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PULSED LASER ABLATED CRATERS ON ALUMINIUM IN GASEOUS AND AQUEOUS ENVIRONMENTS

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Abstract. Here we investigate the dependence of the dimensions of the laser produced craters on aluminium targets on the fluence of nanosecond laser pulses at 532 nm wavelength in atmospheric air and aqueous hydrochloric acid solution of different concentrations. The laser fluence at the target surface was varied between 30 and 3000 J/cm^2 by using a variable attenuator, whereas the pulse number was set to 10 in order to maintain an approximately constant material removing rate during multiple pulses. The microscopy measurements indicate material removing rates as high as 10 microns/pulse at high fluences as compared to 0.7 microns/pulse at small fluences. The craters are shallower but wider, are well defined and have smooth walls and practically no rims and no re-deposited material around when produced in aqueous solutions as compared to air. The depth and the diameter of the craters increase approximately linearly with the 1/3 power of the laser fluence regardless of the environment condition. The fitting curves enabled us to estimate a higher ablation threshold fluence when irradiating the target in aqueous solutions as compared to air. The removed volume increases approximately linearly with fluence and is slightly larger when irradiating the target in acid solution. The material removal efficiency is also demonstrated to increase slightly with the solution concentration.

These results could be connected mainly to photo-thermal and electrochemical phenomena induced by the absorption of the laser radiation at the target surface. Thus, the smaller temperature rise induced by the laser at the target surface when immersed in aqueous solutions due to the enhanced metal-liquid thermal contact determines the increase of the threshold fluence required for initiating the material removal in solutions as compared to air. Moreover, the colder target surface in aqueous solutions results in smaller ablation rates and smoother crater walls as compared to air, and in colder ablation plasma induced above the target which in turn exerts smaller recoil pressure onto the target which reduces the rims. On the other hand, the electrochemically generated thermo-battery at the irradiated metal-liquid interface due to the non-uniform temperature distribution determines an enlargement of the craters due to crater edge etching, and a certain flattering of the crater bottom through a net mass transport from the 'cold' edge toward the hot center of the crater.

Key words: laser ablation, wet etching, ablation plasma.

1. INTRODUCTION

The efficiency of material removal upon irradiation with short and intense laser pulses in different non-etching or etching ambient conditions is described by the ablation/etching rate, which gives the maximum thickness of the layer removed during irradiation with a laser pulse. Understanding and controlling the ablation/etching rate is essential for determining the production efficiency, dimensions, and the quality of the laser produced structures in laser processing and pulsed laser-deposition [1–7].

The most suitable laser sources for obtaining very small (micrometer and sub-micrometer) and high quality structures are the femtosecond lasers due to the reduced thermal effects induced into the irradiated material [4, 5, 8]. Nevertheless, due to the high costs for acquisition and maintenance of the femtosecond lasers, there is an ongoing effort to develop new techniques based on nanosecond laser sources [5, 8, 9]. The studies propose to determine the optimum laser and ambient parameters that allow one to obtain high quality micro- and nano-structures on different metallic or non-metallic materials.

Previous experiments on nanosecond-pulsed laser ablation of metals in different non-reactive gas atmospheres indicated that high quality structures could be obtained at small laser fluences, *i.e.* slightly above the ablation threshold fluence which is demonstrated to be within the range of 1 to 10 J/cm^2 [1, 2, 5, 8, 9]. In these conditions, the ablation rate is rather small (tens to hundreds of nm per pulse) which leads to small processing speeds of large areas. The ablation rate increases logarithmically with the fluence in a certain range above the ablation threshold but to the detriment of the quality [1, 2]. Laser material removal may be enhanced or only induced by a proper choice of a gaseous or liquid etchant ambient [1, 10, 11]. Depending on the laser parameters and on the etchant properties (electrolytic or non-electrolytic), the material removal process may be thermally or electrochemically activated [1]. At higher fluences (*i.e.* above ignition threshold fluence), depending on the ambient, the critical thermo-dynamical conditions come into play along with the phenomena associated to the ablation plasma, and the laser-plasma interaction could influence very strongly the dimensions and the quality of the structures [6, 7, 12–17].

Here, we investigate the dependence of the removal rate of aluminium on the fluence of nanosecond laser pulses at 532 nm wavelengths in ambient atmosphere and aqueous acid solutions of different concentrations. The main purpose is to determine the optimum irradiation and ambient conditions for obtaining high processing rates and, at the same time, good quality of the laser produced structures. We demonstrate the influence of the solution concentration on the activation threshold fluence, on the removal rate, dimensions and quality of the laser produced structures. The results obtained in aqueous solutions are presented comparatively with those obtained normal ambient atmosphere.

2. EXPERIMENTS

The experimental setup consists of a frequency doubled 'Quantel-Brilliant' Q-switched Nd-YAG laser system, a large dynamic range 'Newport' variable attenuator, a 'Newport' beam expander, focusing lens and an aluminium target placed perpendicularly to the laser beam (Fig. 1). The experiments were carried out in ambient atmosphere and aqueous hydrochloric acid solutions of different concentrations, namely 0, 0.5 and 1 N.

The laser system works in the TEM00 mode and generates fundamental pulses at 1 064 nm wavelength which are frequency doubled (532 nm wavelength) by sending them through a second harmonic generator module. The second harmonic pulses are characterized by a duration of 4.5 ns, a maximum repetition rate of 10 Hz, and a maximum energy of 10 mJ.

The laser pulses are focused at normal incidence on a thick aluminium sheet. The target is fixed in air or aqueous solutions in the focal plane of the convergent lens ($f/7$, $f = 18$ cm) and the laser fluence at the target surface was varied between 30 and 3 000 J/cm^2 by using the large dynamic range variable attenuator.

The incident pulse number was set to 10 at 10 Hz repetition frequency in order to maintain a relative constant ablation/etching rate during multiple pulses incidence and, on the other hand, to obtain craters deep enough to allow for small relative errors for the microscopy measurements. The ablated/etched craters were analyzed with a metallographic microscope with a resolution of 1 micron in depth and 2 microns transversally so that, accounting for the craters depths and diameters, we estimated a maximum relative error of the measurements of ~10%. The material removing rate was calculated subsequently by dividing the crater depth by the pulse number.

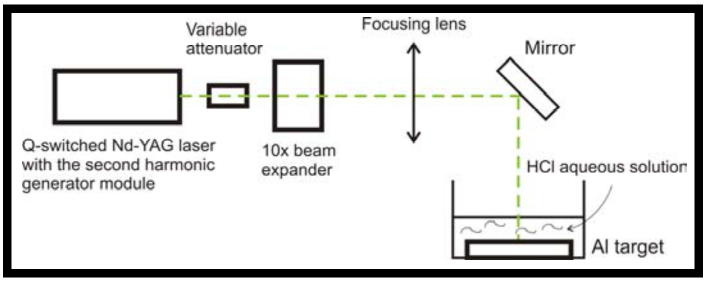


Fig. 1 – Experimental setup.

3. RESULTS AND DISCUSSION

The microscopy measurements indicate that for small fluences (*e.g.* 30 J/cm^2), the removal rates are between 0.7 and 1.5 microns/pulse depending on the ambient.

In this fluence regime the craters are practically free of rims and, in particular, the craters are very well defined when produced in aqueous solutions. At high laser fluences (*e.g.* 3 000 J/cm^2) the measurements indicate very high removal rates of 6 and 10 microns/pulse depending on the ambient medium. In this fluence regime the craters are surrounded by rims and large re-deposited material when produced in air, whereas the craters become better defined, smoother, with no rims and very small redeposit around when produced in aqueous solutions.

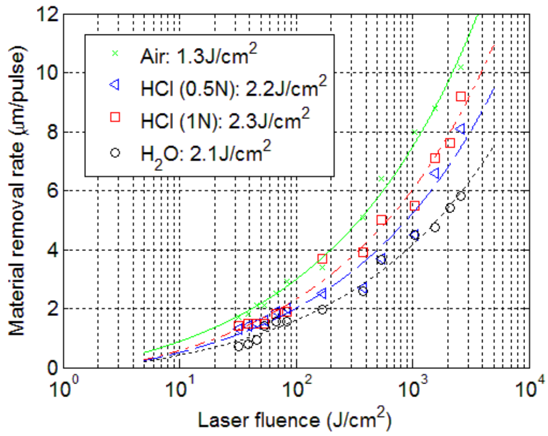
Figure 2a indicates that the removal rate and, consequently, the depth of the craters, increases linearly with the 1/3 power of fluence in all environment conditions. The removal rate is slightly higher when irradiating the target in air as compared to the irradiation in aqueous solutions. By comparing the removal rates in aqueous solutions we can see ~20 % higher removal rates in 1N and 0.5 N acid solutions than in pure water ambient.

By extrapolating toward a zero removal rate the 1/3 power fitting curves we can estimate the minimum threshold fluence for material removing. Thus, we can see that in air the threshold fluence is ~1.3 J/cm^2, which is smaller than in aqueous acid solutions (~2.2 J/cm^2).

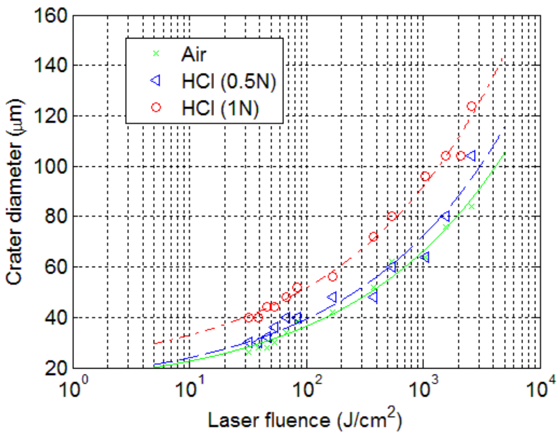
The microscopy measurements indicate additionally that the diameter of the craters increases also linearly with the 1/3 power of fluence in all environment conditions (Fig. 2b). In opposition to the crater depth, the diameter is larger when irradiating the target within the aqueous medium as compared to air.

Considering the craters as approximately conic structures for which the depth and diameter varies linearly with the cubic root of the fluence, we get a linear dependence of the crater volume on the fluence. This is in total agreement with the results presented in Fig. 3. Here we can see that the removed volume increases linearly with fluence, the removed volumes being slightly larger when irradiating in aqueous acid solutions as compared to pure water and air. Another result indicates that the structures are smoother and better defined in aqueous solutions as compared to air.

These experimental results can be interpreted in terms of photo-thermal and photo-chemical material removal under the laser radiation. Considering the photo-thermal activation of the material removal in open air, the excitation laser energy propagates mainly within the target material due to the poor thermal contact between the target surface and the surrounding air, resulting in deep craters rather than wide. At large fluences, strong heating of the target surface and the instabilities within the melted layer of the target surface heated up to the critical temperature may result in the rough craters surface that we observed experimentally. The presence of rims around the craters can be also explained by the high temperature rises of the target surface which in turn lead to hot and dense ablation plasmas and, consequently, to high recoil pressure exerted onto the melted layer.



a)



b)

Fig. 2 – a) The removal rate *vs* laser fluence in different ambient conditions. The legend indicates the threshold fluences as resulted from extrapolation of the fitting curves towards zero removal rate; b) dependence of the crater diameter on the laser fluence for different ambient mediums.

On the contrary, when irradiating the target in aqueous solution, the excitation laser energy propagates both within the target material and within the surrounding liquid due to the good thermal contact between the target surface and the surrounding liquid medium. At small fluences, the temperature rise induced by the laser absorption at the target surface is smaller than in the case of air. Thus, the thermal activation of material removal is more difficult in aqueous ambient and the minimum threshold fluence required for material removal increases in this case. At large fluences, the localized overheating of the target and the instabilities within the melted layer are reduced. Thereby, the removal rate decreases whereas the smoothness of the craters walls is improved. Moreover, the lack of rims around the craters can also be explained by the small temperature rises of the target surface which in turn lead to colder ablation plasmas and, consequently, to smaller recoil pressure exerted onto the melted layer.

The results regarding the crater diameter in different mediums can be understood in terms of laser induced electrochemistry: the electrochemical potential of the metal sheet with respect to the electrolytic acid solution is directly dependent on the local temperature induced at the target surface and on the ion density within the solution [1]. A thermo-battery is generated in the laser irradiated area which determines a net mass transport from the spot edge toward the center through the solution. Thereby, we expect a plating of the crater in the strong heated center due to material deposition and, simultaneously, enhanced etching at the ‘cold’ crater edge. This is consistent with the microscopy observations presented above: in aqueous solutions, the craters are larger and the depths are slightly smaller as compared to air, the craters bottoms are flatter whereas the well defined craters walls become steeper.

The results regarding the approximate equal removed volumes in water and air at different fleunces could be explained similarly, as follows. The strong photo-thermal ablation mechanism in air determines deep craters but with the same volume as in the case of the large and shallow craters produced by the superposition of electrochemical and the weaker photo-thermal mechanisms in water. As the acid concentration in the aqueous solutions increases the electrochemical mechanism become more important, the removed volume increasing slightly as compared to water and air.

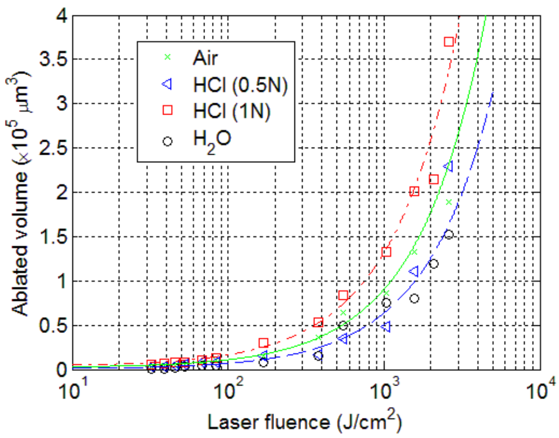


Fig. 3 – Dependence of the laser removed volume on the laser fluence in different ambient conditions.

4. CONCLUSION

We investigated the dependence of the dimensions of the laser produced craters in aluminium on the fluence of nanosecond laser pulses at 532 nm wavelength in atmospheric air and hydrochloric acid solution of different concentrations. The laser fluence at the target surface was varied between 30 and 3 000 J/cm^2 by using a variable attenuator. The incident pulse number was set to 10 in order to maintain an approximate constant material removing rate during multiple pulses, and additionally, to ensure small relative errors for the microscopy measurements on the crater dimensions. The microscopy measurements indicate a small increase of the material removal threshold fluence when irradiating the target in aqueous solutions as compared to the irradiation in air. The increase of the laser fluence leads to shallower but wider craters in aqueous solutions as compared to air, the depth and the diameter of the craters increasing approximately linearly with the 1/3 power of the laser fluence regardless of the environment condition. The removed volume increases approximately linearly with fluence and is slightly larger when irradiating the target in aqueous acid solutions. The material removing efficiency is also demonstrated to increase slightly when using acid solutions with high concentrations as compared to pure water.

These results are connected to two phenomena: the enhanced metal-liquid thermal contact and the consequent poor ablation plasma in liquid medium as compared to air, and a laser induced thermo-electro-chemical effect at the metal-liquid interface. The enhanced metal-liquid thermal contact prevents the overheating of the target surface due to the laser absorption and the instabilities within the melt surface which determine the rough surfaces of the craters in air. Moreover, the smaller temperature rises induced by the laser at the target surface when immersed in a liquid leads to the increase of the threshold fluence for initiating the material removal, and to much colder ablation plasma with small recoil pressure exerted onto the target which reduces the height of the rims around the craters.

The thermo-electrochemically induced ‘battery’ at the laser irradiated metal-liquid interface determines a net mass transport from the crater edge toward the center through the solution. This could be the cause for the enhanced etching of the craters at the well defined crater edge and, simultaneously, for the relative crater flattening in the strong heated bottom of the craters.

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