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Ultrasonic approach for surface nanostructuring

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ABSTRACT

The review is about solid surface modifications by cavitation induced in strong ultrasonic fields. The topic is worth to be discussed in a special issue of surface cleaning by cavitation induced processes since it is important question if we always find surface cleaning when surface modifications occur, or vice versa. While these aspects are extremely interesting it is important for applications to follow possible pathways during ultrasonic treatment of the surface: (i) solely cleaning; (ii) cleaning with following surface nanostructuring; and (iii) topic of this particular review, surface modification with controllably changing its characteristics for advanced applications. It is important to know what can happen and which parameters should be taking into account in the case of surface modification when actually the aim is solely cleaning or aim is surface nanostructuring. Nanostructuring should be taking into account since is often accidentally applied in cleaning. Surface hydrophilicity, stability to Red/Ox reactions, adhesion of surface layers to substrate, stiffness and melting temperature are important to predict the ultrasonic influence on a surface and discussed from these points for various materials and intermetallics, silicon, hybrid materials. Important solid surface characteristics which determine resistivity and kinetics of surface response to ultrasonic treatment are discussed. It is also discussed treatment in different solvents and presents in solution of metal ions.

1. Introduction

The generation of bubbles by acoustic cavitation has been studied for many years [1–5] also because of great prospects of using "green" ultrasonic treatment for surface cleaning [6–8] and nanostructuring [9–15]. The mechanism of bubble formation (Table 1, inset) may be qualitatively understood as follows: in the zone of negative pressure of the sound wave small volumes of lower liquid density or gas clusters may expand to form bubble nuclei. These do not fully collapse during the high pressure phase and are further expanded in the next low pressure phases. This process continues until reaching a maximum critical diameter depending on ultrasound frequency and solvent [16]. These bubbles inside liquids upon collapse create transiently temperatures more than 5000 K, pressures higher than 1000 atm with cooling rates above 10^8 K/s. Hence there is the potential of performing high temperature and high pressure processes, but with a reactor near room temperature and ambient pressure. Much knowledge of a behavior of homogeneous bubble cavitation and collapse dependent on ultrasonic reactor parameters is obtained by studying single bubble systems [17–19]. Important ultrasonic reactor parameters are presented in Table 1: (i) frequency, intensity and duration of ultrasonic process; (ii) temperature, pressure and gas content; (iii) solution and chemical species which can be added to the solution.

For surface cleaning and nanostructuring the processes of homogeneous bubble oscillations and following collapse are studied in multi-bubble systems [20–22]. Shock waves created during bubble collapse create microscopic turbulences [23]. This phenomenon increases the transfer of mass across the solid surface, thus increasing the intrinsic mass-transfer coefficient, as well as possibly creating or modifying existing coatings, such as thick hybrid metal/polymer coatings [24]. Alternatively, this phenomenon may result in thinning/pitting of the film [25].

When the bubble collapse occurs near a solid surface that is several orders of magnitude more extended than the cavitation bubble [26], the collapse occurs asymmetrically [27] and bubble microjetting is formed perpendicular to the solid surface (Fig. 1). These microjets have an estimated speed of ca. several hundreds of m/s and lead to pitting and erosion of the surface [28].

Microscopic turbulences and jetting lead to an enhancement in heterogeneous reactions (secondary cavitation-assisted processes) with active species formed in the reactor. Thus, a part of the vaporized molecules from the surrounding medium can dissociate to form radical species, such as $OH^{\cdot}$ and $H^{\cdot}$, for water sonolysis [29]. The radicals form by the hydrogen abstraction of RH additive

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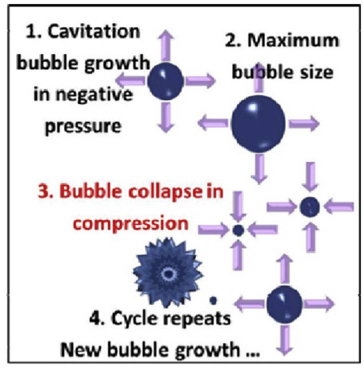
Table 1
Important aspects for fundamental cavitation assisted modeling as reactor parameters and initial material. Inset shows the mechanism of the cycle of homogeneous generation of bubbles by acoustic cavitation, according to Ref. [16] approximate time of a cycle ca. 400 µs.

Reactor conditions	Frequency, intensity and duration	
	T, p, gas content	
	Concentration of chemical species	solvent
		additives -surfactant -monomer -polymer - µ- and nano-particles
Surface Nature	Crystal structure:	molecular
		atom
	Mechanical property e.g. hardness:	(bio)polymers – "soft"
		others – "hard"
	Melting point	high
		low
	Reactivity e.g. tendency to oxidation:	oxidized
		resistant
	Hydrophilicity	hydrophilic
		hydrophobic



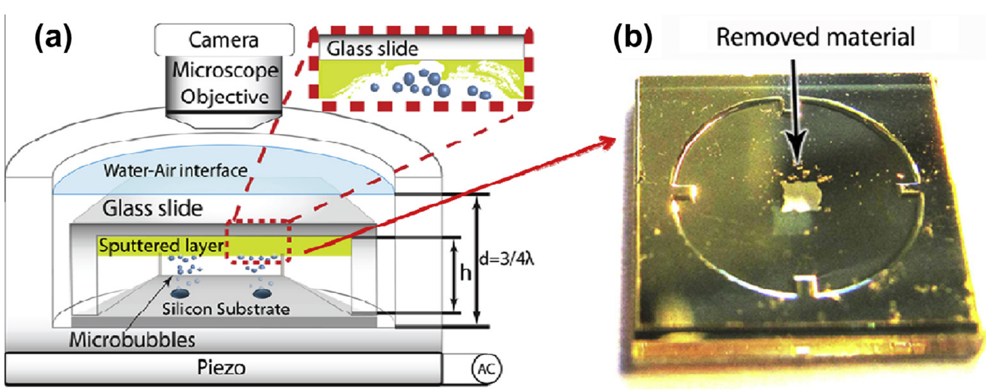


Fig. 1. (a) Schematic representation of the experimental ultrasonic device for controllable surface cleaning by cavitating bubbles. The gap between the glass slide and the silicon substrate $h = 100$ µm. The water column height is 5 mm. (b) A zoomed view of the same glass slide after exposure to cavitating bubbles from four pits in the cavitation cell described in this paper. The glass slide has sides of 10 mm. Reproduced with permission [6]. Copyright 2012, AIP Publishing.

molecules to form R$^{\cdot}$ and/or by the pyrolysis of RH molecules during bubble collapse [30].

There are efforts directed to predict or model the consequences, cleaning or nanostructuring, of ultrasonic surface treatment. In the work of Rivas et al. [6] a special ultrasonic device with in situ processes control was studied with the ability to locally remove deposited layers from a glass slide in a controlled and rapid manner (Fig. 1). The cleaning takes place as the result of cavitating bubbles near the deposited layers and not due to acoustic streaming. The bubbles are ejected from air-filled cavities micromachined in a silicon surface, which, when vibrating ultrasonically, generate a stream of bubbles that travels to the layer deposited on an opposing glass slide. Depending on the pressure amplitude, the bubble clouds ejected from the micropits attain different shapes as a result of complex bubble interaction forces, leading to distinct shapes of the cleaned areas. Acoustic droplet vaporization uses ultrasound to induce a phase transition of liquid droplets that are near their boiling point thus plays important role for surface modifications especially in the cases of high-temperature vaporized droplets. Thus it is important to control the modification of the surfaces via the concentrations of additives in the system (monomer, polymer) and establish the role of initial cavitation in acoustic droplet vaporization in different solutions. It was shown that the cleaning rates for several inorganic and organic materials can be more efficient compared to conventional cleaning equipment.

The influence of dissolved gases, for example CO_2 [31], also can regulate cavitation intensity and consequently cleaning efficiency.

There is still not sufficient knowledge of view of (i) identified for both aspects of cleaning and nanostructuring separately mechanistic causes of cleaning and surface modifications (e.g. shock wave, jet, shear flow, local heating), (ii) one not always finds surface cleaning if one sees surface modification or vice versa, however aspects of cleaning and nanostructuring can be intimately connected.

In our studies and the review we have focused on studies of the consequences of processes that occur at the cavitation interface and solid surface. We focus on further prospects of selective