Smoluchowski model. Consider the transformation of particle size distribution in particles over time. The balance equation is an integral version of the Smoluchowski equation, and it describes the change in the vector of the mass function of particle size distribution over time. Following (KUDRYASHOVA et al., 2015; 2018), the balance equation can be derived:

$$\frac{\partial f(D, t)}{\partial t} = I_1 + I_2 + I_3, \quad (13)$$

where $I_1$ describes the reduction in the particle number with diameter $D$ per unit time in unit volume due to the collision of a particle of diameter $D$ with a particle of diameter $D_1$:

$$I_1 = -f(D, t) \int_0^\infty K(D, D_1) f(D_1, t) \, dt,$$

where $K(D, D_1)$ is a probability of particle collision.

The equation term $I_2$ defines the appearance of particles of diameter $D$ due to the collision of particles with diameters $D_1$ and $D - D_1$:

$$I_2 = \frac{1}{2} \int_0^D K(D - D_1, D_1) f(D_1, t) f(D - D_1, t) \, dt.$$
Table 2. Time of ultrasonic cavitation processing of aluminium melt for deagglomeration of $\gamma$Al$_2$O$_3$ particles: experiment (ESKIN, 1974) and calculation by the formula (3).

<table>
<thead>
<tr>
<th>$t_{\text{wet}}$ [min]</th>
<th>$D$ [$\mu$m]</th>
<th>Experiment</th>
<th>Calculation by the Eq. (3), $\underbrace{\lbrack 0.01-0.1 \rbrack}$</th>
<th>$\underbrace{0.1-1 \rbrack}$</th>
<th>$\underbrace{1-10 \rbrack}$</th>
<th>$\underbrace{10-20 \rbrack}$</th>
<th>$\underbrace{80-100 \rbrack}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30–45</td>
<td>0.01–0.1</td>
<td>12–15</td>
<td>8–10</td>
<td>3–5</td>
<td>1–2</td>
<td></td>
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</tr>
<tr>
<td>Calculation by the Eq. (3), $\underbrace{\lbrack 0.01-0.1 \rbrack}$</td>
<td>$\underbrace{0.1-1 \rbrack}$</td>
<td>$\underbrace{1-10 \rbrack}$</td>
<td>$\underbrace{10-20 \rbrack}$</td>
<td>$\underbrace{80-100 \rbrack}$</td>
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As can be noted from the results above, the size and wettability of particles are crucial for determining the effective time of ultrasonic processing of the melt containing such particles. The smaller the size of the particle and the worse they are wetted by the liquid, the more the time is required for the melt processing. An estimate of the required time can be obtained by calculating the wetting time of particles according to the formula (3). The scale factor $l_{cp}/R_{wp}$ and the total pressure in pores are unknown parameters in this formula. The scale factor is determined primarily by the particle size and can be estimated based on the specific surface area of the powder. The total pressure depends on the wetting angle of particle surface with this metal and on the cavitation intensity.

The dependence of processing time on the particle size for 1 wt% $\gamma$-Al$_2$O$_3$-particles in pure aluminium was obtained experimentally by Eskin (1974). The results are shown in Table 2. If we consider the dependence of scale factor $l_{cp}/R_{wp}$ as a function of the particle diameter $A D^{-B}$, where $A$ and $B$ are approximating constants, the calculation of wetting time obtained by the formula (3) was found to be in good agreement with the experimental data.

Our model gives estimation for treatment time for TiB$_2$-particles with a size of 25 nm in magnesium alloy AZ91D melt as 17 min (15 min according to the experiment (CHoi et al., 2012b)). However, 15 minutes of processing of magnesium AM60B alloy melt with Al$_4$C$_3$-particles with a size of less than 44 $\mu$m (NIMITYONGSKUL et al., 2010) seems superfluous. Our estimates give about 1.5 minutes of processing. This difference can be explained with smaller characteristic sizes of particles (in work the maximum, but not mean diameter is specified).

The time of agglomerate penetration is the main characteristic that determines the processing time of the ultrasonic field. If the melt treatment is discontinued for the time $t < t_w$, particles can coarsen instead of a fragment.

Coagulation can be the leading mechanism for larger particles and their relatively high concentrations (CF < 1). In this case, ultrasonic processing of the melt leads to coarsening and sedimentation of particles instead of expected effects: the fragmentation of agglomerates and the uniform distribution of fine particles in the melt volume.

4. Conclusions

A physical and mathematical model describing the dynamics of the behaviour of nanoparticles in a liquid metal during ultrasonic processing has been proposed. Ultrasonic processing either can lead to coagulation and coarsening of particles but can also lead to fragmentation of aggregates. In this case, the fragmentation of agglomerates and their uniform distribution of particles in the melt volume is the desired result under ultrasonic processing.

The criterion defining the leading mechanism (fragmentation or coagulation) under ultrasonic processing of nano-dispersed metal composites has been discussed. It is a ratio of characteristic times of particle convergence and the penetration of the pores of aggregates with the liquid metal. If the coagulation is the main mechanism, the coarsening of particles is observed during ultrasonic processing. If the fragmentation is the main mechanism, nevertheless, there is a period of time during which the particles will coagulate. This time is necessary for the liquid penetration of the pores of aggregates. Then the fragmentation of particles begins with further processing by ultrasound up to a certain minimum size, determined by the strength of aggregates and the treatment intensity.

The obtained results allow to predict the behaviour of particles in the liquid metal under ultrasonic processing and to evaluate the time required to deagglomerate particles.

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