Formation of microstructure on liquid metal surface under nanosecond laser ablation

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Abstract: Formations of stable micro-protrusions and microstructures on the surfaces of liquid metals during multipulse action of a UV-IR laser in different ambient gases was discovered for the first time. The rate of the structure formation was measured which can reach $5 - 20$ μm/pulse depending on the metal and ambient gas sort. Single micro-protrusions of $1 - 2$ mm in length were formed with the diameter approximately two times greater than the focal spot size. The possibility to control the microstructure shape was shown and their potential applications were also discussed.

Key words: liquid metal; surface; microstructure; nanosecond laser ablation

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(1.   634055;

2.

130033;

3.   630090)

:   UV-IR   。

(5 ~ 20) μm/pulse   1 ~ 2 mm

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1　Introduction

At present　the investigation of powerful laser pulse action on different substances are widely performed and various technology applications based on laser ablation are developed [1]. It was reported inRef. 2 – 6　that micro-nanostructures can be formed on the solid surface after laser action　mechanisms of the structure formation are listed in Ref. 4. However　at all variety of laser action variants only insufficient attention was given to ablation of liquid metals in Ref. 7 – 9. The ablation threshold and dynamics of liquid and solid Ga and In were compared [7-9]　the laser ablation of melted Sn and Bi and processes on the liquid surface were studied [10] and the relaxation time of melted surface of Ga　Ga-In alloy and wood metal after laser pulse were measured [11].

Here we report a new phenomenon which has been observed for the first time to our knowledge namely formation of microstructures on multishot ns laser irradiation(IR and UV) of liquid metals in the presence of reactive ambient gases. Instead of the formation of a crater　as takes place under vacuum conditions or in inert gases　a tower-like structure with diameter somewhat exceeding the irradiation spot size grows on the irradiated surface at a rate of 3 – 20 μm per pulse　depending on laser fluence and metal type.

2　Experimental arrangement

The experimental setup is shown schematically in Fig. 1. Molten metals(Ga　In　Sn Pb alloy　Wood′s metal) were placed in a Gas Chamber (GC) equipped with a heater whose temperature was kept constant during the experiments. The chamber can be pumped down to 1. 33 Pa or filled with different gases(air　Ne　N_2　SF_6　NF_3). Metals were maintained in a liquid state　and their temperature was

controlled with a thermocouple. Multishot irradiation (repetition rate in 1 – 10 Hz) was carried out with several lasers　a Q-switched Nd : YAG laser　λ = 1 064 nm　pulse duration in 2. 5 ns at Full-width Half-maximum(FWHM)　maximal pulse energy in 0. 25 mJ　a nitrogen laser(λ = 337 nm　pulse duration in 4. 5 ns at FWHM　maximal pulse energy in 0. 25 mJ) or excimer KrCl laser (λ = 222 nm pulse duration in 9 ns at FWHM　maximal pulse energy in 2 mJ). The laser beams were focused by a quartz lens (with focal length of 5 cm) and could couple to the targets horizontally. The irradiation spot diameter on the target surface was typically about 0. 1 mm　and the maximum power density was 1. 4 × 10^9 W/cm^2　0. 9 × 10^9 W/cm^2 and 1. 5 × 10^8 W/cm^2 for the Nd : YAG　N_2 and KrCl lasers respectively.
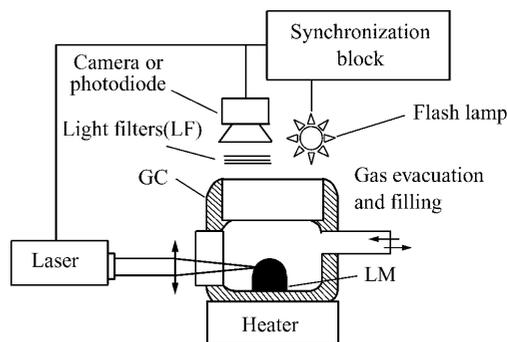

Fig. 1　Schematic diagram of experimental setup

The state of the target surface was analyzed with a digital camera or a high-speed CCD camera(SensisCam) in front of which Light Filters (LF) were placed to ensure a linear operation regime. The target surface was illuminated by a Flash Lamp(FL) and photographs were taken after each laser shot. The temporal evolution of the laser induced plume emission was measured by using a photocell and a TDS-3034 digital oscilloscope. The surface layer structure was analyzed with a Scanning Electron Microscope (SEM) with the type of PHILIPS SEM-515.

3   Experimental results

Fig. 2 presents the microstructure structures grown by multishot irradiation(Nd: YAG laser 200 pulses fluence $F_0 = 3.2$ J/cm^2) of the molten targets. The initial temperature T_0 of gallium (30 ℃) was only slightly above its melting point ($T_m = 29.76$ ℃) while the other targets were heated to about 250 ℃. Under vacuum conditions at the applied fluence a luminous laser plasma is observed above the irradiated surfaces indicating a strong ablation regime and a crater is formed which is healed within several ms [11]. In air at 1 bar a bright plasma plume is also seen. However instead of a crater a tower-like structure is seen to grow on the irradiated surface as illustrated in Fig. 2. The microstructure diameters are typically twice the size of the irradiation spot. The average growth rate V_g is estimated to be 3 − 5 μm per pulse for all metals except the Sn Pb alloy which grew at a rate almost three times slower. It should also be noted that the Sn Pb microtower diameters are approximately 1. 5 times larger than those of the other metals.
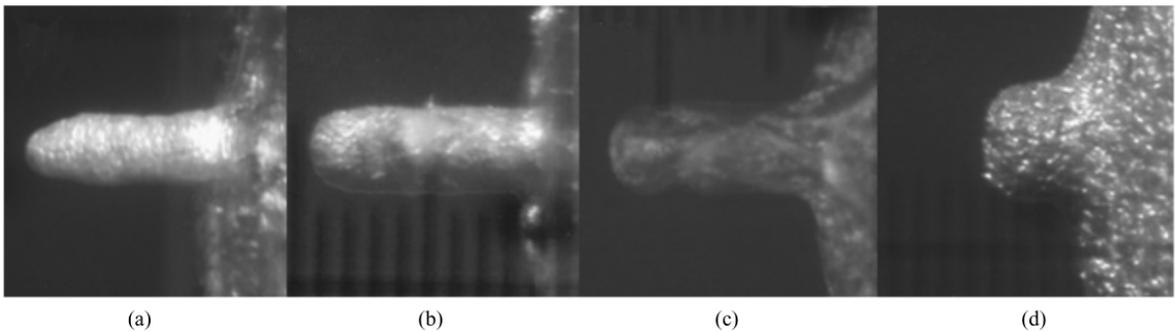

(a)   (b)   (c)   (d)

Fig. 2   Microstructures grown in air by 200 pulses of Nd: YAG laser on Ga(a)   In(b)   Wood's metal(c)   and Sn Pb alloy
(d) liquid targets. The initial temperature T_0 is 30 ℃ for gallium and ~250 ℃ for other metals. F_0 is 3. 2 J/cm^2
and a scale bar is 500 μm.

Increasing the liquid target temperature results in a higher growth rate as demonstrated in Fig. 3. The microtower structures on Sn Pb alloy and gallium which were grown in air with the use of the N$_2$-
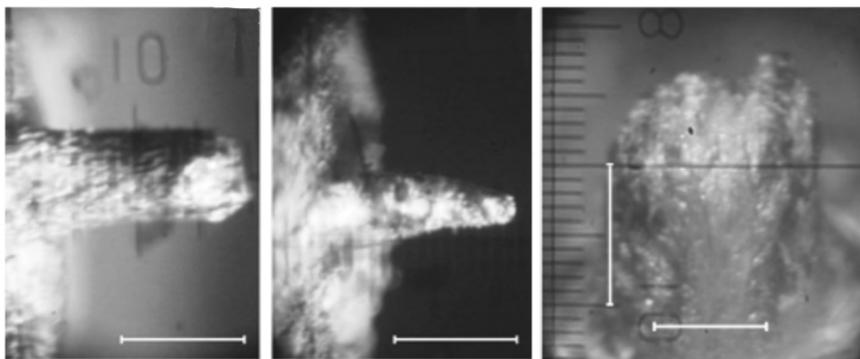

Fig. 3   Microstructures on liquid Sn Pb alloy(a) and Ga(b)   (c) obtained with N$_2$(a)   (b) and KrCl-laser(c) in air.
The numbers of pulses are 350(a)   450(b)   and 75(c). The initial temperature is 450 ℃ for Sn Pb alloy and 30 ℃
for gallium. Laser fluence is 3. 2 J/cm^2(a) and 1 J/cm^2(b)   (c). Scale bars is 1 mm(a)   (b) and 0. 25 mm(c).

laser have the same lengths. This was achieved by increasing the Sn Pb target temperature to 450 ℃ while keeping the gallium target at 30 ℃. Note that although the microstructure growth on Ga requires a larger number of pulses the laser fluence is considerably smaller compared to that needed for the Sn Pb microstructure growth. Fig. 3 shows that by varying the irradiation parameters one can easily control the growth process of these unusual structures. However under similar irradiation conditions the Sn Pb microstructures were found to grow less readily compared to the other studied metals. It should be mentioned that we have not found a strong difference in using Nd：YAG or N_2 lasers for microstructure formation. The only differences are in the higher reflection coefficient and the higher plasma screening effect on IR radiation that requires a higher value of applied laser fluence（or a larger number of pulses） for microtower formation of the same length compared to UV laser light.

Maximal growth rate in our experiment was observed in SF_6. In air the rate was $2 - 3$ times lower when the rate falls by one order of magnitude in N_2. This means that the rate of microstructure formation is controlled by the chemical reactivity of the ambient gas.

In the case of KrCl laser the structure is formed at specific radiation power of about 5 times lower due to relatively high radiation divergency than in the case of Nd：YAG and N_2 lasers. The growth rate about 7 μm/pulse is close to that obtained with lasers at 1 054 and 337 nm.

The SEM analysis by 30 keV electrons of the microstructure shows that the surface of the molten target is highly oxidized outside the irradiation zone and the microstructure walls are also covered by oxidized metals with the Me：O ratio being very close to 1：1. However the microstructure tip is oxygen-deficient compared to the microstructure walls and the nonirradiated target sites. As the estimated penetration depth for 30 keV electrons is slightly less than 2

μm one may conclude that either the oxide layer on the microstructure tip is much thinner than 2 μm or the oxide and metal are mixed due to complicated hydrodynamics within the laser irradiation spot during the ablation process. This allows to conclude that the microstructure is a capillary with walls from metal oxide（nitride fluoride） filled with liquid metal.

4　Theoretical analysis and discussion

As the process of microstructure formation is clearly connected with the regime where liquid metal ablation occurs we have applied a thermal model in order to evaluate the heating and ablation depths resulting from single pulse irradiation and the corresponding temperature profiles. The thermal model details are described in the Ref. 12 13 . According to modeling for 3. 2 J/cm^2 the irradiated Ga surface is heated up to 4 800 K that causes ablation of a layer with the thickness about 5 nm. However such a high temperature level exists only for a few nanoseconds whereupon the heat is conducted towards the target depth. A layer of at least 1 μm thickness reaches the temperature on the order of 1 000 K. Taking into account the linear expansion coefficient of molten gallium（$1. 8 \times 10^{-5}$ K^{-1}） we evaluate the linear expansion to be about 20 nm that is larger than the ablation depth. Hence immediately after an ablation event a bump of liquid metal should be formed instead of a crater. Then the surfaces of the generated microbump experience rapid chemical reaction with ambient gas and "chemical envelope" from oxide（nitride fluoride *etc.* depending on gas environment） is formed.

Note that heating of the oxide layer covering the metal surface is not considered in the modeling. The existence of such a layer can also influence the ablation dynamics. For laser wavelengths applied here to ablate liquid metals the most metal nonmetal compounds are either transparent or have much smaller absorption coefficients compared to metallic sol-

ids [14]. As a result the laser pulse couples to the metal surface through a thin covering oxide(nitride fluoride etc.) film. Due to the contact with the laser-heated metal the outer film will heat up and will either thermally decompose when reaching the de-composition temperature or with higher probability will fracture under the high thermal stress [15].

Thus we can propose a scenario of microstructure formation which is presented in Fig. 4.
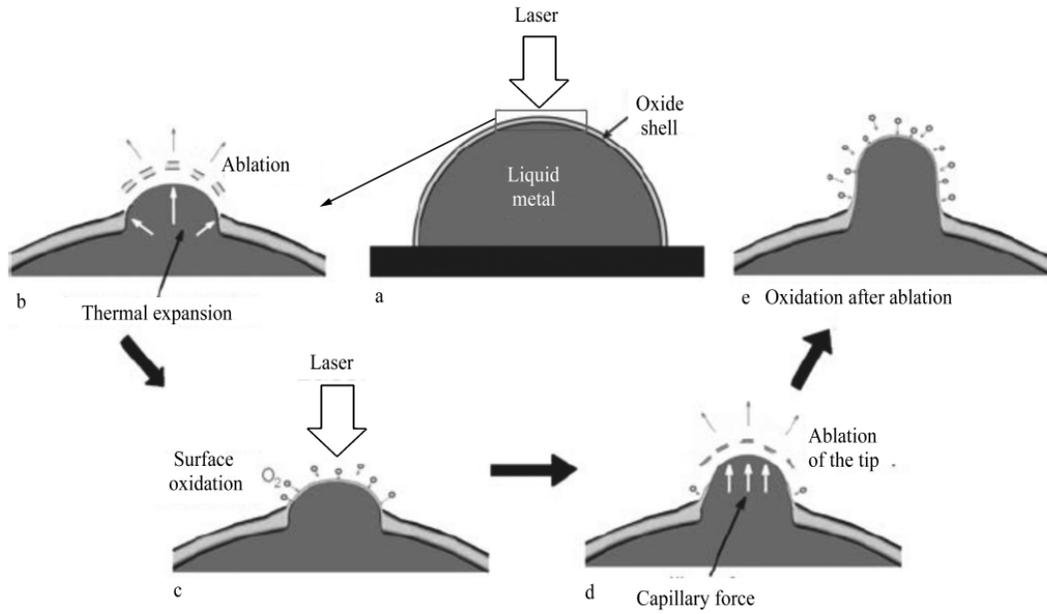

Fig. 4　Schematic representation of the microstructure growth process on laser ablation of liquid metals in reactive atmosphere(air as an example). For explanation see text.

A liquid metal drop subjected to surface oxidation is covered by a solid oxide layer which poorly absorbs laser irradiation. A laser pulse couples to the metal surface through the oxide layer(see Fig. 4 (a)).

The metal layer heated by laser radiation expands and partially vaporizes (up to few nm see Fig. 4(c)) causing fracturing of the oxide layer(see Fig. 4(b)). The ablation products(metal vapor and oxide debris) expand into the atmosphere. The hot liquid metal due to thermal expansion protrudes through the hole produced in the oxide shell by the laser.

During the time interval between two subsequent pulses the surface of the protruded metal is subjected to oxidation(see Fig. 4(c)).

The next laser pulse couples to the top part of the formed bump and ablates a small amount of met-al. If a thin oxide film has been formed between the pulses it is partially fractured in the top site and its debris is carried away with the laser ablation plume(see Fig. 4 (d)). As the bump top is now bare of oxide while its side walls are preserved capillary forces drive the liquid metal up through the formed oxide tube in the irradiation geometry as in Fig. 4. If the laser pulse couples to the target in the horizontal geometry is as shown in Fig. 1 the liquid metal is squeezed out through the oxide tube by the pressure within the droplet. Note that in both irradiation geometries the microstructure growth has been observed in the present experiments.

When irradiation terminates the produced microstructure is covered by an oxide layer(see Fig. 4 (e)).

According to the described scenario the rates of chemical reactions on the surface play a crucial

role for microstructure formation. Here we discuss the microstructure growth through the surface oxidation　assuming that the proposed scenario is also valid for other reactive atmospheres which can create a rigid skeleton on the liquid metal surface. The oxidation process proceeds due to diffusion of metal cations through the growing oxide layer to the sample surface while the oxygen anions diffuse in the opposite direction. Thus　one can expect that a partial oxidation on the tip of a growing microstructure occurs during the time interval between the subsequent laser pulses. Each following laser pulse unseals the top part of the microstructure　thus allowing the molten metal to flow out from the melt volume through the oxide tube under the action of either capillary forces or the pressure of molten material　depending on the irradiation geometry.

5　Conclusion

We have presented a new phenomenon　formation of microstructures　on multishot laser irradiation in the UV‐IR spectral ranges of a number of liquid metals (Ga　In　Sn　Pb alloy　Wood's metal) in reactive ambient gases. To reveal the conditions in the laser irradiated zone　thermal modeling was performed the results of which furnished the clue to understand‐

ing the importance of a number of the process parameters. The microstructure formation is shown to be governed by interplay between different processes　including ablation　thermal expansion　temperature variations of viscosity　surface tension　thermal stresses　and capillary effects. The most important factor is surface chemistry. The rates of chemical reactions on the liquid metal surface control both the microstructure growth rate and stability of the formed coatings on the microstructure walls.

It should be noted that we have touched only the basic mechanisms of microstructure formation and some ways for growth control. It can be expected that microstructure length　radius　and growth rate can be regulated by changing the irradiation spot size　pulse duration(down to femtosecond laser pulses)　ambient gas type　pulse repetition rate　etc. The described microstructures can open ways for a number of possible applications　among which we can conceive of manufacturing a variety of microparts　moulds　and decorations. Another application may be in studying the chemistry of surface reactions under strongly non‐equilibrium conditions. As an example　we can conjecture that the microcones growth observed [16,17] is governed by similar processes to those responsible for microstructure formation.

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