PHYSICO-CHEMICAL ASPECTS OF ULTRASONIC METAL NANOSTRUCTURING

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Nowadays ultrasound appears to be a convenient, safe and time-effective method of solid nanostructuring for materials science and engineering applications. Passing of ultrasonic (US) waves through the liquid results in the formation of cavitation bubbles that can grow either linearly and provide stable cavitation or nonlinearly (attributed to transient cavitation) and collapse creating the local areas with extremely high temperatures and pressures (up to 10000 K and 1000 atm [1]). Such non-equilibrium conditions can provide the possibility of the potential application of ultrasound for surface oxidation for the formation of oxide/hydroxide structures with highly developed porous surface, metastable phases that could not be formed in the absence of ultrasound (*e.g.* in the cases of conventional heat treatment).

Herein, we investigated the aspects of (i) ultrasonic structuring of metals with different chemical activity in various liquids (water, ethanol, ethylene glycol) by means of the cavitation bubbles collapse as well as (ii) the influence of the chemical activity of metal and the formed products on the cavitation activity development.

US treatment of highly reactive metals (magnesium, aluminum, zinc) in water is characterized by the oxidation of metal surface, leading to the transformation of the porous structure in accordance with the duration of US treatment. These processes denote the formation of hydroxide phases and highly developed surface area with the formation of metal sponges [2]. Metals with less chemical activity (*e.g.* titanium) are characterized by the transformations of the surface layer leading to the formation of defective structure [3]. Noble metals such as gold, silver and platinum are not modified during ultrasonic treatment in water [4].

US treatment in non-aqueous media (ethanol, ethylene glycol) showed the tendency to suppress the oxidation of metal surfaces with different reactivity (for reactive magnesium as well as for the high resistant titanium) resulted from the scavenging of the reactive oxygen species by the molecules of ethanol and ethylene glycol [5].

The sonochemical treatment of metal particles is characterized by the oscillations of the crystallite sizes [6] which can be explained by the two opposite processes – recrystallization and growth of the crystallites by means of atomic diffusion. These processes are the sequence of the formation of local high temperatures and pressures occurred after the formation of “hot spots”. These phenomenon depends on the nature of the used liquid dispersed medium (*e.g.* heat capacity, vapor pressure *etc.*), duration of treatment.

For the porous structure preparation for high resistant metal (*e.g.* titanium that is widely exploited in engineering, shipbuilding, biomedicine) the use of medium with higher chemical etching property should be used. In our case we used aqueous alkaline solutions [3]. However, concerning the biomedical applications, titanium implants coated with native oxide layer is regarded as a bio-inert material still possibly leading to high risks of inflammation or abruption inside the organism. Thus, it is necessary to obtain the biocompatible coating with appropriate porous structure, roughness and adhesion. For this reason, US treatment of titanium in alkaline solutions leads to the formation of porous layer based on metal foam with incorporation of titania and sodium titanates [3]. Besides demonstrating good biocompatibility properties, these coatings also possess the photocurrent under 405 nm irradiation [7].

Concerning the study of the evolution of cavitation activity during sonochemical treatment of metal particles, we found out that during US treatment of reactive magnesium particles, the released hydrogen gas is involved in the development of cavitation bubbles. The cavitation bubbles activity is characterized by the complicated behavior, starting from the nucleation of the bubbles, their consequent growth by several mechanisms, fragmentation, reaching the critical value with further collapse. In addition, in the conditions of ultrasonic treatment magnesium particles are characterized not only by the formation of porous hydroxide layer but also the presence of magnesium hydride which was not formed in the absence of ultrasound. On the examples of other metals with lower chemical activity, it has been demonstrated that the ability of metal to produce hydrogen plays an essential role in the development of cavitation activity.

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