Casting technology for ODS steels – dispersion of nanoparticles in liquid metals

M Sarma1, I Grants1,2, I Kaldre2, A Bojarevics2, G Gerbeth1
1 Institute of Fluid Dynamics, Helmholtz-Zentrum Dresden - Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany
2 Institute of Physics, University of Latvia, Salaspils, Latvia
g.gerbeth@hzdr.de

Abstract. Dispersion of particles to produce metal matrix nanocomposites (MMNC) can be achieved by means of ultrasonic vibration of the melt using ultrasound transducers. However, a direct transfer of this method to produce steel composites is not feasible because of the much higher working temperature. Therefore, an inductive technology for contactless treatment by acoustic cavitation was developed. This report describes the samples produced to assess the feasibility of the proposed method for nano-particle separation in steel. Stainless steel samples with inclusions of TiB2, TiO2, Y2O3, CeO2, Al2O3 and TiN have been created and analyzed. Additional experiments have been performed using light metals with an increased value of the steady magnetic field using a superconducting magnet with a field strength of up to 5 T.

1. Introduction
Nonmetallic nano-sized particles in a metal matrix can lead to improved mechanical, physical and chemical properties. One of the most important nanocomposites is the oxide dispersion strengthened (ODS) steel which has been proven of great value in nuclear fusion and fission systems [1,2] because of higher tolerance against radiation, higher operational temperature and creep resistance [3] than standard steels. Another important material group is high modulus steels (HMS) which aim in reducing the weight while increasing the stiffness of the materials [4,5]. Significant effort has been made in developing ways to produce MMNC, but until today they are mostly made in an expensive way by using powder metallurgy, ball milling or infiltration technique. A casting route in which the particles are stirred-in would be highly desirable. In general, a homogeneous dispersion just by stirring can be obtained for micro-sized particles, but not for nano-sized particles which quickly tend to agglomerate due to strong interfacial and van der Waals forces. Problems can also arise from weak particle wetting which supports the creation of particle clusters. A rather inexpensive solution is ultrasonic treatment of the melt – cavitation created by ultrasound could break particle clusters, clean the particle surface and support the dispersion [6,7,8]. Suslick et al. [9] showed that the collapse of bubbles can create “hot spots” with effective temperatures of 5000 K, pressures of 1000 atm, and heating and cooling rates above 1010 K/s. Different methods which incorporate cavitation have been proposed and tested with various aluminum [10,11] and magnesium [12,13] alloys. Due to the much higher melting temperature of steel direct introduction of the ultrasonic probe into the melt is not possible. The interface between the probe and the metal is exposed to harsh working conditions which lead to fast degradation of the probe as well as contamination of the melt. Therefore, a contactless ultrasonic treatment of the melt is needed which can be achieved by electromagnetic vibration – a method first proposed by Vives [14].
A technique that could be used to create steel nanocomposites by a casting route was proposed by Grants et al. [15]. There a steady 0.5 T strong axial magnetic field is applied to a liquid metal zone heated by electromagnetic induction. Superimposition of both fields creates an alternating radial magnetic body force in a molten sample which results in an acoustic pressure field that generates cavitation. In a first step the experiments were limited to light metals. The current study describes the first admixing of different ceramic nanoparticles in stainless steel by using this contactless magnetic sonication of the melt. Additional experiments have been performed with an increased value of the steady magnetic field using a superconducting magnet of up to 5 T for SiC particles in an Al-6%wt.Mg alloy and in Sn [16].

2. Cavitation and nanoparticle dispersion in liquid metals

2.1 Experimental approach

The experimental set-ups can be seen in figure 1. A tablet containing a mixture of matrix metal and nanoparticles (1) is placed between two cooled steel supports (2) that limit the axial oscillations of the molten part. The melting is done in an argon atmosphere the pressure of which is varied between 5-500 mbar in an enclosed quartz tube (5) and water cooled copper caps (3). For additional safety a support from a refractory material (6) is used. An alternating current (AC) induction coil (7) is used for melting the metal and a direct current (DC) magnetic field is directed by the magnet poles (9). Copper caps together with the copper shielding (8) protect the electromagnet poles from the alternating magnetic field. At Institute of Physics of University of Latvia a similar set-up has been installed using for the DC field a superconducting magnet of up to 4 T with a 300mm bore diameter (see figure 1 (c,d)).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Scheme (a) and photo (b) of experiment in the DC field up to 0.5 T; central part scheme (c) and illustration (d) for the experiment in the superconducting magnet.
The combined action of the AC and DC magnetic fields gives rise to pressure oscillations in the sample. The amplitude $p_A$ of those oscillations is, at least for large AC frequencies, simply given by \[ p_A = \frac{B_{AC}B_{DC}}{\mu_0} \] where $\mu_0$ is the vacuum magnetic permeability. In the above described experiments this pressure amplitude reached values of up to 50 kPa in the experiments with a DC field up to 0.5 T, whereas amplitudes up to about 400 kPa have been reached in the experiments with the superconducting magnet. However, the occurrence of cavitation is not characterized by definite threshold of this pressure amplitude but depends heavily on the availability of cavitation nuclei in the melt. Vives [14] estimated $p_A > 16$ kPa for the occurrence of cavitation, whereas Abramov [6] estimated a broad range of 150...800 kPa for it. Hence, for the present experiments not a continuous, but an intermittent observation of cavitation was to be expected.

The cavitation signal is measured by using four piezo elements (4), see figure 1(a). The height of the gap between the poles is 82 mm, the electromagnet provides up to 0.5 T in the melt zone. The maximum inductor r.m.s. current is $I_{AC} = 1300$ A which corresponds to $B_{AC} = 0.130$ T and the frequency of the AC source is around 14 kHz. Stainless steel powder (Cr16-18, Ni10-14, Mo2-3, C0.03, 5-20 µm) was mixed with TiB$_2$ (particle size 2-6 µm), TiO$_2$ (p.s. 0.01-0.03 µm), Y$_2$O$_3$ (p.s. 0.03-0.05 µm), CeO$_2$ (p.s. < 5 µm), Al$_2$O$_3$ (p.s. 0.02 µm) and TiN (p.s. 0.08 µm) with an approximate weight proportion of 2 % and afterwards the mixture was pressed in tablet form. The tablets were created by using a force of around 44 kN. After the melting is done a cylindrical sample with approximate dimensions of $h = 45$ mm, $d = 20$ mm is obtained which then is cut for examination.

For the experiments in the superconducting magnet the sample was prepared by compressing 50 nm SiC particles with coarse Al-6%wt.Mg alloy or Sn powder and then subjected to a superimposed 10 kHz AC field with 0.12 T amplitude and to a DC field of up to 4 T. The AC coil is placed inside the superconducting magnet, which is protected from the AC stray field by a 2 mm thick water cooled copper jacket. After melting of the sample the interaction is maintained for 10 min and then gradually reduced to solidify the sample.

2.2 Results

It is almost impossible to trace individual cavitating bubbles. Instead the noise emitted by numerous collapsing bubbles was recorded by using piezo elements. Cavitation theory suggests that signs of transient cavitation are sub-harmonics of the drive frequency $f_n = f_0/n$, $n = 2, 3...$ as well as ultraharmonics $mf_0 \pm f_n$, $m = 1, 2...$ emitted as sound by the collapsing bubbles [17]. The recorded sound spectra in case of steel with different particles can be seen in figure 2. The graphs show the above mentioned uncertainty of cavitation – with initial as well as working conditions in all cases being more or less the same, the power and character of the observed cavitation differs. The case with Al$_2$O$_3$ (a) shows a very weak sign of the phenomenon as a signal of half frequency which starts around $t = 1000$ s, disappearing in the middle of the experiment and returning before the end. The case with TiB$_2$ (b) has higher signal strength, however, the cavitation is not steady and has frequent interruptions. With TiO$_2$ (c) it was possible to achieve cavitation only in the final period of the experiment, around $t = 2300$ s, while the sample with Y$_2$O$_3$ (e) experiences a rather strong and continuous influence of cavitation. Two experimental trials should be highlighted, namely CeO$_2$ (d) and TiN (f). The increase in pressure in the melting cell leads to the appearance of a wide spectrum noise (marked by a dashed arrow). This change might be explained by cavitation going from stable to unstable oscillating bubble fields [18]. While in theory the ambient pressure should dampen the cavitation and first experiments in [15] were done in an evacuated cell in order to promote cavitation, it was found here that an increase in pressure promotes the occurrence of such unstable oscillating bubble fields. Likely, gas diffusion in
the melt increases the bubble sizes. Apparently, this increase has outweighed the decrease of negative pressure. That may explain the observed stronger cavitation signal under elevated ambient pressure.

![Temporal dependency of the sound power spectrum when cavitation is applied to 6 different samples – with Al₂O₃ (a), TiB₂ (b), TiO₂ (c), CeO₂ (d), Y₂O₃ (e) and TiN (f) particles. Full arrows indicate the start of cavitation, dashed ones the occurrence of a wide spectrum noise. Depth of logarithmic palette is 60 dB.](image)

**Figure 2.** Temporal dependency of the sound power spectrum when cavitation is applied to 6 different samples – with Al₂O₃ (a), TiB₂ (b), TiO₂ (c), CeO₂ (d), Y₂O₃ (e) and TiN (f) particles. Full arrows indicate the start of cavitation, dashed ones the occurrence of a wide spectrum noise. Depth of logarithmic palette is 60 dB.

As mentioned above and seen in figure 2, the cavitation onset varies depending not only on the pressure oscillation amplitude, but obviously also on the added particles and the trapped gas traces. Moreover, cavitation is only a necessary precondition for the dispersion of nanoparticles, the agglomeration and dispersion certainly depends also on the wetting between particles and melt and further influences. Hence, with the cavitation signals of figure 2 as basis, it was almost clear that a full dispersion of the nanoparticles without any regions or periods of agglomeration was not to be expected.

This is reflected in the micrographs shown in figure 3. The sample analysis revealed that particle admixing varies from dispersed to highly agglomerated phases. The most promising results were achieved with TiN (f) and Al₂O₃ (a), where particles, while still being in relatively small clusters (sub-millimeter in (a) and sub-micron sized in (f)) and not dispersed evenly, could be found in the bulk of the steel matrix. TiB₂ (b), TiO₂ (c) and CeO₂ (d) particles agglomerated near the boundaries in large, submillimeter clusters (dark gray). Y₂O₃ (e) can be found inside the steel matrix in a, most likely, eutectic form covered by MgS (light gray) which could be explained with some form of chemical reaction happening between the liquid steel and the particles. The superconducting magnet results showed that in the Al-Mg alloy SiC particles are fully dispersed (g) while in tin they still are concentrated in micron sized agglomerates (dark gray) (h).

The current findings indicate that one of the main factors of successful admixing of particles is the physical and chemical compatibility between the matrix material and the particles. The compound
should be chemically stable and able to withstand the harsh environment in the melt. In addition the admixing of the reinforcements is strongly dependent on the wettability by the matrix material. Research in this field is scarce due to the fact that the wetting varies with the steel composition – each steel grade could have a different contact angle with a particular substrate in a specific temperature range. Most contact angle measurements have been done with TiN and different types of carbon steel [19,20,21], which can be used to explain the current results and suggest possible improvements. It has been concluded that TiN can be wetted well (contact angle in some cases being as low as 40 degrees) by carbon steel which also can be confirmed with stainless steel in the present experiments.

Results obtained with Al$_2$O$_3$, MgO and Ti$_2$O$_3$ in [20], where wettability by iron and steel is examined, shows that oxides (103 degrees for Al$_2$O$_3$, 90 degrees for MgO) are poorly wetted by the iron melt, but in case of Ti$_2$O$_3$ and steel, the contact angle decreased from 140 to 90 degrees. Results from cavitation experiments are similar in tendency – TiO$_2$ and CeO$_2$ seem to be badly wetted by the used steel grade. On the other hand, Al$_2$O$_3$ shows a reasonably good wetting behavior, and the dispersion could be increased with increased cavitation influence.

![Micrographs](image)

**Figure 3.** Micrographs with different particle inclusions in a stainless steel matrix – Al$_2$O$_3$ (a), TiB$_2$ (b), TiO$_2$ (c), CeO$_2$ (d), Y$_2$O$_3$ (e), TiN (f) created using DC magnetic field of 0.5 T. SEM image with samples of Al-6%wt.Mg + 50 nm SiC particles (g), Sn + 50 nm SiC particles (h) and XRF analysis (i) showing Si distribution (white) created in the superconducting magnet. Figures (g,h,i) from [16] with permission.
To improve the dispersion the first idea is to enlarge the period during which the cavitation is applied as the contact angle is expected to decrease with time since the particle surface reacts with the steel and the creation of, e.g., a Ti(N,C,O) precipitation layer on a TiN particle leads to a decrease of the contact angle as TiC is known to have a good wetting behavior by liquid iron [19]. Additionally, the temperature achieved should slightly exceed the melting temperature as in some cases it has been shown that even a 20°C increase in temperature can decrease the contact angle by about 20 degrees [21].

Due to the high level of porosity (\(\rho \approx 5000 \text{ kg/m}^3\) for the samples compared to appr. 7700 kg/m³ as density of stainless steel) in the used tablets, there is reason to assume that TiB₂, TiO₂ and CeO₂ particles could have agglomerated around the gas bubbles in the melt and then were transported out of the matrix even before the application of cavitation. Taking into account these factors as well as searching for chemically stable reinforcement-steel pairs are the necessary next steps for a successful creation of steel composites by a liquid metal route.

2.3 Pulsed AC field

The continuous application of the AC induction heating may overheat the sample, which may limit the time of processing significantly or require an efficient cooling of the sample. Therefore, the idea of using a pulsed magnetic field which provides extremely high peak values while the time averaged heating is moderate was developed. The current pulses are generated with a high capacitance capacitor battery which is periodically discharged. In these experiments from 1 to 10 pulses per second are applied to the inductor which allows reaching a more than 1T peak magnetic field value. At first, a theoretical model was considered in order to understand the penetration of such pulses into a conducting volume [22] which allowed to derive relations for the pressure oscillation amplitude in the melt resulting from the superposition of an additional DC magnetic field. First experiments with such a pulsed AC field approach are in progress.

3. Summary

The experiments on a contactless electromagnetically induced cavitation and its use for the dispersion of nanoparticles in metal melts, although not yet entirely successful in creating steel composites, provide a valuable insight into the process and the related unresolved questions. By analyzing sound measurements it is possible to conclude that transient cavitation was achieved within the steel melt in all cases. The future aim is to develop a process in which by varying induction heating power, magnetic field, pressure and temperature in the melting chamber a full-scale transient cavitation could be achieved continuously.

It is difficult to disperse ceramic particles in a liquid steel, however not all important factors were yet considered in the present experiments. While TiN and Al₂O₃ revealed a good result and focus should be on improving dispersion of these reinforcements, the other particles should be further investigated as the processing time and temperature plays a key role in dispersing them. Only one type of stainless steel grade has been used in the experiments, however, different composition steels, e.g. various low carbon steels, should certainly be tested, although the mostly missing contact angle data leave the trial-and-error approach as the only option to proceed.

In order to reduce the heating action of the AC magnetic field on the sample, the idea of a pulsed AC current generated by a periodic discharge of a capacitor battery instead of a continuous application of the AC induction heater was developed. Related experiments are in progress.

Acknowledgments

The financial support of the Helmholtz Alliance “Liquid Metal Technologies – LIMTECH” is gratefully acknowledged.
References
[1] Verhiest K, Almazouzi A, de Wispelaere N, Petrov R and Claessens S 2009 J. Nucl. Mat. 385 308
[2] Dubuisson P, de Carlan Y, Garat V and Blat M 2012 J. Nucl. Mat. 428 6
[3] Franke P, Heintze C, Bergner F and Weißgärber T 2010 Materials Testing 52 133
[4] Bonnet F, Daeschler V and Petigand G 2014 Canad. J. Met. Mat. Sci 53 243
[5] Aparicio-Fernandez R, Springer H, Szczepaniak A, Zhang H and Raabe D 2016 Acta Materialia 107 38
[6] Abramov O V 1987 Ultrasonics 25 73
[7] Farmer A D, Collings A F and Jameson G J 2000 Int. J. Min. Proc. 60 101
[8] Bittmann B, Haupert F and Schlarb A K 2009 Ultrasonics Sonochemistry 16 622
[9] Suslick K S, Didenko Y, Fang M M, Hyeon T, Kolbeck K J, McNamara W B, Mdleleni M M and Wong M 1999 Phil. Transact. Royal Soc. A 357 (1751) 335
[10] Yang Y, Lan J and Li X 2004 Mat. Sci. Eng. A 380 378
[11] Choi H, Jones M, Konishi H and Li X 2012 Met. Mat. Transact. A 43 738
[12] De Cicco M, Konishi H, Cao G, Choi H S, Turng L S, P e r e p e z k o J H, Kou S, Lakes R and Li X 2009 Met. Mat. Transact. A 40 3038
[13] Shen M J, Wang X J, Li C D, Zhang M F, Hu X S, Zheng M Y and Wu K 2014 Mat. Des. 54 436
[14] Vives C 1996 J. Cryst. Growth 158 118
[15] Grants I, Gerbeth G and Bojarevics A 2015 J. Appl. Phys. 117 204901
[16] Kaldre I, Bojarevics A, Grants I, Beinerts T, Kalvans M, Milgravis M and Gerbeth G 2016 Acta Mat. 118 253
[17] Neppiras E A 1980 Phys. Rep. 61 159
[18] Cramer E and Lauterborn W 1982 Appl. Sci. Res. 38 209
[19] Xuan C, Shibata H, Zhao Z, Jönsson P G and Nakajima K 2015 ISIJ Int. 55 1642
[20] Xuan C, Shibata H, Sukenaga S, Jönsson P G and Nakajima K 2015 ISIJ Int. 55 1882
[21] Amadeh A, Heshmati-Manesh S, Labbe J C, Laimeche A and Quintard P 2001 J. Eur. Ceramic Soc. 21 277
[22] Grants I, Bojarevics A and Gerbeth G 2016 AIP Advances 6 065014