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Controlled “golf ball shape” structuring of Mg surface under acoustic cavitation

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ABSTRACT

This manuscript describes the original structuring of Mg materials under ultrasound irradiation in mild conditions. Golf ball like extended structures can be prepared in dilute oxalic solutions at 20 °C under high frequency ultrasound (200 kHz). An original approach carried out through iterative 3D reconstruction of sonicated surfaces is used to describe surface evolutions and characterize the formed microstructures. A combination of SEM, ICP-AES, contact-angle measurements, and 3D image analyses allows to characterize the roughness and mass loss evolutions, and investigate the mechanism of formation for such architectures. A screening of the sonication experiments clearly points out an ultrasound frequency dependency for the effects generated at the surface. 200 kHz sonication in 0.01 M oxalic acid provides an unprecedented manufacturing of Mg samples which result from a controlled and localized dissolution of the material and characterized by a strong wetting surface with a roughness of 170 nm. The additional formation of newly formed secondary phases appearing with surface dissolution progress is also deciphered. More generally, the ultrasonic procedure used to prepare these engineered surfaces opens new alternatives for the nano- and micro-structuring of metallic materials which may exhibit advanced physical and chemical properties of potential interest for a large community.

1. Introduction

Due to their low density and high specific strength, Mg and its alloys have been widely used in automotive, aerospace, or microelectronic industries [1]. As a result of their additional low toxicity and biodegradability, Mg-based materials have demonstrated a high potential for biomedical applications such as stents, implants, or orthopedic components [2–6]. However, their low corrosion resistance in aqueous physiological environment may hinder such material applications. Several strategies have been therefore proposed to overcome this problem and improve Mg material biodegradability including the development of new Mg alloys, the control of the microstructure, and the development of protective coatings [4–6]. This last is highly linked to surface roughening and structuration which program the efficiency of adherence of the coating [6,7]. Furthermore, surface wetting plays a crucial role for coating developments [6,8]. Several methods have been reported in the literature for metallic surface structuring including electrochemical machining [9], plasma etching and laser irradiation [6,8], chemical etching [7,10], and ultrasound irradiation [11,12]. Among those techniques, ultrasound irradiation presents the advantages of being relatively cheap and simple to use, without direct contact with the samples, and with a relative universality towards the possible materials to be treated.

Ultrasound has been used for decades in homogeneous solutions and heterogeneous systems for surface treatments (degreasing, cleaning and decontamination for instance), materials synthesis, water remediation and catalysis, extraction and emulsification, etc [13–15]. In a liquid medium, effects attributed to ultrasound treatment do not result from the direct interaction of ultrasonic waves with the matter but from the acoustic cavitation phenomenon which refers to the nucleation, growth and rapid implosion of gas- and vapor-filled micro bubbles. At the final stage of collapse, a non-equilibrium plasma is formed in the bubbles, and very high and transient temperatures (several thousands of degrees) and pressures (several hundreds of atmospheres) are reached [16]. Excited and radical species (such as $H^{\cdot}$ and $OH^{\cdot}$ for water sonolysis) are generated that act in chemical reactions while the treated solutions are maintained at ambient temperature and pressure [17,18]. When bubbles implode at the vicinity of extended surfaces, pressure gradients occurring at the bubble interface may leads to an asymmetric collapse generating an inrush of liquid (micro-jet) passing through the bubble and striking the surface with a very high velocity (over 100 m/s at 20 kHz) [19,20]. Besides, shock-waves resulting from the implosion

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of spherical cavitation bubbles are supposed to reach pressures of several GPa that may combine to micro-jets and participate in surface erosion and micro-deformation, fragmentation of grains, and depassivation of metallic surfaces [21–24].

Recently, a study reported the ultrasonic activation of Mg particles through surface depassivation for the reduction of nitrates contaminating water [25]. Although sonication of solutions and particles has often been reported, the ultrasonic control of extended surface structuration and dissolution is an emerging topic that remains scarce in the literature. Most of the researches dedicated to ultrasonic surface treatment are related to cleaning or erosion and mainly focus on stainless steel, aluminum alloys and titanium [26–29], or glass and silicon wafers [23,30]. Furthermore, most of the related studies have been carried out at low frequency ultrasound (20–60 kHz) where mechanical effects of ultrasound are generally said to be more efficient thus neglecting high frequency domain [11,27,29,31]. In addition, the understanding of the non-equilibrium physical conditions and the complexity of the mechanisms involved at the interface remains often elusive and poorly understood. In this study, we focus on the behavior of pure Mg surfaces in aqueous solutions under ultrasonic irradiation. Several important parameters are investigated such as the ultrasonic frequency, duration of treatment, type and concentration of solutes, etc. An original approach carried out through 3D reconstruction of sonicated surfaces is used to describe the surface evolutions. The evolution of the surface morphology and of the chemical composition of the solutions are followed and discussed. A structuration mechanism is then proposed.

2. Experimental

2.1. Materials and solutions

Magnesium discs (99.9% purity) were purchased from Good fellows and were stored under normal conditions at room temperature and atmospheric pressure until use. They exhibit a diameter of 25 mm and a thickness of 0.5 mm. Chemicals with a high purity were provided by Sigma-Aldrich. The various solutions were prepared with milli-Q water having a resistivity higher than 18.2 MΩ.cm at 25 °C.

2.2. Experimental set-up

Sonications were carried out in a home-made thermostated batch reactor (250 mL). The cylindrical reactor is supplied with several entries for the parameter controls and allows several configurations. Low frequency experiments were carried out at 20 kHz with a plunging probe maintained at a reproducible distance from the sonicated sample as already described in the literature [23]. Ultrasound propagates from the top of the cell and the sample is maintained on the bottom with a tight Teflon part. High frequency experiments required a different configuration. The cylindrical reactor was mounted on top of a piezoelectric transducer (scheme presented Fig. S1, Supporting information). A picture of both configurations is presented Fig. 1. For 100 kHz ultrasound a SinapTec Lab500 generator was used, whose maximum electrical power is 120 W. 200 kHz and 1 MHz ultrasound were provided by an Elac Nautik transducer connected to a generator able to supply an electrical power up to 300 W (T & C Power Conversion, Inc.). Depending on the experiment and the generator stability, a frequency deviation of ± 5 kHz can be noticed for the 200 kHz transducer. High frequency experiments required stirring of the sample to avoid the accumulation of bubbles at the surface which could cushion the cavitation and limit the effects.

Unless otherwise specified, stirring for the high frequency experiments was 200 rpm. Preliminary experiments dealing with stirring effect in the presence of ultrasound can be found in Fig. S2, Supporting Information. Low frequency experiments (20 kHz) did not require such stirring. The rotation of the sample was provided with a Teflon bar

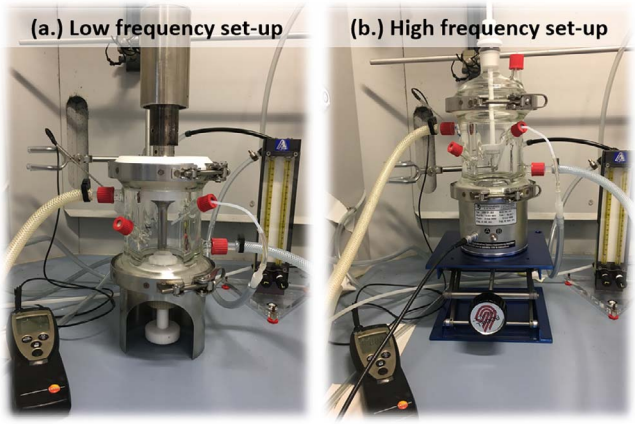

Fig. 1. Picture of the reactors used for Mg surface sonication at (a) low and (b) high frequency ultrasound. Both set-ups enable the control of the temperature and atmosphere and allow solution sampling and the control of the sample position in the cell.

connected from the top of the reactor to a motor (VWR VOS 14 Agitator). The tightness of the reactor was ensured by a machined Teflon stopper on top of the reactor which allowed the rotation of the bar. The Mg surface was stuck with microscopy carbon tabs on a Teflon sample holder which was screwed to a bar and was sonicated at reproducible distance (6 cm and 1.5 cm, for high and low frequency experiments, respectively) from the transducer. Solution sampling was carried out through a septum connected to the cell. Whatever the experiment, a thermocouple was immersed into the solution from the side of the reactor and a cryostat (Huber Pilot One) was used to maintain the solution temperature at 18 ± 2 °C. For sonolysis, the acoustic power density P_{ac} ($W.mL^{-1}$) transmitted to the solution was measured using the conventional thermal probe method in agreement with the literature [23]. An equivalent acoustic power of 0.07 $W.mL^{-1}$ was used for each frequency experiment except for 1 MHz experiments which were carried out at 0.14 $W.mL^{-1}$. The duration of each experiment was comprised between 30 and 90 min. All the solutions were sparged and saturated with Ar gas during sonication or stirring experiments at a stable flow rate of 100 $mL.min^{-1}$.

2.3. Analyses

Mg surface dissolution was evaluated by inductively coupled plasma optical emission spectroscopy (ICP-OES supplied by Spectro Analytical Instruments GmbH and equipped for axial plasma observations). During experiments, solution aliquots (1.5 mL) were sampled through a septum at regular time intervals and were diluted with 0.3 M HNO_3 to the appropriate concentration prior to analyses. Sample concentration was given against an external calibration curve prepared between 0.5 and 15 ppm. Initial dissolution kinetics (W_0) was then calculated from a linear regression by fitting the measurements observed during the first 30 min of sonication. After treatment, Mg surfaces were rinsed with few milliliters of milli-Q water before being dried with an air blow gun.

Surface energy differences were evidenced by contact angle measurements with a Drop Shape Analyzer (DSA100S, KRÜSS). A couple (n) of sessile drops was formed at random on the sample surface by dosing 5 μL of pure water with an automated syringe situated on the top of the surface. An image of each drop was recorded by a camera and transferred to a software which fits the contour of the drop shape with a geometrical model. The contact angle (θ_i) is given by the angle created between the calculated drop shape function (shape line) and the sample surface (baseline). The given contact angle ($\bar{\theta}$) was calculated as an average value ($n > 8$) of all the sessile drops deposited at the surface (Eq. (1)).