Applied Surface Science 257 (2011) 2019–2023

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Dependence of *Cm* on the composition of solid binary propellants in ablative laser propulsion

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ARTICLE INFO

Article history:
Received 16 March 2010
Received in revised form 30 August 2010
Accepted 3 September 2010
Available online 29 September 2010

Keywords:
Laser propulsion
Propellant
Laser ablation
Coupling coefficient

ABSTRACT

Propulsion pellets of different metal/salt (Zn/$CaCO_3$) composition have been prepared. The impulse imparted to the pellet by the laser has been measured using two different methods: a torsion pendulum and a piezoelectric sensor. The dependence of the coupling coefficient, C_m, on the composition of the solid binary propellants in ablative laser propulsion has been investigated under different experimental conditions: in vacuum and at atmospheric pressure as well as with two different wavelengths, IR and UV. The composition of the Zn/$CaCO_3$ propellant mixture that optimizes the coupling coefficient, C_m, has been determined.

1. Introduction

Ablative laser propulsion has demonstrated to be better than other propulsion schemes in terms of specific impulse, that is, of the efficiency of energy conversion to mass–power ratio. In this sense, the most recent experimental results in which micro-spheres of metallic and non-metallic elements have been used show that the coupling efficiency, C_m (momentum transfer per unit incident laser energy) [1] is to a large extent dependent on the diameter and material of the spheres as well as on the laser pulse width. In consequence, the dependence of ablative laser propulsion on the different parameters needs to be further investigated.

Many works on laser ablation have been published in the literature [2]. Most of them have focused on the physical processes that dominate this phenomenon. However, in the literature consulted by these authors, no studies relating these processes to ablative laser propulsion have been found. On the other hand, a lot of research has been carried out using the Laser induced breakdown spectroscopy (LIBS) technique, particularly in the analytical chemistry area [3]. These studies could provide very useful information to enhance the laser propulsion yield. The LIBS technique uses matrices doped with analytes which emit light following ablation. It has been demonstrated in different works in this area that the minor component (analyte) dominates the laser energy absorption process while the major component (matrix) controls the physical behavior (structure, ductility, etc.). These features have enabled the development of stable matrices for metal determination in soils by means of LIBS [3]. The determination of the physical characteristics of a matrix and their relation with the emission of electronically excited particles is a basic requirement for the development of propellants for laser ablation. On the other hand, as it has been demonstrated by Villagrán-Muniz and co-workers [4], it is also possible to determine the energy distribution in the laser ablation processes by using piezoelectric sensors. The opto-acustic signals obtained with this method can be used to characterize the laser propulsion processes.

The measurement of the velocities of the particles ejected during the ablation process cannot be used to perform a correct determination of the coupling coefficient. These measurements constitute a very important topic in the studies of chemical dynamics since the LIBS technique has been used to produce molecular beams with hyper-thermal velocities [5]. In these studies Rossa et al. [6] have determined that the atoms and ions excited in different electronic states possess different velocities. These velocities differ as well from those of the same species in their fundamental states. Therefore, these features hinder a correct measurement

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doi:10.1016/j.apsusc.2010.09.045

of the coupling coefficient, C_m, from the velocities of the ejected particles.

Bearing in mind the precedent information, the concepts of ablation matrix for analytical purposes [3] and utilization of piezoelectric sensors [4] have been applied in this paper to the development of solid propellants composed of metal/salt mixtures and to the optimization of the coupling coefficient. Propellant pellets of different Zn/$CaCO_3$ composition have been prepared. The impulse imparted to the pellet by the laser has been measured using two different methods: a pendulum of torsion and a piezoelectric sensor. Then, ablation of the pellets has been performed in an evacuated system in order to uncouple the impulse imparted by the plasma expansion produced by air breakdown from that transferred by the momentum transmitted by the ablated material. The propellant samples have been irradiated both with IR and UV laser radiation. The composition of the binary propellant mixture that optimizes the coupling coefficient, C_m, has been determined from the results obtained.

2. Experimental

In this section the procedure used to prepare the propellant pellets is presented. In addition, two experimental methods used to measure the coupling coefficient, *Cm*, are described.

2.1. Propellant pellets preparation

In order to determine the composition of the propellant pellet it was necessary to carry out a study to enable the selection of the matrix as well as of the ablation conditions (wavelength, laser fluence). A preliminary analysis was undertaken taking into account that the ablation process is mainly governed and characterized by the matrix composition. As a result the use of Zn as ablation matrix was defined [3]. This selection was performed on the basis that Zn favors the ablation process due to its physical and thermal properties: low ionization potential and high electronic density [7]. It also improves the homogeneity and cohesion of the sample, resists the mechanical shock and allows the vaporization of the surface target avoiding the crumbling effect [8]. On the other hand, there is experimental evidence that a small amount of salt ($CaCO_3$) can produce large effects on the processes of emission of light and particles during the ablation of a Zn matrix [3].

Therefore, in order to determine the coupling coefficient, C_m, and its relation to the propellant composition (metal/salt), pellets with different (Zn/$CaCO_3$) concentration ratio has been prepared.

The pellets of 0.5 g and 10 mm of diameter per 1.5 mm of thickness, were prepared by mixing Zn metal powder (Mallinckrodt, 99.99%) and $CaCO_3$ (Aldrich powder, 99.99%) in a mortar, which were subsequently powdered using a mill and then pressed in two stages. In the first stage, a pressure of 36 kpsi was applied for 10 min and, in a second stage; the pellets were additionally pressed with 54 kpsi during 5 min. This pressure reduces strongly the effects of the size of the particle in the ablation process, increasing the homogeneity of the surface of the sample and reducing its humidity content. The grain size of the powder of the pellets was not determined. Even though it might have an influence on the ablation efficiency, the experiments were performed at laser fluences above the threshold for massive ejection of material [9] and in this condition any effect of grain size should be negligible [10]. The composition of the propellant pellets was also controlled by infrared spectrometry. FTIR spectra of 100% Zn pellets show ZnO and carbonates impurities as expected from exposition to air. Table 1 shows the composition of the propellant pellets.

Table 1
Composition of the propellant pellets.

Pellets	Zn (% w/w)	$CaCO_3$ (% w/w)
1	0	100.00 ± 0.01
2	29.89 ± 0.01	70.10 ± 0.01
3	49.81 ± 0.01	50.19 ± 0.01
4	70.34 ± 0.01	29.66 ± 0.01
5	89.87 ± 0.01	10.13 ± 0.01
6	94.98 ± 0.01	5.02 ± 0.01
7	100.00 ± 0.01	0

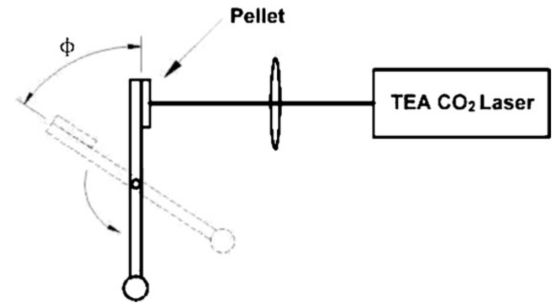

Fig. 1. Experimental set-up for pendulum of torsion measurements.

2.2. Measurement of the impulse with a pendulum of torsion

The pellets were placed in the set-up shown in Fig. 1 which consists of a pendulum of torsion implemented in the laboratory. A pulsed homemade TEA CO_2 laser tuned to the 10P(20), 10.59 μm, emission line was used to produce ablation on the pellet. The laser output energy was 2.5 J *per* pulse and the pulse width was 80 ns. The laser beam was focused on the center of the target, with a flat–convex lens of 12.7 cm focal length and a spot size of 1 mm was obtained in the ablation point on the pellet. The laser fluence, ϕ, was thus estimated in 320 J/cm^2.

The entire procedure was recorded by a video camera operating at 24 fps. The angular velocity was then measured using a program for digital images processing (ImageJ) that allows to process movies [11]. A set of five movies was filmed for each pellet (for statistical propose) in order to measure the C_m as a function of the pellet composition. Then each movie was analyzed with a plug-in incorporated in the ImageJ software. A typical data set obtained after using the ImageJ processing software is shown in Fig. 2.

Fig. 3 shows a diagram of a pendulum of torsion. Its movement can be described by Eq. (1) with the initial conditions given

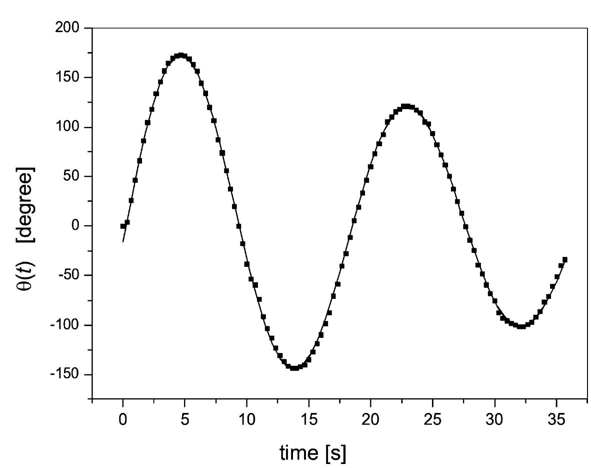

Fig. 2. Typical time-dependent data set obtained after processing the movies.

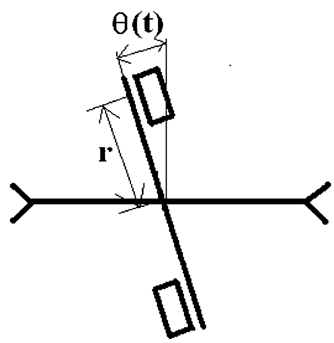

Fig. 3. Scheme of a pendulum of torsion.

by Eq. (2)

$$\frac{d^2\theta}{dt^2} + 2\beta\frac{d\theta}{dt} = \Omega_0^2\theta = 0 \tag{1}$$

$$\theta(t=0) = 0 \quad \frac{d\theta}{dt}(t=0) = \omega_0 \tag{2}$$

where Ω is the angular frequency, ω_0 is the undamped angular frequency of the oscillator and β is the damped constant

The resulting solution is

$$\theta(t) = \frac{\omega_0}{\Omega}e^{-\beta t}\sin(\Omega t) \tag{3}$$

$$\Omega^2 = \Omega_0^2 - \beta^2 \tag{4}$$

In accordance with Gualini et al. [1], the value of C_m can be obtained from Eqs. (3) and (4):

$$Cm = \frac{m\Delta\nu}{E} = \frac{2m\omega_0 r}{E} \tag{5}$$

where m is the mass ejected from the pellet, $\Delta\nu$ the average velocity of this mass and E the energy of the laser pulse.

This method was used to determine the angular velocity of the different pellets. The coupling coefficient as a function of the target composition was obtained from these values and Eq. (5). The fitting of a typical time-dependent data set obtained by the digital images processing using Eq. (3) is shown in Fig. 2. As it can be seen, experimental and fitted data are in excellent agreement, indicating that the system clearly behaves as a pendulum of torsion. The angular velocity thus determined has an error less than 1%. However, due to the pulse-to-pulse variability of the laser fluence, the C_m values have been determined with an uncertainty of about 10%.

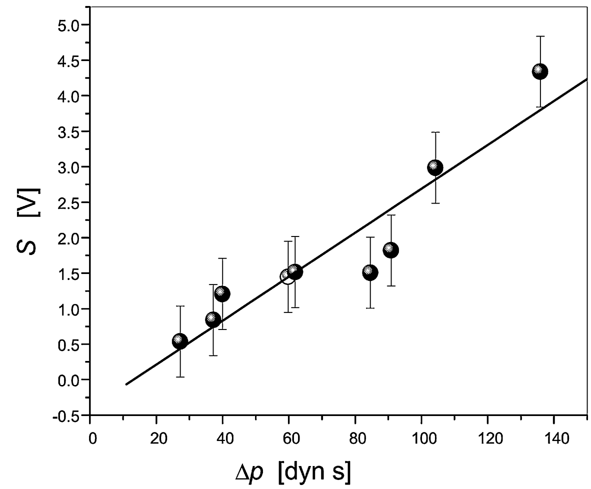

Fig. 5. Piezoelectric sensor calibration curve.

2.3. Measurement of the impulse with a piezoelectric transducer

The impulse transmitted to the sample can be determined in an absolute manner with a pendulum of torsion. A more versatile method of doing so, although not in an absolute way, is by the use of a piezoelectric transducer (PZT). This type of transducer produces, in the linear range, a voltage difference proportional to the mechanical deformation. Assuming that the PZT behaves as an ideal elastic material, such deformation would be proportional to the impulse imparted according to Eq. (6)

$$Cm = \frac{\Delta P}{E} \tag{6}$$

where ΔP is the impulse imparted to the pellet. The root mean square value of the PZT signal was used as an estimator of the impulse transmitted to the pellet. This estimator was chosen since it is an integrated magnitude and, thus, less sensitive to spurious noise. Moreover, this estimator is quite independent of the different oscillation modes of the pellet-PZT system.

The system had to be initially calibrated since, as mentioned before, the impulse measurements performed with the piezoelectric sensor are not absolute. This calibration was performed by registering the PZT signal produced by the impact of stainless steel spheres of different masses in free fall from different heights. Spheres of masses 0.11 g, 0.25 g and 1.26 g were dropped with null velocity from five different heights between 0.31 m and 1.5 m. Fig. 4 shows the time-dependent series obtained with the PZT when

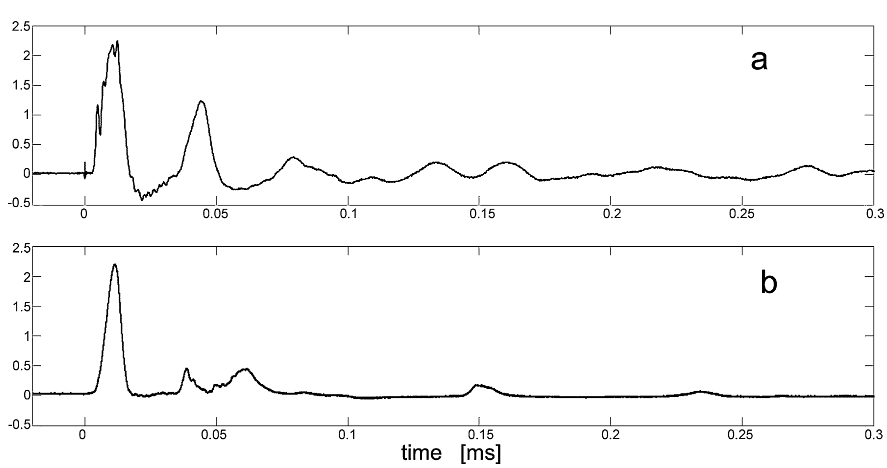

Fig. 4. PZT signal (a.u.) obtained (a) with the laser and (b) with the spheres excitation.

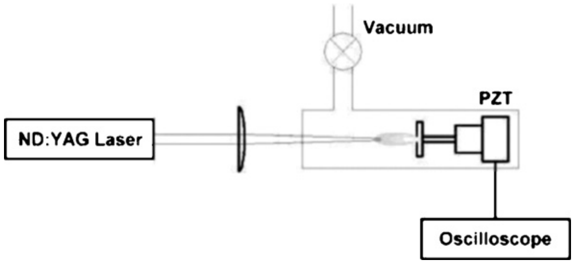

Fig. 6. Experimental set-up for measurement of the impulse with the PZT in an evacuated system.

(a) the laser impacts on the target and (b) a sphere impacts on the PZT.

Fig. 5 shows the linear dependence of the PZT signal standard deviation on the sphere's impulse when it impacts on the PZT.

2.4. Measurement of the impulse in a vacuum system

A series of experiments has been undertaken in order to uncouple the impulse imparted by the momentum transmission of the ablation process from that imparted by the plasma generated by the laser in the area surrounding the focal region (Rayleigh range). The PZT was used as detector in a measurement system set up in vacuum as shown in Fig. 6. This system consisted of a Pyrex cylindrical cell (5 cm diameter and 10 cm long) with a NaCl window on one end and the PZT on the other. The cell was connected to a vacuum pump and a dynamical final pressure of 10^{-2} Torr was achieved.

2.5. Measurement of the impulse varying the irradiation wavelength

Finally, in order to determine a possible irradiation wavelength effect on the ablation process, propellant pellets of different composition have been irradiated with the TEA CO_2 laser (IR, $\lambda = 10.59\,\mu m$) and with a frequency tripled Nd:YAG laser (UV, $\lambda = 355$ nm). The irradiation conditions with the CO_2 laser were the same as those described before. The output energy of the Nd:YAG laser at 355 nm was 25 mJ per pulse and the pulse duration 5 ns. A Pyrex cylindrical cell (1.8 cm diameter and 40 cm long) with a fused silica window on one end and the PZT on the other was used. The cell was connected to a vacuum pump and a dynamical final pressure of 10^{-2} Torr was reached. The laser beam was focused on the center of the target and a spot size of 0.22 mm was obtained in the ablation point on the pellet. The laser fluence, ϕ, was thus estimated in 64 J/cm^2. These experiments were performed in vacuum in order to compare the signals obtained with both wavelengths, avoiding the air plasma effect.

3. Results and discussion

Fig. 7 shows the dependence of C_m on the composition of the pellet determined with both detection methods: the pendulum of torsion and the piezoelectric sensor. A very good correlation between both methods can be observed. These measurements have been performed at atmospheric pressure and under the same irradiation conditions, that is, with the TEA CO_2 laser focused with the 12.7 cm focal length lens and a fluence of 320 J/cm^2.

The C_m values obtained with the different pellets composition (Zn/$CaCO_3$) show a non-linear behavior. As it can be seen, the maximum C_m value that can be achieved under these experimental conditions is determined by the composition of the pellet, independently of the detection method. Lower C_m values are obtained for matrices consisting either of pure metal, Zn, or of pure salt, $CaCO_3$.

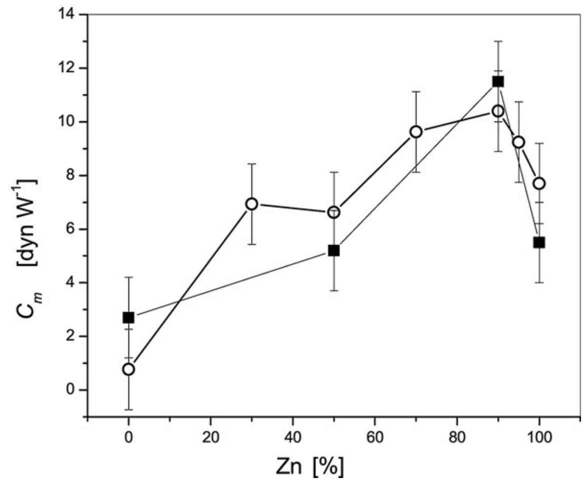

Fig. 7. C_m dependence on the pellet metal/salt composition measured using (■) pendulum and (○) PZT.

However, in binary propellants it has been found that the C_m values increase as the concentration of $CaCO_3$ decreases. The maximum value has been determined for metal proportions of 90%.

Later, the dependence of C_m on the composition of the pellet has been investigated both in vacuum and at atmospheric pressure. These experiments have been performed irradiating the target with the TEA CO_2 laser and detecting the impulse with the piezoelectric sensor. Fig. 8 shows the superposition of the C_m values obtained in both conditions. In both cases the dependence of C_m on the pellet metal/salt composition is qualitatively similar. The lower signal levels achieved in the vacuum system evidence the contribution of the impulse of the plasma expansion from air breakdown.

Finally, the dependence of C_m on the composition of the pellet has been investigated with two different wavelengths. These experiments have been performed irradiating the target in vacuum with the TEA CO_2 laser, 10.6 μm, and the frequency tripled Nd:YAG laser, 355 nm. The irradiation conditions with both lasers were those previously described and the impulse was detected with the piezoelectric sensor. Lasers parameters are listed in Table 2. Fig. 9 shows the superposition of the C_m values obtained in both conditions. Larger C_m values were obtained when irradiating the pellets with IR radiation. The dependence of C_m on the target composition with the two different wavelengths does not differ significantly. The maximum value has been determined for metal proportions of 70%.

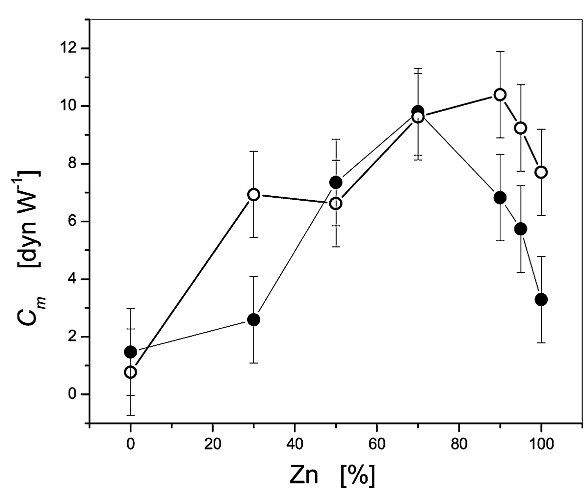

Fig. 8. Dependence of C_m on the pellet metal/salt composition in (●) vacuum and at (○) atmospheric pressure.

Table 2
Irradiation lasers parameters.

Parameter	Symbol	IR	UV
Wavelength	λ	10.59 μm	355 nm
Energy	E	2.5 J	25 mJ
Spot area	A	7.8×10^{-3} cm^2	0.39×10^{-3} cm^2
Fluence	Φ	320 J cm^{-2}	64 J cm^{-2}
Pulse width	τ	180 ns	5 ns
Peak power	*P*peak	13.9 MW	5 MW
Peak intensity	*I*peak	1.8 GW cm^{-2}	12.8 GW cm^{-2}

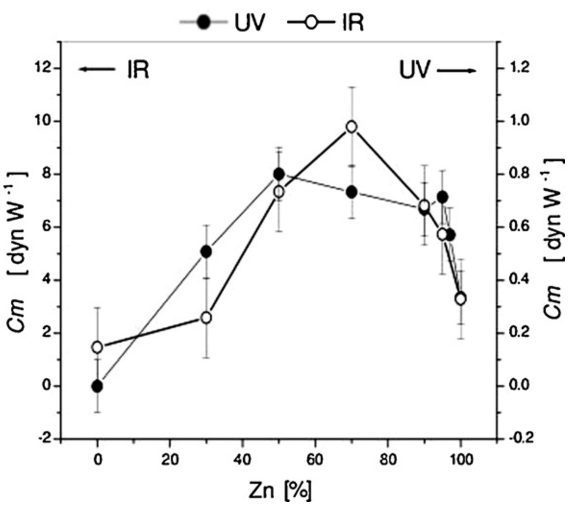

Fig. 9. Dependence of C_m on the pellet metal/salt composition. (○) IR 10.6 μm; (●) UV 355 nm.

From the laser parameters listed in Table 2, it can be inferred that although the IR to UV energy ratio is 100, the IR to UV fluence ratio is only 5 due to the spot size. At the same time, the IR to the UV peak pulse intensity ratio is 0.17. Therefore, it becomes apparent that the coupling coefficient is essentially dependent on the laser fluence and not on the wavelength. Also, the ablation process would not be a resonant phenomenon.

4. Conclusions

The dependence of the coupling coefficient, C_m, on the composition of solid binary propellants in ablative laser propulsion has been investigated under different experimental conditions. Propellant pellets of different metal/salt composition have been prepared. Mixtures of Zn and $CaCO_3$ have been chosen as binary propellant due to their intrinsic properties which favor the ablation process.

The impulses imparted by the laser determined with two different methods: a pendulum of torsion and a piezoelectric transducer (PZT), have been compared. The experiments with the pendulum of torsion detection allowed us to determine the dependence of the coupling coefficient, C_m, on the metal/salt composition of the propulsion pellets. The calibration of the impulse determined from the opto-acoustic signals of the piezoelectric transducer permitted the performance of the experiments in a faster and easier way. Particularly, detection with the PZT enabled us to perform measurements in vacuum.

The difference in the C_m values determined at atmospheric pressure and in vacuum evidences a contribution from the impulse imparted by air breakdown produced in the laser focus surroundings.

The experiments performed with two different wavelengths, IR and UV, evidence that C_m depends essentially on the laser fluence and not on the wavelength indicating, thus, that resonant absorption does not predominate in the ablation process.

The behavior of the dependence of Cm on the composition of the propellant pellets has been found to be similar in all experimental conditions. Maximum values of *Cm* have been obtained for metal proportions between 70% and 90%. It has been shown that the addition of small amounts of salt ($CaCO_3$) can produce large effects on the particle emission process during the ablation of a Zn matrix.

Finally, this work has integrated the knowledge derived from LIBS studies in analytical chemistry and photoacoustic signals induced by laser ablation in energy distribution processes, in order to optimize the design of targets for laser propulsion. The experiments performed have enabled us to establish the influence of the laser parameters on ablative laser propulsion and the $Zn/CaCO_3$ concentration ratios in the matrix to achieve the highest C_m value. Further experiments tending to elucidate this point are going to be carried out in short. In these experiments scanning electron micrograph studies of the pellets surface after laser irradiation will be undertaken. We hope these studies will allow us to elucidate the effect of the addition of a small amount of salt on the Cm.

Acknowledgments

This work was supported by CONICET, ANPCyT and SeCyT-UBA.

References

[1] M.M. Gualini, S.A. Khan, K. Zulfiqar, Development of laser propelled “Semi-perpetual” rotary machine, in: BEAMED ENERGY PROPULSION: Fourth International Symposium on Beamed Energy Propulsion, AIP Conferencie Proceedings 830, 2006, pp. 591–599.
[2] M. Villagran-Muñiz, H. Sobral, C.A. Rinaldi, I. Cabanillas-Vidosa, J.C. Ferrero, Optical emission and energy disposal characterization of the laser ablation process of CaF_2, BaF_2, and NaCl at 1064 nm, J. Appl. Phys. 104 (2008) 112–117.
[3] A.M. Beccaglia, C.A. Rinaldi, J.C. Ferrero, Analysis of arsenic and calcium in soil samples by laser ablation mass spectrometry, Anal. Chim. Acta 579 (1) (2006) 11–16.
[4] F. Bredice, D. Orzi, D. Schinca, H. Sobral, M. Villagrán-Muniz, Characterization of pulsed laser generated plasma through its perturbation in an electric field, IEEE Trans. Plasma Sci. 30 (6) (2002) 2139–2143.
[5] M. Rossa, C.A. Rinaldi, J.C. Ferrero, Chemiluminescent reaction of Ba(^{3}P) with N_2O at hyperthermal collision energies: Rotational alignment of the BaO($A^1\Sigma^+$) product, J. Chem. Phys. 127 (6) (2007) 064309.
[6] M. Rossa, C.A. Rinaldi, J.C. Ferrero, Velocity distributions of Ba($^1S_0$, ^3D_J, $^1D_2$, $^3P_1$ and $^1P_1$) and Ba$^+$($^2P_{3/2}$) produced by 1064 nm pulsed laser ablation of barium in vacuum, J. Appl. Phys. 100 (6) (2006) 063305.
[7] P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 2010, 20899 http://webbook.nist.gov.
[8] P. Musil, V. Otruba, V. Kanický, J. Mermet, Determination of elements in agricultural soils using IR laser ablation inductively coupled plasma atomic emission spectrometry, Spectrochim. Acta B 55 (2000) 1747–1758.
[9] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, Molecular dynamics model for laser ablation of organic solids, J. Phys. Chem. B 101 (1997) 2028–2037.
[10] J.T. Dickinson, L.C. Jensen, R.L. Webb, M.L. Dawes, S.C. Langford, Interactions of wide band gap single crystals with 248 nm excimer laser radiation, Appl. Phys. 74 (6) (1993) 3758–3767.
[11] Wayne Rasband, National Institute of Health, USA http://rsb.info.nih.gov/ij/.