

Effect of Ultrasounds Irradiation on the Electrolytic Growth of Nanocrystalline Ni Films

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The present study reports the effects of ultrasounds irradiation on both charge transfer processes and interfacial structures in acid nickel sulfate electrolytes by various electrochemical methods. Moreover, the surface structure of electrolysis product-Ni film was evidenced by AFM. In order to determine optimum electrolysis parameters, we investigated the current-potential curves (voltammograms) at copper electrode and Ni ion collision speed with Cu substrate for different powers of ultrasonication processes. The bath efficiency has been also studied as a function of the time and the current density applied. The ion collision speed, bath efficiency, the hardness, the brightness and the adherence of the electrodeposits increase with the ultrasonic agitation, in comparison with the same film produced from still or magnetic stirred baths. Surface analyses of Ni films are performed using atomic force microscopy (AFM). Both surface roughness and grain size are the important factors in all areas of nanotribology and in evaluating the quality of a nanostructured surface operation. The results show that there exists optimum ultrasound sonication intensity where the mechanical properties of the Ni films are mostly enhanced. Moreover, results indicate that the grain size of nanocrystalline Ni film change with different sonicating intensity.

Keywords: sonoelectrochemistry, electrodeposition, nanocrystalline film, atomic force microscopy

It has been showed that making less in size of materials to nanoscale brings out peculiar properties which have not been observed in the bulk materials [1]. The quantum size effects of nanomaterials may induce unique electronic, optical and magnetic properties compared with those in traditional bulk materials. Their nanometer-scale dimensions may allow new structures that could serve as potential building blocks new devices. The quantum size effects of nanomaterials may induce unique electronic, optical and magnetic properties compared with those in traditional bulk materials. Their nanometer-scale dimensions may allow new structures that could serve as potential building blocks new devices. In the last decade, many methods have been explored to produce various nanomaterials, such as gas-liquid precipitation, molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), organometallic vapor phase epitaxy (MVPE), electrochemical methods, solvothermal methods, ac-radiation synthesis, microwave assisted preparation and sonochemical synthesis et al [2, 3]. Among these methods, sonochemical synthesis has been paid more extensive attention due to its special potential applications. Currently, the sonochemical process has been proved to be a useful technique for generating novel materials with unusual properties, since it results in particles of a much smaller size and high surface area than those produced by other methods. The chemical effects of ultrasound, which arise from acoustic cavitation, formation growth and implosive collapse of a bubble in a liquid, will produce unusual chemical and physical environments [4, 5].

Previous works [6-12] have shown that ultrasonic irradiation yield interesting effects (e.g. good yields, short reaction times and mild reaction conditions) and that the plating rates and deposit properties can be improved

considerably, especially if ultrasonic irradiation takes place during both activation and plating steps [13]. Moreover, there is an upsurge of interests in the use of sonoelectrochemistry in other subject areas such as the production of active metal particles, electrosynthesis, corrosion and electrochemical dissolution, the deposition of polymer films [14-18]. In sonoelectrochemistry, the effects of ultrasonic irradiation on mass transport processes in reversible electrochemical systems have been widely reported [1, 2]. However, it was evidenced that the imposition of an ultrasound accelerated charge transfer processes in electroplating systems of nickel [3] and copper [4], the mechanism of contributions of ultrasound to charge transfer processes has not been elucidated in detail.

Here, the application of ultrasound in electrodeposition process of metallic (Ni) coating (thin films) is discussed. A critical review concerning to cathode process under ultrasound irradiation, e.g. the voltage-current characteristic of the electrolyze cell irradiated at various ultrasonic intensities and the estimation of average collision velocity of Ni ions on the cathode, is discussed. Moreover, the surface structure of deposits obtained from silent and, respectively, under ultrasounds electrolyte irradiation is also given. Finally, criteria for electrodeposition of thin films under ultrasounds irradiation are discussed.

Experiment description

Experimental apparatus

Figure 1 shows a schematic representation of the electrodeposition cell used in our experiments. Halfway between two Ni anodes fixed to the lateral walls of the parallelepipedic electrolyze cell, a mobile cathode is suspended by a torsion metal thread, rigidly fixed by two consoles.

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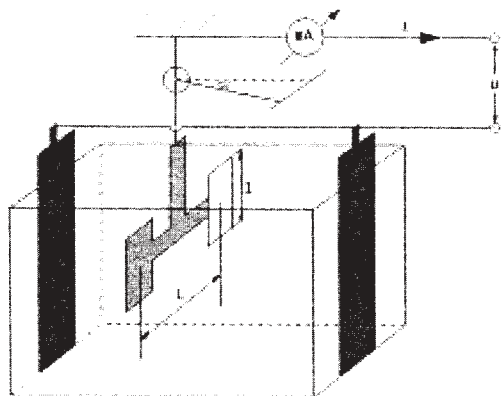


Fig. 1. Schematic representation of the electrodeposition cell

The mobile cathode was made of thin copper sheet having the shape shown in figure 1. Lateral blades are square ($l = 3 \times 10^{-3} \text{ m}$) and are separated by a copper strap of 2 mm width; the distance between the centres of the lateral blades is $L = 5 \times 10^{-2} \text{ m}$. One of the lateral blades as well as the linking strap was covered with varnish to avoid electrodeposition (the hachured surface in fig. 1). A mirror O is attached to the torsion thread whose torsion constant is $c = 7.2 \times 10^{-6} \text{ Nm/rad}$. Using a light beam and a ruler R we can determine the rotation angle $\alpha = d/D$ ($D = 2 \text{ m}$).

Ultrasound generation

All experiments were performed with a high frequency generator of 2 MHz from electronic service, at various ultrasonic intensities: 1, 2, 4, 6, 8 and 10 kW/m^2 , in a electrolyze cell filled with 400 mL liquid electrolyte. Ultrasonication is produced perpendicular to the electrolyte surface that is perpendicular to the ionic current and parallel to the surface of mobile cathode hung up vertically. In order to determine precisely both ultrasound parameters in bath and agitation-induced effects, the characterization of exposure conditions was needed. The transducer emission surface was 3.2 cm^2 and the ultrasonication time of 30 s. Acoustic power transmitted to the liquid electrolyte was determined by calorimetry [21]. Mass transfer measurements were characterized by electro-diffusion method [22–24].

Electrodeposition process

As supports of Ni deposits (thin films) copper conductive substrates of $50 \times 5 \times 3 \text{ mm}$ were used previously electrodeposited on a sensitized and activated polycarbonate plates. Table 1 summarizes the condition for Ni film electrodeposition.

Before Ni electrodeposition, the copper substrate was chemically cleaned with sodium hydroxide aqueous solution for 5 min. It was used an aqueous electrolyte based on nickel sulphate. For solution $\text{pH} = 1.8$ and bath temperature 300 K, the current density was adjusted during deposition to 12 mA/cm^2 .

Table 1

CHEMICAL COMPOSITION AND OPERATING CONDITIONS OF THE PLATING BATH

Bath composition	
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	250 g/l
H_3BO_3	15 g/l
$\text{NaC}_2\text{H}_3\text{SO}_3$	0.8 g/l
Operating conditions	
pH	1,8
Deposition time	36 min
Temperature	300 K

Results and discussion

The use of ultrasounds during the electroplating causes the formation of cavitation bubbles, which collapse on the solid surface and promote the agitation of the solution. These microjets directed towards the surface enhance the momentum, heat and mass transfer into the electrolytic bath [2, 3]. So, the diffusion layer near the cathode is decreased [4] and the electrode surface is activated, advancing conditions to obtain good electrodeposits.

The current-voltage characteristic of electrolytic cell

A typical voltametric curve exhibits a sigmoidal current response yielding a signal plateau at mass transport limited potential. Only the steady state value is considered. Figure 2 shows the current-voltage characteristic of the electrolytic cell. This characteristic has a linear variation between 2V and 4V applied voltage.

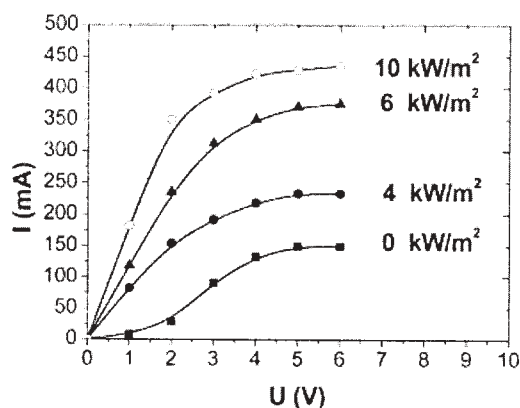


Fig.2. The current-voltage characteristic of the Ni electrodeposition cell

By applying a continuous voltage U on electrolytic cell electrodes, an electric field occurs between the anode and cathode. In the presence of this field, in the electrolyte occurs a continuous electric current with two components faradic electric current and non-faradic electric current. As a result of the faradic current positive ions cross the boundary of potential and, in the end, „fall” on the cathode with a certain average velocity v_f . Because after the ion neutralization their adsorption at the surface cathode takes place, we can consider that the ions plastically „collide” the cathode. Due to the irreversible processes that take place in electrolytic cell, the electric current I changes function on tension voltage U . The silent system (fig. 2, curve-0 kW/m^2) shows a flat plateau, the ‘limiting current’, while in the case of ultrasonication, the shape is a characteristic smooth increase for all ultrasounds intensities as shown in figure 2 (curves: 4, 6, 10 kW/m^2). As a consequence, the surface efficiency of an electrode increases when is exposed to the ultrasonication and this may be useful in the design and assembly of practical sensor systems [25]. The current-voltage characteristic is specific for each electrolytic cell.

The collision velocity between the Ni ions and the cathode in silent electrolyte

For the begining, we attempt to calculate the expression for average velocity of collision of the Ni^{2+} ions with the Cu cathode [7, 8]. At the same time, we will emphasize the way in which the mentioned proportion changes when the electrolyte is under the effect of ultrasounds.

Considering that between 2V and 4V the number of ions which change collision speed with one unit is proportional

to the voltage applied to the clamps of the electrolytic cell, that is:

$$\frac{dN}{dv_i} = aU \quad (1)$$

The first member can also be written as:

$$\frac{dN}{dU} \frac{dU}{dv_i} = b \frac{dU}{dv_i} \quad (2)$$

Here a and b are proportionally constants. From relations (1) and (2) results:

$$\frac{dU}{dv_i} = A \cdot U \quad (3)$$

where $A = a/b$, respectively

$$\frac{dU}{U} = A \cdot dv_i \quad (4)$$

By integration we get:

$$\ln U = A \cdot v_i + C \quad (5)$$

We consider $C = \ln U_0 = 0$, ($U_0 = 1$ V) and, finally, results:

$$v_i = \frac{1}{A} \cdot \ln U \quad (6)$$

Because $\frac{1}{A}$ has the physical dimension of velocity, we

consider that the proportion is the same as one tenth of the average velocity of the molecules according to Maxwell's distribution, that is:

$$\frac{1}{A} = 0.16 \sqrt{\frac{RT}{M}} = 33 \text{ m/s} \quad (7)$$

with $R=8310$ J/kg K; $M=59.7$ kg/kmol; $T=300$ K.

From (6) and (7) results the theoretical expression of the average velocity of collision between Ni ions and cathode (substrate), v_i :

$$v_i = 33 \cdot \ln U \quad (\text{m/s}) \quad (8)$$

Due to the collision between Ni ions and substrate (fig. 1), the system rotates with an angle α . At the equilibrium we can write:

$$\frac{FL}{2} = c \frac{d}{D} \quad (9)$$

$$F = \sum_{i=1}^N m_i \frac{|\Delta v|}{\Delta t} = m \frac{|\Delta v|}{\Delta t} = m \frac{v_i}{\Delta t} \quad (10)$$

Here, m is the deposited mass, $|\Delta v| = |v_f - v_i| = v_i$ that is approximately the same as the average velocity of the incidental ions \bar{v} and Δt is time after that the Ni ion velocity becomes zero.

According to Faraday's law:

$$m = \frac{1}{2} k i \Delta t \quad (11)$$

Considering $\Delta t \approx \Delta t$, we obtain the following expression for the experimental value of the average velocity of collision between Ni ions and the cathode:

$$\bar{v} = \frac{2cd}{kild} = 0.48 \frac{d}{i} \left(\frac{m}{s} \right) \quad (12)$$

Figure 3 shows the tension voltage dependence of current density and Ni ion collision velocity for a silent electrolysis bath.

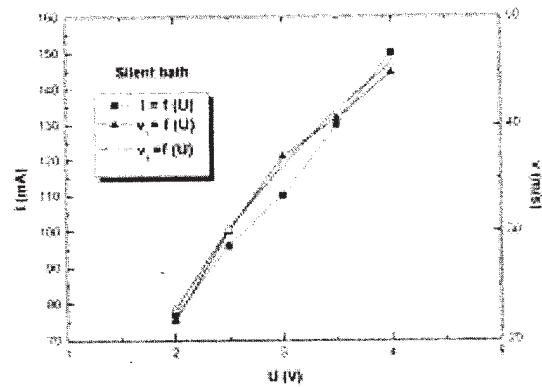


Fig. 3. Current density and ion collision velocity as a function of tension voltage in silent electrolysis bath

The collision velocity of the ions against the cathode and current intensity in the silent bath continuously increases with the increase of the voltage. A good correlation was found between experimental values (fig. 3) and those calculated (12).

In the case of the electrolyte ultrasonication, at the place of the mobile cathode with the frequency of $f = 2$ MHz and different intensities I , it was found an increase of the average collision velocity with the increase of the intensity of ultrasounds.

Figure 4 shows the experimental ultrasound intensity dependence of current density and Ni ion collision velocity for an ultrasonicated bath. The collision velocity reaches a plateau value at high ultrasound intensities, while the current intensity continuously increases in an ultrasonicated bath. This means that at higher ultrasonication intensity, higher than $5-6 \times 10^3$ kW/m², the effects of ultrasounds irradiation on the electrode process keep the same.

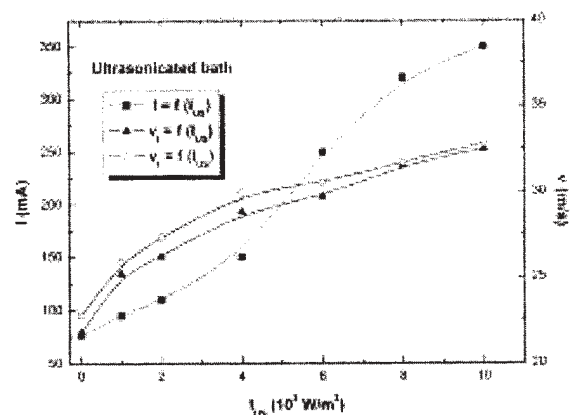


Fig. 4. Current density and Ni ion collision velocity as function of ultrasound intensity at 2 V tension voltage between electrodes

Through empirical trials we established a relation for the calculation of the average collision velocity according to the intensity I of the ultrasounds:

$$\bar{v}_i = 22.8 + 0.1\sqrt{I} \quad (13)$$

Therefore, normal collision velocity changes function of ultrasounds intensity as $I^{1/2}$. A good correlation between experimental and theoretical values is observed.

The changes in average collision speed under the effect of ultrasounds are mainly due to the changes in various characteristic values of the electrolytic process under action

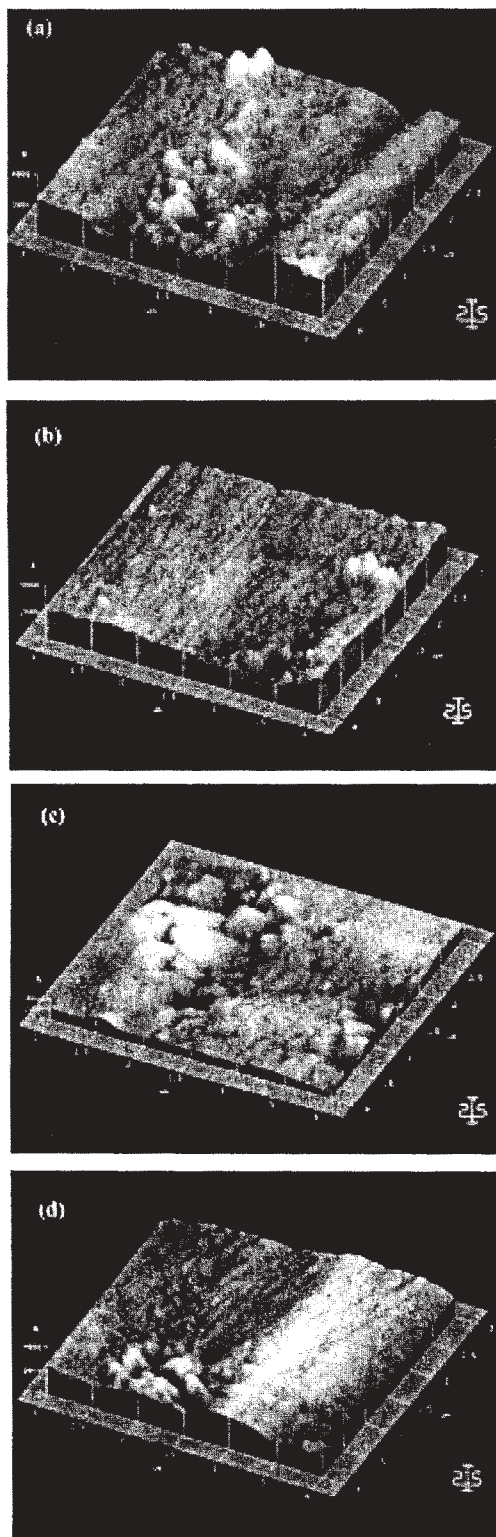


Fig. 5. Surface AFM images of nanocrystalline Ni films as function of ultrasound power realized under ultrasonic irradiation at 2 MHz. Picture (a): silent conditions. Picture (b): ultrasonic irradiation at 2 kW/m². Picture (c): at 6 kW/m². Picture (d): at 10 kW/m²

of ultrasounds such as: electrolyte conductivity, dehydration degree, electric permittivity. The imposition of ultrasound gave rise to decreasing cathodic overpotential, increasing exchange current density and accelerated the charge transfer process at the metal–electrolyte interface in the electrodeposition, and these effects depended upon the ultrasonic frequency. The values of exchange current density were dependent upon the measured electrode potentials.

The surface microstructure of Ni films

Figure 5 shows AFM images for some selected Ni films. The grain average size varies as function of ultrasound power, for 2 Mhz frequency, and their distribution all along the sample is altered (fig. 5). For a 2 kW/m² intensity, a smooth film surface with fine grain structure (nanograins) is evidenced (fig. 5, Picture b). An analogous surface structure was evidenced in a previous work [3] where such fine grained surface structure was observed on Ni electrodeposited in presence of organic inhibitor, such is thiourea [27]. AFM pictures of ultrasonicated films (fig. 5, Picture b-d) illustrate this, showing grain arrangements in the mat areas as though the deposit were made without ultrasound irradiation (fig. 5, Picture a), with small, rounded and unorganised grains. In the bright areas, grains are organised in perpendicular lines to wave propagation direction. Because grain size depends on ultrasonic power, this leads us to consider that mat areas correspond to pressure nodes. We can see that in bright area which corresponds to wave propagation direction, nanograins have pyramidal forms and do not exhibit a privileged orientation, with low ultrasound influences. Finally, ultrasonic irradiation does not modify deposit thickness for low and high ultrasonic power (2 or 10 kW/m²), but it seems that there is a little thickness diminution for intermediary ultrasonic power (fig. 5, Picture c: 6 kW/m²).

AFM is the perfect tool for quantitatively detecting and making visible roughness and textures in the nano range. Controlling roughness and texture down to only a few nanometers is very important in various areas of research and industry. Certain optical and/or mechanical characteristics of materials, e.g. friction characteristics, depend on the nano roughness. The AFM images can be cut and various parameters, such as the mean roughness depth Rzm, the arithmetic average roughness depth Rza, the root mean square roughness Rqm or the arithmetic average roughness Rqa, can be quantitatively detected and visualized along these cuts. The measured and calculated values of roughness for Ni film irradiated at different ultrasound powers are summarized in table 2.

Table 2
ROUGHNESS OF ULTRASOUND IRRADIATED NI FILMS FOR DIFFERENT ULTRASOUND POWERS

I _{US} (kW/m ²)	Rzm (nm)	Rza (nm)	Rm (nm)	Rqa (nm)
0	3.120	0.034	34.946	25.501
2	1.170	0.075	36.827	27.109
6	5.070	0.289	90.421	69.700
10	3.120	9.005	41.252	33.571

The properties of ultrasound irradiated Ni films are improved using low ultrasonic power, short irradiation times and high frequencies. It is known that normal grain growth requires a certain optimum current density [26]. Finally, under ultrasound waves, the film is compact and the effect of the typical mechanical action imposed by bubbles cavitation can be seen on the surface of electrodeposited metal [7]. This structure confirms the effect of ultrasounds in the production of harder deposits.

Conclusions

The speed at which the ions collide the cathode during the deposition processes has a significant importance concerning the structure of the thin films. The fact that ion speed is different when the electrolyte is under the action of the ultrasounds leads to changes in their properties. In

the future, the changes in the structure of the thin electrodeposited films, as well as the changes of the coercive field and of the saturation magnetization of the film must be analyzed at the same time with the changes of the velocity at which the ions collide the cathode.

It may be pointed out that the experimental results have shown that the physico-mechanical properties of electrodeposited nickel undergo substantial changes when the process is accompanied by high current densities.

Ultrasounds action on nickel electrodeposits reduces substantially the polarization phenomena, enhances the efficiency of the plating rate and changes the physicochemical properties of the electrolytic nickel.

Under the influence of ultrasound it is possible to produce hard, compact and adherent electrodeposits even using high current densities in the electroplating process.

References

1. MASON, T.J., LUCHE, J.-L., R.V. ELDICK, R.V., HUBBARD, C.D. (Eds.), *Chemistry under Extreme or Non-Classical Conditions*, Wiley, New York, 1997, p. 317
2. KELSALL, R., HAMLEY, I.W., GEOGHEGAN, M. (Eds.), *Nanoscale Science and Technology*, Wiley, New York, 2005
3. SULTANU, N., SANDU, I., SANDU, I.-G., *Rev Chim (București)* **54**, 2003, p. 670
4. SUSLICK, K.S., DOKTYCZ, S.J., *Advances in Sonochemistry*, 1, Mason, T.J. (Ed.), Elsevier-JAI Press, 1990
5. WALKER, R., *Advances in Sonochemistry*, **3**, Mason, T.J. (Ed.), Elsevier-JAI Press, 1993.
6. SUSLICK, K.S., *Ultrasound, its Chemical, Physical and Biological Effect*, VCH, Weinheim, Germany, 1988
7. ZHAO, Y., BAO, C., FENG, R., CHEN, Z., *Ultrasonics Sonochemistry* **2**, 1995, p. 99
8. TOUYERAS, F., HIHN, J.Y., DOCHE, M.L., ROISARD, X., *Ultrasonics Sonochemistry* **8**, 2001, p. 285
9. COHEN, R.L., WEST, K.W., *Technologies Internationales* **80**, 2002, p. 26
10. BONRATH, W., *Ultrasonics Sonochemistry* **10**, 2003, p. 55
11. SCHEFFEL, M., PH.D. Thesis, Iași, 1979
12. MASON, T.J., LORIMER, J.P., *Applied Sonochemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2003.
13. TOUYERAS, F., HIHN, J.Y., DELALANDE, S., VIENNET, R., DOCHE, M.L., *Ultrasonics Sonochemistry* **10**, 2003, p. 363
14. LIGIER, V., HIHN, J.-Y., WÉRY, M., TACHEZ, M., *J. Appl. Electrochem.* **31**, 2001, p. 213
15. DOCHE, M.L., HIHN, J.-Y., TOUYERAS, F., LORIMER, J.P., MASON, T.J., PLATTES, M., *Ultrasonics Sonochemistry* **8**, 2001, p. 291.
16. MIZUKOSHI, Y., SEINO, S., OKITSU, K., KINOSHITA, T., OTOME, Y., NAKAGAWA, T., YAMAMOTO, T.A., *Ultrasonics Sonochemistry* **12**, 2005, p. 191
17. ZHANG, X., ZHAO, H., TAO, X., ZHAO, Y., ZHANG, Z., *Materials Letters* **59**, 2005, p. 1745
18. SULTANU, N., SANDU, I., *Rev. Chim. (București)*, **54**, 2003, p. 561
19. KOBAYASHI, K., CHIBA, A., MINAMI, N., *Ultrasonics* **38**, 2000, p. 676
20. KOBAYASHI, K., CHIBA, A., TSUZUKI, K., MINAMI, N., *Proceedings of the 17th International Congress on Acoustics*, Rome, Italy, 2-7, September 2001, p. 393
21. MASON, T.J., LORIMER, J.P., D.M. BATES, D.M., *Ultrasonics* **30**, 1992, p. 40
22. F. TRABELSI, F., LYAZIDI, H.A., BERLAN, J., FABRE, P.L., DELMAS, H., WILHELM, A.M., *Ultrasonics Sonochemistry* **3**, 1996, p. 125
23. COOPER, E.L., COURY, L.A., *J. Electrochem. Soc.* **145**, 1998, p. 1994
24. DOCHE, M.L., HIHN, J.Y., LORIMER, J.P., MASON, T.J., PLATTES, M., *Ultrasonics Sonochemistry* **8**, 2001, p. 291
25. PHULL, S.J., WALTON, D.J., *Advances in Sonochemistry*, **4**, Mason, T.J. (Ed.), Elsevier-JAI Press, 1996
26. BERGENSTOF NIELESEN, C., A. HORSEWELL, A., M.J.L. OSTERGARD, M.J.L., *J. Appl. Electrochem.* **27**, 1997, p. 839
27. SULTANU, N., BRINZA, F., *Mater. Sci. Eng.* **B106**, 2004, p. 155

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