

Contents lists available at ScienceDirect

Optics and Laser Technology



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

Full length article

Capturing the final stage of the collapse of cavitation bubbles generated during nanosecond laser ablation of submerged targets

Jiangyou Long ^{a, b, c, *}, Matthew H. Eliceiri ^b, Letian Wang ^b, Zacharias Vangelatos ^b, Yuexing Ouyang ^a, Xiaozhu Xie ^{a, c}, Yongkang Zhang ^c, Costas P. Grigoropoulos ^{b, *}

^a Laser Micro/Nano Processing Lab, School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

^b Laser Thermal Laboratory, Department of Mechanical Engineering, University of California, Berkeley, CA 94720-1740, USA

^c State Key Laboratory of Precision Electronic Manufacturing Technology and Equipment, Guangdong University of Technology, Guangzhou 510006, PR China

ARTICLE INFO

Keywords: Laser ablation Cavitation Bubble collapse PLAL Sonoluminescence

ABSTRACT

We observe and study the growth and collapse of cavitation bubbles generated during the pulsed laser ablation of submerged targets in three liquid environments, water, ethanol, and *n*-butanol, utilizing a stroboscopic shadowgraphy system. The transient images of the final stage of bubble collapse when the bubble volume is at a minimum are captured. Ethanol and *n*-butanol are subject to cavitation-induced reactions, which produce gaseous products that hinder the implosive collapse of the bubbles. In contrast, laser-produced cavitation bubbles in water achieve the smallest radii at the final stage of collapse, resulting in a sharper increase in localized temperature and pressure that can drive a potential second etching. Our results emphasize the role of the chemical effects of liquids on the implosive collapse of cavitation bubbles, providing a deeper understanding of cavitation-related phenomena and liquid-assisted laser processing.

1. Introduction

The energy of cavitation bubbles is stored in the bubble/liquid system during the growth stage and is focused and released during their implosive collapse. It is this focusing of energy in both space and time that produces the intense local heating, high pressure, and enormous heating and cooling rates that result in the remarkable effects of cavitation such as cavitation erosion and the emission of shockwaves and light [1–3]. Previous studies on single-bubble sonoluminescence (SL) have proved that the chemical nature of liquids has a significant effect on the implosive collapse of cavitation bubbles [4]. SL occurs when a trapped bubble of gas in the liquid is driven into high-amplitude pulsations by a strong sound wave, emitting an instantaneous flash of light around the point of maximum implosion. Studies have revealed that SL can be widely observed in aqueous liquids but is very weak in common organic liquids [5–7]. At room temperature, the intensity of SL from a single xenon bubble trapped in ethanol is only $\sim 0.2\%$ of that in water [7]. An explanation for this phenomenon is that the cavitation-induced reactions in organic liquids yield insoluble gaseous polyatomic products inside the bubble that obstruct the compressional heating necessary to generate SL [8]. In contrast, N₂ and O₂ dissolved in water can be removed from the bubble's interior by reactions to form NO_x, which dissolves in and reacts with bulk water, leaving primarily monatomic noble gases inside the bubble [9,10]. In addition, the decomposition of water produces hydrogen atoms and hydroxyl radicals, which are scavenged by the recombination or reactions with other gas molecules, leading to an enhanced gas removal effect [11,12]. Although these hypotheses have been verified by the spectral results of SL [8,13], there is still no image-based evidence of residual gaseous products in common organic liquids.

Despite the use of various imaging techniques in the study of cavitation bubbles such as high-speed photography [14,15], time-resolved shadowgraphy imaging [16], and pump-probe microscopy [17], it is still challenging to capture high temporal resolution images of the final stage of bubble collapse at its minimum size. Because cavitation bubbles collapse tens of microseconds after their origination and the final stage of collapse lasts only a few nanoseconds or less, most imaging techniques fail because of limited temporal resolution and recording time.

Pulsed laser ablation of submerged solid targets has been studied in diverse applications including underwater laser micromachining

E-mail addresses: longjy@gdut.edu.cn (J. Long), cgrigoro@berkeley.edu (C.P. Grigoropoulos).

https://doi.org/10.1016/j.optlastec.2020.106647

Received 20 July 2020; Received in revised form 7 September 2020; Accepted 28 September 2020 Available online 14 October 2020 0030-3992/© 2020 Elsevier Ltd. All rights reserved.

^{*} Corresponding authors at: Laser Micro/Nano Processing Lab, School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou 510006, PR China (J. Long).

[18,19], laser shock peening [20], and the preparation of nanomaterials [21]. Due to the strong confinement of a liquid environment, a cavitation bubble forms after a laser shot and affects the subsequent processes. In laser shock peening, previous studies have proven that the violent collapse of a laser-produced cavitation bubble triggers the generation of a strong shockwave that propagates through the targets [22]. When preparing nanomaterials by pulsed laser ablation in liquid (PLAL), the transient high temperature and high pressure reached inside the cavitation bubble at the final stage of bubble collapse may result in the aggregation and phase transition of the already formed nanomaterials [23]. An in-principle feasible method to observe the final stage of the collapse of cavitation bubbles generated during pulsed laser ablation of submerged targets is time-resolved shadowgraphy in which one shadowgraph image at a specified delay time is acquired in one experiment. Nevertheless, as the instant of final collapse slightly changes in every experiment (\sim 1–2 µs) due to fluctuations in experimental conditions, e.g., laser pulse energy and impurities in the liquid, capturing a transient image of the elusive instant of the final collapse is very challenging. Additionally, understanding how to confirm the time interval between the acquired images and the instant of final collapse (t_i) is another challenge.

In our earlier work, we observed the temporal evolution of cavitation bubbles generated during nanosecond (ns) laser ablation of submerged metal targets within 1 µs after the laser shot [24]. We found that the formation of shockwaves and cavitation bubbles are highly synchronous when using low-energy laser pulses. Owing to the much higher propagation velocity of the shockwaves, the profiles of the shockwaves and cavitation bubbles can be distinguished several nanoseconds after the origination. This finding provided us with the idea that the position of the emitted shockwave after the bubble collapse can be employed as a benchmark that approximately indicates the time interval between the acquired image and the instant of final collapse. In this study, we provide high-resolution images specifically at and after the final stage of bubble collapse. The transient images captured at the final stage of collapse confirm the concept of a suppressed bubble collapse in ethanol and *n*-butanol, providing image evidence that supports the theoretical assumptions in previous studies [7,8].

2. Materials and methods

The experimental setup is described in detail in an earlier study [24]. In brief, a 1064 nm and a 532 nm Nd:YAG ns laser are employed for the ablation and imaging, respectively. The focused 1064 nm laser beam with a diameter of 48 µm and a pulse width of 20 ns irradiates the polished titanium sample that is immersed at a depth of 5 mm below the liquid's surface. The energy of the laser pulses (e) used for the study of the bubble dynamics is 620 μ J, which corresponds to a laser fluence (F) of 68.5 J/cm^2 . Deionized water, chemically pure ethanol, and *n*-butanol are used as the liquids. Table 1 summarizes the basic properties of these liquids [25]. The experiment is conducted in ambient air without additional gas dissolution in the liquid. Titanium samples are chosen for this study because of their high boiling point (3560 K) [25], which minimizes the production of laser-ablated materials that could affect the bubble dynamics. The expanded 532 nm laser beam with a pulse width of 4 ns passes parallel to the target's surface, providing a shadowgraph image on a CCD camera coupled with a 12X zoom lens and a 2X long working distance objective. The delay time (t) of the two laser beams is

Table 1

Surface tension (σ), dynamic viscosity (μ), density (ρ), and vapor pressure (p_v) of the used liquids at 298 K.

Liquid	σ (mN/m)	μ (mPa·s)	ρ (kg/m ³)	$p_{\rm v}$ (kPa)
Water	72.0	0.85	997	3.17
Ethanol	21.9	1.07	790	7.87
n-Butanol	24.1	2.54	815	0.86

controlled by a delay generator and confirmed by two photodetectors connected to an oscilloscope. Each acquisition triggers a single laser shot, allowing one photograph to be acquired at a given delay time. The laser ablation rate is calculated by measuring the volume of the laserablated pits through a three-dimensional (3D) laser scanning microscope (OLS4100, Olympus). The morphology of the laser-ablated surfaces is observed using a scanning electron microscope (SEM, FEI Quanta 3D FEG).

3. Results and discussion

The pulsed laser ablation of submerged targets results in the formation of plasmas accompanied by the emission of shockwaves. The laser-induced plasmas propel the rapid expansion of the surrounding liquids and thus lead to the formation of a cavitation bubble. When the focused laser spot is relatively small, this process can be treated as an intense point explosion underwater, and the initial (<900 ns after the laser incidence) fluid displacement outside the bubble is a hemispherical self-similar motion [24]. Afterward, the laser-induced bubbles further expand to a maximum size and then collapse, as shown in Fig. 1. After the collapse, a new shockwave is emitted, and the cavitation bubble rebounds. The maximum radius of the laser-induced cavitation bubble (R_{max}) in water, ethanol, and *n*-butanol is 700 µm, 745 µm, and 740 µm, respectively, and the lifetime of the cavitation bubble from origination to the first collapse (*T*) in the three liquids is 120 µs, 114 µs, and 113 µs, respectively.

Fig. 2a shows the details regarding the changes in bubble radius (R) with *t* for the three liquids. Although the properties of the three liquids differ, there are only minor differences in the maximum bubble size and the bubble duration, which is consistent with previous results obtained by high-speed photography [26]. The temporal development of the Weber number ($We = \rho \dot{R}^2 R / \sigma$), which represents the ratio of the inertial force to surface tension, and the Reynolds number ($Re = \rho |\dot{R}| R/\mu$), which expresses the ratio of the inertial force to viscous force, are depicted in Fig. 2b and c respectively, where \dot{R} represents the velocity of the bubble wall. Here, the changes of *R* as a function of *t* are fitted with 7th order polynomial regressions. As shown in Fig. 2b, the We decreases rapidly with the expansion of the cavitation bubbles. When the bubbles grow to a size that approaches the maximum size, the We decreases to a value $<10^2$ (shown in the inset of Fig. 2b). In comparison, the *Re* decreases more slowly with t and is $\gg 10^3$ during most of the evolution (Fig. 2c). These results prove that the bubbles' growth and collapse are dominated by the inertial force. In other words, the liquid density plays a more critical role than the surface tension and viscosity.

By further comparing the temporal development of *Re* in the three liquids, we found that the *Re* in *n*-butanol is much lower than that in the other two liquids due to its higher viscosity. As the dynamic viscosity of some organic liquids reaches hundreds of mPa·s, which are two orders of magnitude higher than that of *n*-butanol, the effect of viscosity on the bubble dynamics can be significant in these liquids, as demonstrated in previous reports [27].

Considering an ideal situation by neglecting the thermal effects and gas contents in the bubble, the time t_c required for a total collapse from $R = R_{\text{max}}$ to R = 0 of the bubble can be given by $t_c = 0.915R_{\text{max}}\sqrt{\rho/\Delta p}$, where $\Delta p \equiv p_{\infty} - p_0$, p_{∞} is the liquid pressure far from the bubble (~0.1 MPa), and p_0 is the pressure within the bubble as it grows to its maximum size (~0 MPa) [14,28]. The measured collapse time of the laser-induced cavitation bubbles in water, ethanol, and *n*-butanol are 65 µs, 60 µs, and 56 µs, respectively, which are approximately equal to the calculated t_c (~64 µs, 61 µs, and 61 µs, respectively). This agreement implies that there is a limited gas content inside the bubble and the thermal effects are not evident during the bubbles' growth and collapse.

We further observed the final stage of the bubble collapse under high magnification. A shockwave is emitted after both the laser shot



Fig. 1. Temporal evolution of the laser-induced cavitation bubbles in (a) water, (b) ethanol, and (c) *n*-butanol. Related videos describing the bubble evolution in water and ethanol are provided in Supplementary Materials (Video S1 and S2).



Fig. 2. (a) Changes in bubble radius (R) with t. Solid lines: fitted curves with 7th order polynomial regressions. (b, c) Changes in the Weber number (We) and the Reynolds number (Re) with t. The inset in (b) shows the We near the maximum bubble radii.

and the bubble collapse. The propagation velocity of the emitted shockwave, which decays rapidly with time and then quickly reaches a constant, depends on the released energy that drives the shockwave propagation [29,30]. In our earlier work [24], we found that the shockwaves emitted after the laser shots propagate with a nearly constant velocity after ~ 20 ns when using low-energy laser pulses (e <1.02 mJ). When $e = 620 \mu$ J, the average propagation velocity of the emitted shockwaves in water, ethanol, and n-butanol within the initial 300 ns (s) is 1613 m/s, 1344 m/s, and 1443 m/s, respectively. The change in e from 270 µJ to 1020 µJ only results in slight changes in these values. Previous studies on the shockwave emission upon the collapse of a cavitation bubble attached to a rigid wall also show that the shockwave velocity decreases rapidly from 2520 m/s to 1500 m/s in \sim 25 ns [30]. It is, therefore, reasonable to assume that the emitted shockwaves after bubble collapse propagate with a nearly constant velocity after the incipient stage. Thus, the position of the shock front can be employed as a benchmark to estimate the time interval between the acquired images and the instant of final collapse. We acquired thousands of photographs around the instant of final collapse and selected the ones that captured the shockwaves for analysis. The t_i is estimated based on the position of shock front: $t_i = R_s/s$, where R_s is the radius of the observed shock front.

Fig. 3 shows the acquired images when the size of the bubble was at a minimum and immediately after. The first figures in Fig. 3(a-c) depict the instant of final collapse as the shockwaves are not fully formed. Traces of multiple shockwaves can be observed after the collapse. This phenomenon is probably caused by the rugged surfaces that are formed after the laser ablation, which may affect the propagation of the emitted shockwaves. The position of the most visible shock front is employed to calculate the t_i . In water, the cavitation bubble is compressed into a minuscule size during the collapse and then rapidly expands to a height (*H*) of ~28 µm and a width (*W*) of ~179 µm after ~134 ns (Fig. 3a). However, the implosive collapse of cavitation bubbles in ethanol and *n*-butanol is hindered, and flat residual bubble layers are observed at the instant of the final collapse, as shown in Fig. 3b and c. The *H* and *W* of the residual bubble layers are ~42 µm and ~223 µm, respectively, in ethanol and ~37 µm and ~199 µm, respectively, in *n*-butanol.

During the final stage of bubble collapse, the strong compression of the bubble contents results in a dramatic increase in temperature and pressure inside the bubble. It is difficult to quantitatively describe the collapse of a bubble because, at the final stage of collapse, the fluid pressure increases so dramatically that the assumption of liquid incompressibility is no longer appropriate, and the pressure and temperature within the bubble reach such high values that the thermal effects are not negligible. Consequently, we only compare the differences in the development of the bubble collapse in the three liquids but we do not give a precise calculation of the bubble pressure and temperature.

It is customarily assumed that the behavior of gas in the bubble is polytropic; thus, the gas pressure and temperature can be determined by [31]:



Fig. 3. Shadowgraph images after the first collapse of the laser-produced cavitation bubbles in (a) water, (b) ethanol, and (c) n-butanol. H and W represent the height and width, respectively, of the bubble layer when the bubble volume is at a minimum.

$$P_g(R) = \frac{P_0 R_0^{3\gamma}}{(R^3 - a^3)^{\gamma}},\tag{1}$$

$$T_g(R) = \frac{T_0 R_0^{3(\gamma-1)}}{(R^3 - a^3)^{\gamma-1}}.$$
(2)

Here, R_0 is the ambient radius corresponding to the size at which the bubble contents are at P_0 (=1 atm) and T_0 (=298 K), and *a* is the van der Waals hard-core radius. When the bubble wall moves slowly compared with the sound velocity in the gas, the pressure in the gas is uniform throughout the bubble. The value of γ depends on the rate of heat transfer across the bubble wall relative to the collapse rate of the bubble. If the heat transfer rate is high compared with the time scale of bubble motion, then the gas in the bubble is maintained at the temperature of the liquid and the pressure can be determined by an isothermal equation of state with $\gamma = 1$. In contrast, if the bubble wall moves very quickly relative to the rate of heat transfer, the heat cannot escape from the bubble and adiabatically heats the bubble on collapse. Thus, γ is the ratio of specific heats. The dimensionless Peclet number (*Pe*) can be used to distinguish the relative strength of the heat transfer and is expressed as

 $Pe = |\dot{R}|R/x_l$, where x_l is the thermal diffusivity of the liquid [4].

Fig. 4 shows the changes in *Pe* with *t* in the three liquids during the collapse. The *Pe* in ethanol and *n*-butanol is $\gg 10^4$ even at the final stage of collapse, which indicates that the bubble's collapse is almost adiabatic. Thus, the pressure and temperature within the bubbles rise rapidly during the collapse, particularly at the final stage of collapse. Although the bubble collapses adiabatically, a thin thermal boundary layer exits in which the temperature also rises dramatically [32]. The generation of gases due to the decomposition of organic compounds may occur both in the boundary layer and inside the bubble and hinder further compression of the bubble. As a result, the residual bubble layers, as shown in Fig. 3b and c, can be observed at the instant of final collapse in ethanol and *n*-butanol. The decomposition of organic liquids during the collapse of cavitation bubbles has been verified in the study of sonochemistry. For instance, Tauber proved that the decomposition products of tbutanol within a collapsing cavitation bubble include ethane, ethylene, and acetylene [33]. Kerboua et al. proposed that the sonolysis of a watermethanol mixture generates CH2OH, CH3O, CH2O, HCO, CO2, and CO [34].

The *Pe* in water is $\gg 10^3$ during most of the collapse, as shown in Fig. 4, but decreases to $\sim 10^2$ at the final stage of collapse. Nevertheless, this condition only lasts for $\sim 0.1 \,\mu$ s when the effect of heat transfer is obvious. Consequently, although the heat transfer is more evident in water than in ethanol and *n*-butanol, the collapse of laser-produced cavitation bubbles in water can also be regarded as adiabatic. However, water is more stable than organic compounds and only fractionally decomposes at temperatures higher than 2200 °C in which its decomposition products are partially soluble and reactive [35]. According to Eqs. (1) and (2), if we assume an identical initial state with the cavitation bubble containing few noble gases whose specific heat ratio is ~ 1.67 and neglect the van der Waals hard-core, the pressure and temperature within the cavitation bubbles at the instant of final collapse are proportional to $R_{\min}^{5,01}$ and $R_{\min}^{2,01}$, respectively, where R_{\min} represents the minimum bubble radius at the final stage of collapse. Here, the R_{\min} in



Fig. 4. Changes of the Pe with t.

water is assumed to be 5 µm, which is approximately the resolution limit of our imaging system. The R_{\min} in ethanol and *n*-butanol is approximated by the volume of the residual bubble layer (*V*), assuming a cylindrical shape $[V = \pi (W/2)^2 H = 2\pi R_{\min}^3/3]$, and is 95 µm and 82 µm, respectively. Thus, in this case, the maximum pressure reached at the minimum bubble volume is $\sim 10^6$ times higher in water than in ethanol and *n*-butanol, and the maximum temperature is ~ 370 and ~ 280 times higher in water than in ethanol and *n*-butanol, respectively. This simplified estimation shows that the temperature and pressure within the bubbles can be much higher in water due to the much smaller R_{\min} . However, even under these extreme conditions, no residual gas is visible in our experiment at the instant of final collapse in water, as demonstrated in Fig. 3a.

The pressure and temperature inside a cavitation bubble at its minimum size have already been studied theoretically and experimentally. In the study of SL, many models have been developed, with different degrees of sophistication, to predict the peak temperature within the cavitation bubble in water during the collapse. The predicted temperature ranges from 6000 K to 20000 K [36,37]. Based on the spectrum of the luminescence pulse generated during the bubble collapse, the maximum temperature inside the collapsing bubble in water has also been experimentally measured to be ~8150 K for bubbles with $R_{max} =$ 650 µm [38]. Furthermore, the maximum pressure acting on the rigid wall at the bubble's minimum size has been estimated in several previous works via the temporal evolution of the emitted shockwave after the bubble collapse. Vogel et al. estimated a maximum pressure of 6 GPa inside a laser-produced cavitation bubble with an R_{max} of ~3.5 mm that collapsed down to an R_{\min} of 50 μ m [39]. Using high-speed photography with 200 million frames per second, Brujan et al. observed and studied the shockwave emitted upon the collapse of a cavitation bubble attached to a rigid wall in water and produced by ultrasonic irradiation [30]. The Rmax and Rmin were measured to be 1.7 mm and 30 µm, respectively, and the maximum pressure acting on the rigid wall was estimated to be ~ 8 GPa. They also studied the shockwave emission from the collapse of a hemispherical cloud of bubbles [40]. The results show that the R_{\min} of the cloud increases with increasing R_{max} and ranges from 18 µm at R_{max} = 250 μ m up to 35 μ m at R_{max} = 1260 μ m. The maximum pressure acting on the boundary materials is estimated to be 265 MPa for a bubble cloud with $R_{\text{max}} = 300 \,\mu\text{m}$ and 1750 MPa for $R_{\text{max}} = 1260 \,\mu\text{m}$. Compared with these results, the observed R_{\min} in our study is smaller due to the higher temporal resolution of the imaging method. Thus, the pressure inside the bubble could be even higher than the reported values. It is worth noting that the pressure and temperature within the cavitation bubbles are affected by the gas composition inside the bubble. Several properties, such as the heat capacity ratio and the thermal conductivity, of the gas in the bubble have dramatic effects on the bubble collapse. Because the cavitation bubbles in our study are produced by laser ablation of a solid target, the gas composition inside the bubble may be more complicated due to the existence of laser-ablated products. Consequently, the real pressure and temperature within the bubbles in our study may differ from reported results.

Brujan et al. found that the maximum pressure of the shockwave emitted during the bubble collapse is reduced when adding a few organic polymers in water [41]. Many studies have also proved that even a small addition of polymer additives to the test fluid can strongly influence cavitation erosion and noise [42,43]. Previous studies on these phenomena focus on the effects of viscoelasticity on the dynamics of cavitation bubbles [44], whereas our results indicate that thermochemical effects may also be significant. The potential decomposition of the polymer additives can result in the generation of insoluble gaseous products inside the bubbles, and thus the compressive heating and pressure that increase during the collapse are dramatically suppressed.

The ablation rate and morphology of titanium specimens immersed in the three liquids were further studied. As shown in Fig. 5a, the ablation rate is higher in water than in ethanol and *n*-butanol, which is consistent with previous reports [45,46]. Fig. 5b-d show the morphology



Fig. 5. (a) Average ablation rate δ after 20 laser shots under a laser repetition rate of 0.2 Hz. (b-d) SEM images of laser-ablated areas in (a) water, (b) ethanol, and (c) *n*-butanol. *F*: 68.5 J/cm².

of the laser-ablated areas. Due to the impact of the high-speed micro-jets produced by the collapsing cavitation bubbles [39], the inner walls of the laser-ablated pits are smooth without a pile-up of laser-ablated materials. Crown-like structures can be observed around the laserablated pits, which are formed due to the molten material movement attributed to the recoil pressure caused by the ejection of laser-ablated materials [47,48]. Additionally, there is a thermal damage zone around the crown-like structures where a thin resolidified surface layer can be found. Compared with that in water (Fig. 5b), this thermal damage zone expands in ethanol and *n*-butanol (Fig. 5c and d). These differences may mainly originate from the different thermophysical and optical properties of the liquids and can also be partly explained by the different bubble collapse evolution in the three liquids. The intense compression of cavitation bubbles during the collapse triggers a dramatic increase in localized temperature and pressure. Previous studies on SL have demonstrated that the time duration of a luminescence pulse, which is caused by the strong heating of the gas content inside the collapsing bubble, is ~5 ns when $R_{\text{max}} \sim 700 \ \mu\text{m}$ [38]. Because the temperature and pressure inside the bubble are extremely high at the final stage of collapse, the collapsing bubbles may cause thermal damage to the metal substrate. In water, the laser-induced cavitation bubbles become minuscule at the final stage of collapse. Thus, the thermal effect is concentrated in the laser-ablated pits, which, combined with the impact of high-speed micro-jets, may drive a second etching and increase the ablation rate. In contrast, the cavitation bubbles in ethanol and n-butanol cannot be fully compressed due to the existence of insoluble gases inside the bubble, and thus the thermal damage zone expands. It is worth noting that we used a low laser repetition rate during the measurement of the ablation rate. After each laser shot, residual bubbles were observed near the ablated areas, affecting the following laser incidence and resulting in drastic fluctuations of the ablation rate. This effect becomes substantial for high-repetition-rate laser pulses. With this mechanism, the surface tension and viscosity of the liquid may also have an impact on the laser ablation rate under highrepetition-rate laser shots by affecting the stability of these residual bubbles.

4. Conclusions

The growth and shrinkage of laser-induced cavitation bubbles are dominated by the inertial force and thus the evolution of cavitation bubbles in water, ethanol, and *n*-butanol is similar except at the final stage of collapse. In ethanol and *n*-butanol, the cavitation-induced reactions generate gaseous products inside the bubble that hinder the bubble collapse. However, in water, the cavitation bubbles can be compressed into a minuscule size, resulting in a more dramatic increase of localized temperature and pressure, which can trigger a potential second etching. Our results show that although the maximum size and lifetime of laser-induced cavitation bubbles are similar in the three liquids, the collapse of cavitation bubbles is disparate due to the differences in the chemical nature of the liquids.

CRediT authorship contribution statement

Jiangyou Long: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. Matthew H. Eliceiri: Methodology, Resources, Writing - review & editing. Letian Wang: Methodology, Resources. Zacharias Vangelatos: Resources, Writing - review & editing. Yuexing Ouyang: Resources. Xiaozhu Xie: Funding acquisition. Yongkang Zhang: Funding acquisition. Costas P. Grigoropoulos: Supervision, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was conducted at the Laser Thermal Laboratory. The ablation rate measurement and SEM observation were carried out at the Marvell Nanofabrication Laboratory and the California Institute of Quantitative Bioscience (QB3) of UC Berkeley. Dr. Jiangyou Long acknowledges the support from the National Natural Science Foundation of China (51805093), National Key R&D Program of China (2018YFB1107700, 2017YFB1103600), Natural Science Foundation of Guangdong Province (2018A030310578), Ordinary University Characteristics Innovation Project of Guangdong Province (2017KTSCX056), Science and Technology Planning Project of Guangdong Province (2017B090911013), and Chinese Scholars Council.

Appendix A. Supplementary material

See supplementary materials for the videos describing the bubble evolution in water (Video S1) and ethanol (Video S2). Supplementary data to this article can be found online at https://doi.org/10.1016/j.op tlastec.2020.106647.

References

- K.S. Suslick, D.J. Flannigan, Inside a collapsing bubble: sonoluminescence and the conditions during cavitation, Annu. Rev. Phys. Chem. 59 (2008) 659–683, https:// doi.org/10.1146/annurev.physchem.59.032607.093739.
- [2] C.E. Brennen, Cavitation in medicine, Interface Focus. 5 (2015) 1–12, https://doi. org/10.1098/rsfs.2015.0022.

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- [3] H. Xu, B.W. Zeiger, K.S. Suslick, Sonochemical synthesis of nanomaterials, Chem. Soc. Rev. 42 (2013) 2555–2567, https://doi.org/10.1039/c2cs35282f.
- [4] M.P. Brenner, S. Hilgenfeldt, D. Lohse, Single-bubble sonoluminescence, Rev. Mod. Phys. 74 (2002) 425–484, https://doi.org/10.1103/RevModPhys.74.425.
- [5] P.-K. Choi, S. Abe, Y. Hayashi, Sonoluminescence of Na Atom from NaCl Solutions Doped with Ethanol, J. Phys. Chem. B. 112 (2008) 918–922, https://doi.org/ 10.1021/jp709661z.
- [6] M. Ashokkumar, R. Hall, P. Mulvaney, F. Grieser, Sonoluminescence from aqueous alcohol and surfactant solutions, J. Phys. Chem. B. 101 (1997) 10845–10850, https://doi.org/10.1021/ip972477b.
- [7] K. Weninger, R. Hiller, B.P. Barber, D. Lacoste, S.J. Putterman, Sonoluminescence from single bubbles in nonaqueous liquids: New parameter space for sonochemistry, J. Phys. Chem. 99 (1995) 14195–14197, https://doi.org/10.1021/ i100039a001.
- [8] Y.T. Didenko, W.B. McNamara, K.S. Suslick, Molecular emission from single-bubble sonoluminescence, Nature. 407 (2000) 877–879, https://doi.org/10.1038/ 35038020.
- [9] D. Lohse, M.P. Brenner, T.F. Dupont, S. Hilgenfeldt, B. Johnston, Sonoluminescing air bubbles rectify argon, Phys. Rev. Lett. 78 (1997) 1359–1362, https://doi.org/ 10.1103/PhysRevLett.78.1359.
- [10] D. Lohse, S. Hilgenfeldt, Inert gas accumulation in sonoluminescing bubbles, J. Chem. Phys. 107 (1997) 6986–6997, https://doi.org/10.1063/1.474939.
- [11] P. Riesz, T. Kondo, Free radical formation induced by ultrasound and its biological implications, Free Radic. Biol. Med. 13 (1992) 247–270, https://doi.org/10.1016/ 0891-5849(92)90021-8.
- [12] A. Henglein, C. Kormann, Scavenging of OH radicals produced in the sonolysis of water, Int. J. Radiat. Biol. 48 (1985) 251–258, https://doi.org/10.1080/ 09553008514551241.
- [13] D.J. Flannigan, K.S. Suslick, Plasma formation and temperature measurement during single-bubble cavitation, Nature. 434 (2005) 52–55, https://doi.org/ 10.1038/nature03361.
- [14] A. Philipp, W. Lauterborn, Cavitation erosion by single laser-produced bubbles, J. Fluid Mech. 361 (1998) 75–116, https://doi.org/10.1017/ S002211208008738
- [15] E.A. Brujan, G.S. Keen, A. Vogel, J.R. Blake, The final stage of the collapse of a cavitation bubble close to a rigid boundary, Phys. Fluids. 14 (2002) 85–92, https:// doi.org/10.1063/1.1421102.
- [16] T. Tsuji, Y. Okazaki, Y. Tsuboi, M. Tsuji, Nanosecond time-resolved observations of laser ablation of silver in water, Jpn. J. Appl. Phys. 46 (2007) 1533–1535, https:// doi.org/10.1143/JJAP.46.1533.
- [17] H. Hu, T. Liu, H. Zhai, Comparison of femtosecond laser ablation of aluminum in water and in air by time-resolved optical diagnosis, Opt. Express. 23 (2015) 628, https://doi.org/10.1364/oe.23.000628.
- [18] T. Wuttisarn, V. Tangwarodomnukun, C. Dumkum, Laser micromachining of titanium alloy in water and ice at different temperatures, Opt. Laser Technol. 125 (2020), https://doi.org/10.1016/j.optlastec.2019.106024.
- [19] W. Feng, J. Guo, W. Yan, Y.C. Wan, H. Zheng, Deep channel fabrication on copper by multi-scan underwater laser machining, Opt. Laser Technol. 111 (2019) 653–663, https://doi.org/10.1016/j.optlastec.2018.10.046.
- [20] Y. Tong, C. Wang, S. Yuan, K. Han, X. Chen, N. Yang, X. Ren, Compound strengthening and dynamic characteristics of laser-induced double bubbles, Opt. Laser Technol. 113 (2019) 310–316, https://doi.org/10.1016/j. optlaster 2018.11.003
- [21] V. Amendola, M. Meneghetti, Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles, Phys. Chem. Chem. Phys. 11 (2009) 3805–3821, https://doi.org/10.1039/b900654k.
- [22] T. Takata, M. Enoki, P. Chivavibul, A. Matsui, Y. Kobayashi, Effect of confinement layer on laser ablation and cavitation bubble during laser shock peening, Mater. Trans. 57 (2016) 1776–1783, https://doi.org/10.2320/matertrans.M2016150.
- [23] V. Amendola, M. Meneghetti, What controls the composition and the structure of nanomaterials generated by laser ablation in liquid solution? Phys. Chem. Chem. Phys. 15 (2013) 3027–3046, https://doi.org/10.1039/c2cp42895d.
- [24] J. Long, M. Eliceiri, Z. Vangelatos, Y. Rho, L. Wang, Z. Su, X. Xie, Y. Zhang, C. Grigoropoulos, Early dynamics of cavitation bubbles generated during ns laser ablation of submerged targets, Opt. Express. 28 (2020) 14300–14309, https://doi. org/10.1364/OE.391584.
- [25] J.R. Rumble, CRC Handbook of Chemistry and Physics, 100th ed., CRC Press, 2019.

- [26] J. Lam, J. Lombard, C. Dujardin, G. Ledoux, S. Merabia, D. Amans, Dynamical study of bubble expansion following laser ablation in liquids, Appl. Phys. Lett. 108 (2016), https://doi.org/10.1063/1.4942389.
- [27] T. Hupfeld, G. Laurens, S. Merabia, S. Barcikowski, B. Gökce, D. Amans, Dynamics of laser-induced cavitation bubbles at a solid-liquid interface in high viscosity and high capillary number regimes, J. Appl. Phys. 127 (2020), https://doi.org/ 10.1063/1.5116111.
- [28] Lord Rayleigh, On the pressure developed in a liquid during the collapse of a spherical cavity, Philos. Mag. 34 (1917) 94–98, https://doi.org/10.1080/ 14786440808635681.
- [29] A. Vogel, S. Busch, U. Parlitz, Shock wave emission and cavitation bubble generation by picosecond and nanosecond optical breakdown in water, J. Acoust. Soc. Am. 100 (1996) 148–165, https://doi.org/10.1121/1.415878.
- [30] E.A. Brujan, T. Ikeda, Y. Matsumoto, On the pressure of cavitation bubbles, Exp. Therm. Fluid Sci. 32 (2008) 1188–1191, https://doi.org/10.1016/j. expthermflusci.2008.01.006.
- [31] R. Löfstedt, B.P. Barber, S.J. Putterman, Toward a hydrodynamic theory of sonoluminescence, Phys. Fluids A. 5 (1992) 2911–2928, https://doi.org/10.1063/ 1.858700.
- [32] F.N. Egolfopoulos, A. Prosperetti, A theoretical study of sonoluminescence, J. Acoust. Soc. Am. 94 (1993) 248–260, https://doi.org/10.1121/1.407083.
- [33] A. Tauber, G. Mark, H.P. Schuchmann, C. Von Sonntag, Sonolysis of tert-butyl alcohol in aqueous solution, J. Chem. Soc. Perkin Trans. 2 (1999) 1129–1135, https://doi.org/10.1039/a901085h.
- [34] K. Kerboua, O. Hamdaoui, Oxygen-argon acoustic cavitation bubble in a watermethanol mixture: Effects of medium composition on sonochemical activity, Ultrason. Sonochem. 61 (2020), https://doi.org/10.1016/j.ultsonch.2019.104811.
- [35] J.E. Funk, Thermochemical hydrogen production: Past and present, Int. J. Hydrogen Energy. 26 (2001) 185–190, https://doi.org/10.1016/S0360-3199(00) 00062-8.
- [36] V.Q. Vuong, A.J. Szeri, Sonoluminescence and diffusive transport, Phys. Fluids. 8 (1996) 2354–2364, https://doi.org/10.1063/1.869020.
- [37] B.D. Storey, A.J. Szeri, Water vapour, sonoluminescence and sonochemistry, Proc. R. Soc. London. Ser. A Math. Phys. Eng. Sci 456 (2000) 1685–1709, https://doi. org/10.1098/rspa.2000.0582.
- [38] E.A. Brujan, D.S. Hecht, F. Lee, G.A. Williams, Properties of luminescence from laser-created bubbles in pressurized water, Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys. 72 (2005), https://doi.org/10.1103/PhysRevE.72.066310.
- [39] A. Vogel, W. Lauterborn, R. Timm, Optical and acoustic investigations of the dynamics of laser-produced cavitation bubbles near a solid boundary, J. Fluid Mech. 206 (1989) 299–338, https://doi.org/10.1017/S0022112089002314.
- [40] E.A. Brujan, T. Ikeda, Y. Matsumoto, Shock wave emission from a cloud of bubbles, Soft Matter. 8 (2012) 5777–5783, https://doi.org/10.1039/c2sm25379h.
- [41] E.A. Brujan, Shock wave emission and cavitation bubble dynamics by femtosecond optical breakdown in polymer solutions, Ultrason. Sonochem. 58 (2019), https:// doi.org/10.1016/j.ultsonch.2019.104694.
- [42] T. Tsujino, Cavitation damage and noise spectra in a polymer solution, Ultrasonics. 25 (1987) 67–72, https://doi.org/10.1016/0041-624X(87)90062-X.
- [43] E.A. Brujan, A.F.H. Al-Hussany, R.L. Williams, P.R. Williams, Cavitation erosion in polymer aqueous solutions, Wear. 264 (2008) 1035–1042, https://doi.org/ 10.1016/j.wear.2007.08.007.
- [44] S.J. Lind, T.N. Phillips, Spherical bubble collapse in viscoelastic fluids, J. Nonnewton. Fluid Mech. 165 (2010) 56–64, https://doi.org/10.1016/j jnnfm.2009.09.002.
- [45] A. Kanitz, J.S. Hoppius, M. del Mar Sanz, M. Maicas, A. Ostendorf, E.L. Gurevich, Synthesis of magnetic nanoparticles by ultrashort pulsed laser ablation of iron in different liquids, ChemPhysChem. 18 (2017) 1155–1164, https://doi.org/ 10.1002/cphc.201601252.
- [46] A. Kanitz, J.S. Hoppius, M. Fiebrandt, P. Awakowicz, C. Esen, A. Ostendorf, E. L. Gurevich, Impact of liquid environment on femtosecond laser ablation, Appl. Phys. A Mater. Sci. Process. 123 (2017), https://doi.org/10.1007/s00339-017-1280-z.
- [47] E. György, I.N. Mihailescu, P. Serra, A. Pérez del Pino, J.L. Morenza, Crown-like structure development on titanium exposed to multipulse Nd:YAG laser irradiation, Appl. Phys. A Mater. Sci. Process. 74 (2002) 755–759, https://doi.org/10.1007/ s003390201307.
- [48] J. Long, Z. Cao, C. Lin, C. Zhou, Z. He, X. Xie, Formation mechanism of hierarchical Micro- and nanostructures on copper induced by low-cost nanosecond lasers, Appl. Surf. Sci. 464 (2019) 412–421, https://doi.org/10.1016/J.APSUSC.2018.09.055.