Advanced Laser Science Research Section

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1. Introduction

Laser is a versatile technique to probe various dynamics and also fabricate various devices. This year we have developed a few different techniques to probe the electrochemical processes during hydrogen evolution, fabricate the functional metal surfaces, and modify the size and shape of nanoparticles for the utilization toward green energy.

2. Influence of liquid viscosity and temperature on the morphologies of laser-induced microstructures

Laser materials processing is a useful technique to fabricate micro/nanostructures on the material surface, and performed not only in air but also in liquids in some cases to fabricate desired surface morphologies. How and how much the property of the liquid influences the surface morphology of the laser-irradiated target is not yet completely understood. This is particularly true in terms of liquid viscosity. To clarify the role of liquid viscosity in laser materials processing we undertake the study to ablate the metal target in different liquids at different temperatures and compare the morphology of the ablation crater. The liquids we employ in this study are water (H_2O), ethanol (ET), ethylene glycol (EG), and glycerol (GOL) at room temperature (RT), and additionally EG and GOL at 100 °C, since their viscosities significantly change at different temperatures. Representative results with Ni targets are shown in Fig. 1. In Fig. 1(a) we clearly see the confinement effects. From Fig. 1(b), we notice that the diameter of the crater in each liquid linearly increases with laser fluence, and at a given laser fluence, the crater diameters are air < ET < water < EG at 100 °C < EG at RT < GOL at 100 °C < GOL at RT. Similar is true for the volume (Fig. 1(c)). To explain the different ablation efficiencies in different liquids at different temperatures we consider the pressure exerted to the target under the confined geometry by laser-induced plasma, and estimate the plasma-induced recoil pressure. The relative pressures exerted to the target during the laser pulse are found to be 1:0.78:1.09:1.20:1.26 in water, ET, EG at RT, GOL at RT, and GOL at 100 °C, respectively, and this order is in good agreement with those of the experimentally obtained diameters and volumes of ablation craters shown in Fig. 1(b) and (c). This clearly shows that it is not the liquid viscosity but the plasma-induced recoil pressure that plays an important role on the ablation efficiency in liquids.

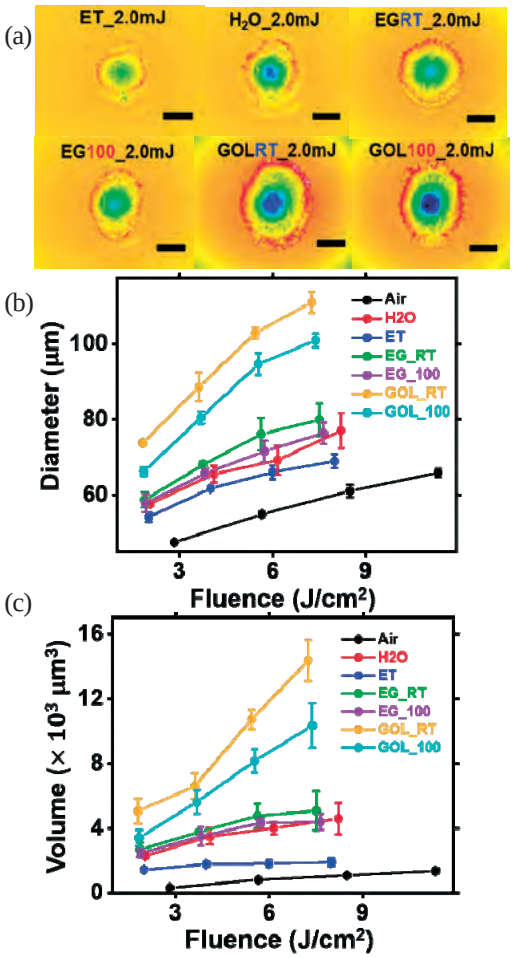

Fig. 1 (a) Morphologies of the ablation craters in air and various liquids at different temperatures. Variation of (b) diameters and (c) volumes of ablation craters as a function of laser fluence.

3. Correlation between the bubble forming sites and micro/nanostructures on the electrode surface during hydrogen evolution

Production of hydrogen gas through water electrolysis using the excess electricity is one of the promising candidates for green energy. For the efficient production and transportation of hydrogen gas through water electrolysis it is very important to

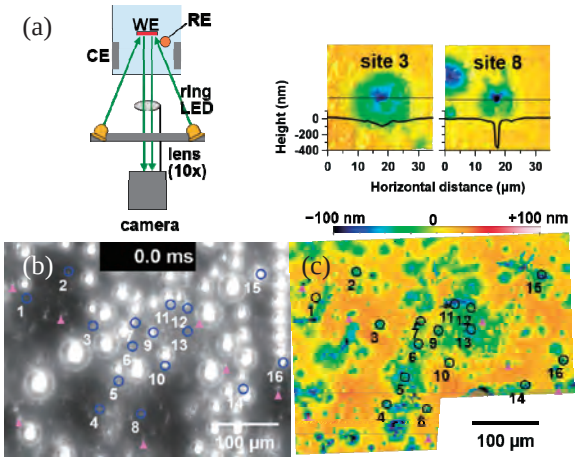

Fig. 2 (a) Experimental setup. (b) Optical image of hydrogen bubbles where all bubble forming sites are numbered. (c) Corresponding false-colored surface profile of the electrode. The figures above panel (c) are the blow-ups of the surface profiles at sites 3 and 8.

know where on the electrode the hydrogen bubbles are formed, since the deeper understanding of formation mechanism will enable us to design the surface morphology of the electrode. For this purpose we optically monitor the formation of hydrogen bubbles on a Ni disk cathode from the front side (Fig. 2(a)) to identify the bubble forming sites (Fig. 2(b)), and correlate them with the surface profile with ~μm accuracy (Fig. 2(c)). We notice that the bubble forming sites are located at the shallow structures, but their structures are not necessarily similar, as shown by the surface profiles of bubble forming sites 3 and 8. To better understand the local bubble dynamics we analyze the optical images of the bubbles at sites 3 and 8 using many successive images taken with the time interval of 1 ms, and obtain the temporal variations of the squared radius, R^2, and rising velocities, v, of the bubbles formed at sites 3 and 8 (Fig. 3). We find that the growth rates and formation periods of the bubbles are completely different at those sites, and the formation period is very long at site 8. The

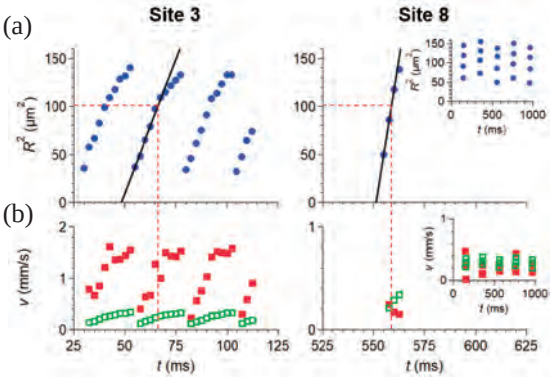

Fig. 3 (a) Temporal variations of the squared radius, R^2, and (b) experimental (closed squares) and theoretical (open squares) rising velocities, v, of the bubbles formed at sites 3 and 8.

difference of the experimental and theoretical rising velocities of the bubble at site 3 implies the presence of local convection flowing upward near site 3 since the theoretical rising velocity is obtained using the Stokes law without taking into account the convection. In contrast, there is practically no local flow near site 8. These results suggest that, although sites 3 and 8 are only ~120 μm apart, the dynamics of the bubbles as well as the local convections at those sites are very different. This is the first study to correlate the bubble forming sites and surface morphologies of the electrode and clarify the dynamics of bubbles.

4. Dynamics of hydrogen bubbles formed at a laser-induced microstructure on the electrode during hydrogen evolution

What we have learned from the study described in the previous section is that, although there is a clear correlation between the bubble forming sites and their local surface morphologies, the local surface morphology itself does not seem to determine the bubble dynamics. Knowing this, we fabricate a single microstructure on a polished Ni electrode by single-shot laser irradiation, and study the formation of hydrogen bubbles at a laser-induced microstructure through the optical detection. The results are summarized in Fig. 4. From the optical image of the laser-induced microstructure with bubbles shown in Fig. 4(a) we notice that the bubbles are never formed at the central area of the microstructure, and all the bubble forming sites numbered 1-7 are located at the periphery of the microstructure where there are bumps (Fig. 4(b)) with so many micro/nanostructures (Fig. 4(c) and (d)). It is interesting to point out that the growth rates and formation periods of the bubbles under the constant current operation are different at different bubble forming sites. This finding clearly implies that a subtle local structure within a single microstructure strongly influences the bubble forming activity of the individual sites, although they are only a few tens of μm apart.

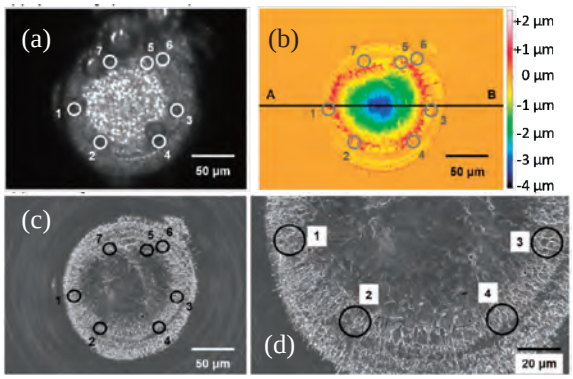

Fig. 4 (a) Optical image of the laser-induced microstructure with bubbles and (b) surface profile of the corresponding area. (c) SEM image of the microstructure and (d) its blow-up.

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