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On the Mechanism of Ultrasound-Driven Deagglomeration of Nanoparticle Agglomerates in Aluminum Melt

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One of the promising directions in the technology of composite alloys with improved mechanical properties is reinforcement of the metallic matrix with nanopowders introduced in the liquid metal. Ultrasonic processing is known to significantly improve the introduction of submicrone particles to the metallic melt. This study focuses on the mechanisms of deagglomeration and wettability of such particles by the melt under the action of ultrasound. The suggested mechanism involves the penetration of the liquid metal into the pores and cracks of the agglomerates under the excess pressure created by imploding cavitation bubbles and further destruction of the agglomerate by the sound wave. The main dependences connecting the acoustic parameters and processing time with the physical and chemical properties of particles and the melt are obtained through analytical modeling. The mathematical description of the ultrasonic deagglomeration in liquid metal is presented; a dependence of the threshold intensity of ultrasound for the break-up of agglomerates on their size is reported.

INTRODUCTION

The processing of metallic melts by sonic or ultrasonic waves favorably influences grain refinement, particle dispersion, mixing, degassing, and mold filling.[1,2] This also applies to the processing of melts modified or reinforced with nanopowders. However, there are specific problems associated with the introduction of nanopowders in the molten metal, specifically to liquid aluminum.[3] Due to the high surface tension, considerable hydrogen solubility, and strong oxide film, the particles introduced into molten aluminum are often agglomerated, surrounded by oxide film, and have absorbed hydrogen on the surface.[2] As a result, these particles and their agglomerates are not wetted by the melt and notoriously difficult to introduce and distribute in the liquid matrix. Ultrasonic processing is reported to facilitate introduction of small particles to the melt and their deagglomeration.

The purpose of this work is to consider a possible mechanism of deagglomeration under ultrasonic melt processing. It is known that ultrasound increases the efficiency of filtration and impregnation of filters and preforms.[2,4–7] The intensification of these processes is related to the excessive pressure formed close to the capillary entry by pulsating and imploding cavitation bubbles, the so-called "sono-capillary" or "ultrasonic capillary effect" (UCE), which is the sharp increase of depth and speed at which liquid penetrates micro-capillary channels (e.g., filtration channels, cracks, and pores). Ultrasonic cavitation is the leading phenomenon in this effect.

For processing of a metallic melt and introduction of particles into the melt, there is a practice of using the ultrasonic field.[2,8,9] It is shown that ultrasonic cavitation promotes deagglomeration and better distribution of nonmetallic particles in the liquid. One of these hypotheses explaining the increased apparent wettability connects it to the improved access of the melt to a surface of nonmetallic particles and penetration of the melt into defects of the surface (capillaries) with the ultrasonic cavitation.[2]

In this work, we extend the sono-capillary effect to the process of deagglomeration of nonmetallic particles, including nanoporous particles.

Qualitatively, the process can be described as follows. Cavitation bubbles, pulsing and collapsing near agglomerates, create overpressure, allowing

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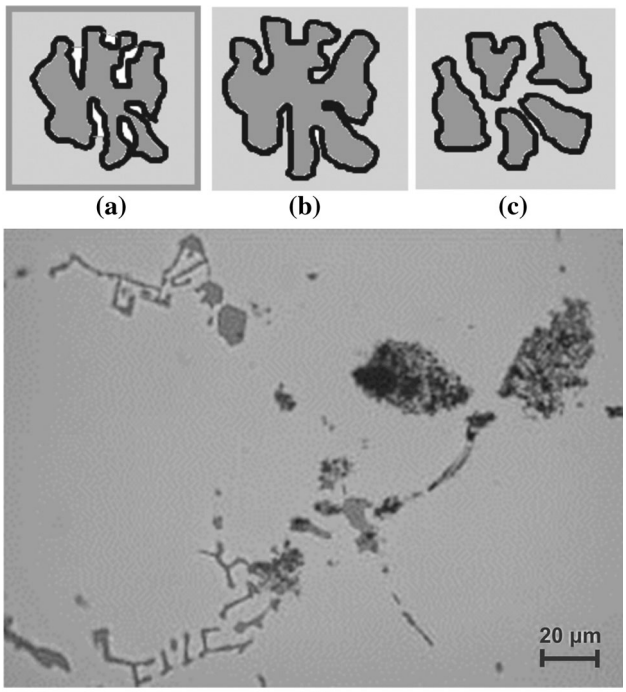

Fig. 1. Deagglomeration of particles in liquid metal under ultrasound: porous agglomerate not yet filled with metal (a); under the overpressure of the collapsing cavitation bubbles the pores are filled with liquid metal (b); agglomerate is divided into separate fragments under acoustic wave (c); an agglomerate of alumina nanoparticles in an aluminum alloy (d) (courtesy J. Tamajo and D. Eskin).

liquid to get into the narrow pores and to overcome the capillary pressure. The melt is "pushed" in capillary channels and pores of the particles, even if they are badly wetted by the liquid metal. Saturation of agglomerated particles with the melt significantly changes the properties of the agglomerate and facilitates its separation into individual particles (deagglomeration) by using the force of viscous friction at the front of the ultrasonic wave (Fig. 1).

MATHEMATICAL DESCRIPTION OF THE PROBLEM

The nanoparticles introduced into aluminum melt exist in the form of agglomerates ranging in size from several to tens of microns (Fig. 1d). Nanoparticles agglomerate already during their production or handling because of their developed surface. Such agglomerates have nanopores and nanochannels. The size of cavitation bubbles depends on the frequency of ultrasound, viscosity of liquid, and surface tension.[10] An estimate for the diameter of a cavitation bubble in the aluminum melt is 50/300 of micron at a frequency of 17.5 kHz.[11] In the mode of the developed cavitation, each agglomerate placed or passing through a cavitation zone is surrounded by numerous pulsing and collapsing bubbles because the cavitation index (the ratio of volume of bubbles to the volume of cavitation zone) in the mode of the developed cavitation approaches unity.[10] Therefore, it is possible to assume that in each point of time, at least one cavitation bubble will implode near the entry of a capillary. It creates a pressure impulse, promoting the filling of the capillary with the matrix liquid. In this case, the pressure p_{ex} generated when cavitation bubbles collapses is proportional to the intensity of the ultrasound.[10]

Let us assume that all particles have a spherical form, the same size, and pores (capillaries) of identical radius and depth. When imposing excessive pressure p_{ex}, the meniscus velocity in the capillary can be defined as follows:

$$v_{cf} = \frac{R_{cr}^2 p}{8\eta_l l_l} \tag{1}$$

where R_{cr} is the capillary radius, η_l is the viscosity of the melt, l_l is the capillary length filled with the melt, and p is the total pressure:

$$p = p_{ex} + \frac{2\sigma\cos\theta}{R_{cr}} = p_{ex} + \Delta p \tag{2}$$

Here Δp is the Laplace capillary pressure, θ is the wetting (contact) angle, and σ is the surface tension.

In the case of poor wettability of particles by metallic melt, the second member in Eq. 2 is negative and can reach large values for small capillary radii. Therefore, to achieve the effect of melt infiltration into the pores, the necessary condition is that the excessive pressure exceeds the Laplace pressure.

Under the conditions of $p_{ex} > \Delta p$, the capillary will be filled with liquid metal after some time. This time can be obtained by integrating Eq. 1:

$$t_{wt} = \frac{4\eta_l l_{cr}^2}{R_{cr}^2 p} \tag{3}$$

The ratio l_{cr}/R_{cr} can be found by using the following simple model. Let all particles have the identical diameter of D; their surface is evenly covered with cone-shaped pores of radius R_{cr} and depth l_{cr}. The diameter of nanoparticles and the specific surface of S_m can be determined experimentally. Based on these assumptions and by using simple geometric transformations, one can find:

$$\frac{l_{cr}}{R_{cr}} = \frac{8}{3} S_m D \rho_p \tag{4}$$

where ρ_p is the real density of a particle. Typical values for nanoparticles from tens of nanometers to several microns in size are listed in Table I.[12]

Table I. Size, specific surface of powder particles (experimental[12]) and the ratio of the length of the pores to their radius (Eq. 4)

Powder	Average particle diameter	Specific surface (m^2/g)	l_{cr}/R_{cr} (Eq. 4)
α-Al_2O_3	36 nm	35–40	14.2
ZrO_2 (Y_2O_3)[10]	1.5 μm	7	110
Al_2O_3	0.2–5 μm	60	465

In considering an agglomerate with a diameter of D located at the front of the sound wave and analyzing the forces exerted on it, it is possible to estimate the threshold intensity of deagglomeration:

$$I_t = 2W_l\left(\frac{\sigma_{stp}}{D\omega\rho_l}\right)^2 \quad (5)$$

where σ_{stp} is tensile strength of a particle or agglomerate. It must be kept in mind that the tensile strength of agglomerates can be an order of magnitude smaller than that of a monolithic particle. For example, aluminum oxide has a high strength of about 500 MPa, whereas the agglomerates fracture at $\sigma_{stp} \sim 75$ MPa and less.[13]

RESULTS AND DISCUSSION

The amount of pressure $p_{ex} + \Delta p$ needs to be estimated for the calculation of the penetration time of the melt into the agglomerate pores. The excessive pressure created in capillaries at a collapse of cavitation bubbles under ultrasonic cavitation in aluminum melt was estimated in Ref. 14 Such pressure can reach very high values (depending on the proximity of the imploding bubble to the entry of a capillary), in the range from 1 MPa to over 4 GPa; on average, 10–400 MPa. On the other hand, the negative pressure Δp can reach magnitudes of the same order for very narrow channels. For example, according to Eq. 1, $\Delta p \sim$ 80–320 MPa for R_{cr} = 5–20 nm in the system of liquid aluminum–aluminum oxide (wetting angle $\theta = 152°$, σ = 0.9 N/m).[13,15]

Figure 2 shows the calculated dependencies of the Laplace pressure module $|\Delta p|$ and $p_{ex} + \Delta p$ in a pore capillary on the radius of the capillary and overpressure p_{ex}. In practically important modes, when the overpressure in the melt is tens of MPa, infiltration of melt into the capillaries of the particles becomes possible. In this case, for filling relatively large pores (R_{cr} = 100–1000 nm), the condition $p_{ex} \gg \Delta p$ is fulfilled and the Laplace pressure in Eq. 2 can be neglected. However, if the pores and channels are considerably smaller (R_{cr} = 5/100 nm), the Laplace part of the total pore pressure is essential, and the sum of the pressures will be in the range 10–100 Pa.

The impregnation time for an agglomerate in accordance with Eq. 3 is proportional to the squared length of the pores of l_{cr}^2 and the viscosity of melt η_l, and inversely proportional to the cross-sectional area and the pressure $p = p_{ex} + \Delta p$.

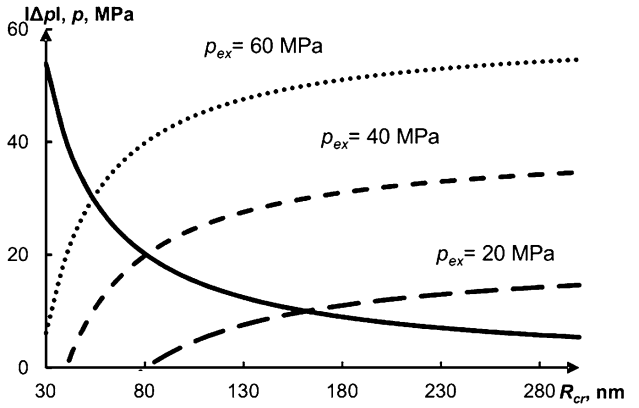

Fig. 2. Dependence of $|\Delta p|$and the total pressure $p = p_{ex} + \Delta p$ in the pore on its radius.

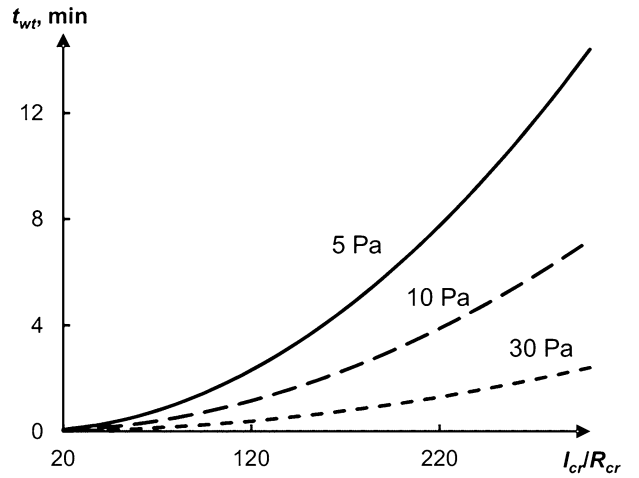

Fig. 3. Dependence of the penetration time of melt into the pores of the particles on the ratio of length to radius of the pore for various values of the total pressure p.

In experiments on the introduction of fine particles into metallic melt, the duration of ultrasonic processing is measured in minutes.[2,8,9,12] Figure 3 shows the dependence of the penetration time of metallic melt into the pores of the particles on the ratio of the length of the pores to their radius for various values of pressure p. Figure 4 shows the dependence of the penetration time on pressure p for various values l_{cr}/R_{cr}.

The increase of pressure (in proportion to the intensity of ultrasound) first leads to a sharp reduction of penetration time, but the further increase in pressure does not give a noticeable gain in time.

Figure 5 shows the calculated (Eq. 5) dependence of the threshold ultrasonic intensity for deagglomeration of aluminum oxide particles in aluminum melt at (ultra)sound frequencies of 15 kHz, 12 kHz, and 10 kHz.

For large agglomerates, with a radius of about 40–50 μm, less intensity is required, whereas with the reduction of the agglomerate size, the threshold intensity sharply increases. Also the lower the sound frequency, the higher the intensity required for the deagglomeration, which justifies the use of ultrasonic frequencies.

The obtained theoretical results are indirectly confirmed by experimental data on ultrasonic processing of aluminum melts containing particles of oxides, borides, and carbides (see, for example, the review in Ref. 2). The main parameters affecting the deagglomeration and dispersion of particles are the processing time and the amplitude of vibration (ultrasonic intensity). The wettability of particles and their distribution in the liquid volume are improved with an increase in processing time.[2,3,16]

An experimental dependence of the duration of ultrasonic processing on the particle size for γAl_2O_3 in 99.99% Al melt at 700°C to 720°C and an acoustic power of 500 W was reported in Ref. 16 and shows that with reduction of particle size, the required time of processing increases. By using Eq. 3 for p = 50 Pa, assuming that the scale factor l_{cr}/R_{cr} of particles decreases inversely with their diameter, we calculated the processing time for the experimental case described in Ref. 16; the results of calculated and experiment data are shown in Table II.

Despite the fact that the estimated impregnation time of particles grows faster with the reduction in their size than is observed in the experiment, one can consider the match satisfactory, especially taking into account that some parameters used in the calculation have been assumed.

SUMMARY

The suggested mechanism of penetration of metallic melt into submicronic particles and their agglomerates under ultrasonic processing is based on the sono-capillary phenomena and ultrasonic cavitation. The parametrical study allows us to draw the following conclusions:

– Ultrasonic cavitation facilitates impregnation of agglomerates by liquid metal, which affectively means their deagglomeration.
– The time required for the impregnation is proportional to the viscosity of the melt; the squared ratio of length to radius of a pore (capillary) that

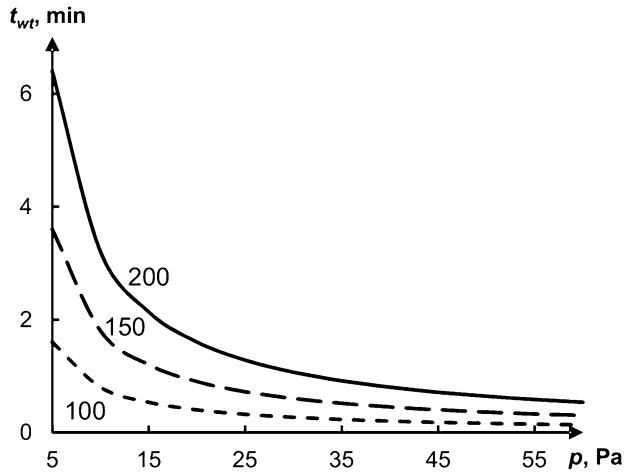

Fig. 4. Dependence of the penetration time of melt into the pores of the particles on the total pressure in the pore for various values of the scale factor l_{cr}/R_{cr}.

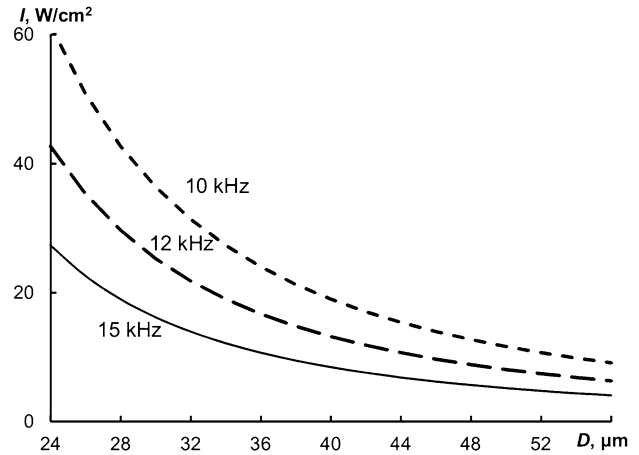

Fig. 5. Dependence of the threshold (ultra)sound intensity for break-up of agglomerates in liquid aluminum melt on the particle diameter for various values of the sound frequency.

Table II. Time of ultrasonic cavitation processing of aluminum melt for dispersion of γAl_2O_3 agglomerates: experiment[14] and calculation (this work)

D (μm)	0.01–0.1	0.1–1	1–10	10–20	80–100
t_{wt} (min)					
Experiment[12]	37.5	14	9	4	1.5
Calculation (Eq. 3)	810	20	3.2	0.4	0.01

can be estimated from the size of a specific surface of powder and the size of agglomerates; and inversely proportional to the external pressure at the entry of a pore and the intensity of ultrasound.
- In the important case of processing of the particles having a large number of a nanopores (with a radius less than 100 nm), the Laplace capillary pressure is comparable to the excessive pressure created at the collapse of the cavitation bubbles; the time of impregnation of such particles with the melt will be in the range from minutes to tens of minutes.
- Dispersing of agglomerates requires a threshold ultrasonic intensity that is inversely proportional to the squared radius of agglomerates.
- A comparison of calculated values of impregnation time of aluminum oxide particles by liquid aluminum with an experimental data gives satisfactory results and validates the model.
- The suggested analytical formulas allow one to estimate intensity, frequency, and time of the ultrasonic processing that are necessary for successful introduction of particles to the metallic melt.

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