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Short communication

# Experimental study of cavitation damage on hydrogen-terminated and oxygen-terminated diamond film surfaces

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**Abstract**

To investigate the effect of hydrophobic surface on cavitation damage, hydrogen-terminated diamond film and oxygen-terminated diamond film are prepared for the cavitation damage experiment. Because the film surfaces have the same roughness and hardness, the hydrophobic property effect is focused on. Obvious damage pits appear on the hydrogen-terminated surface after 4 h cavitation experiment, while no such pits are found on oxygen-terminated surface. Surface testing results also show that the surface roughness of hydrogen-terminated surface is higher than that of oxygen-terminated surface after the experiment. Such results indicate that the collapse of bubbles growing from the hydrophobic wall to be damaged plays important role in the generation of cavitation damage.


*Keywords:* Heterogeneous nucleation; Cavitation damage; Surface roughness; Diamond film

## 1. Introduction

The studies on the bubble collapse and cavitation damage have accumulated since the pioneering work of Rayleigh [1] in 1917. It is commonly agreed that a collapsing bubble has the potential for generating extremely high pressures and velocities to damage solid surfaces according to Rayleigh's analysis [1]. This loss of material on solid surface is known as "cavitation damage". This statement is supported by experimental photographs [2,3] as well as theoretical analyses [4,5], which are enumerated by Hammitt [6] in a short review. On the other hand, the heterogeneous nucleation is thought to be a necessary step before cavitation damage. This theory was first proposed by Harvey [7] and later demonstrated by Scardina [8]. It was thought that the gas nuclei exist in the crevices on solid surfaces submerged in water, and then they grow and collapse to cause cavitation damage. But now a question is arising: whether the surface is damaged by the bubbles generating from the solid surfaces of particles contained in water, or by the bubbles generating from surface of the wall to be damaged? Numerical results have proved that the bubble should be close to the wall to cause the damage [6]. It seems that the bubbles growing from the wall surface have more probability to cause cavitation damage, but this assumption still needs the experimental validation.

So in the undergoing study, two different surfaces are prepared in the cavitation damage experiment. One is a hydrophobic hydrogen-terminated diamond film, and the other is a hydrophilic oxygen-terminated diamond film. It is known that a hydrophobic rough surface is necessary for pre-existing nuclei on solid surface [8], so the heterogeneous nucleation condition on the two film surfaces are not the same. Comparing the damage level on the two surfaces after the experiment, the question mentioned above is investigated. It should be noted that the diamond film is very smooth and hard, pits on its surface are easily observed and determined, so it is chosen as the surface in the experiment.

## 2. Experimental

### 2.1. Experimental apparatus

Fig. 1 shows the schematics of a rotating-disk cavitation apparatus. The diameter of the rotating-disk is 300 mm and four samples are installed on the rotating disk. To induce the cav-

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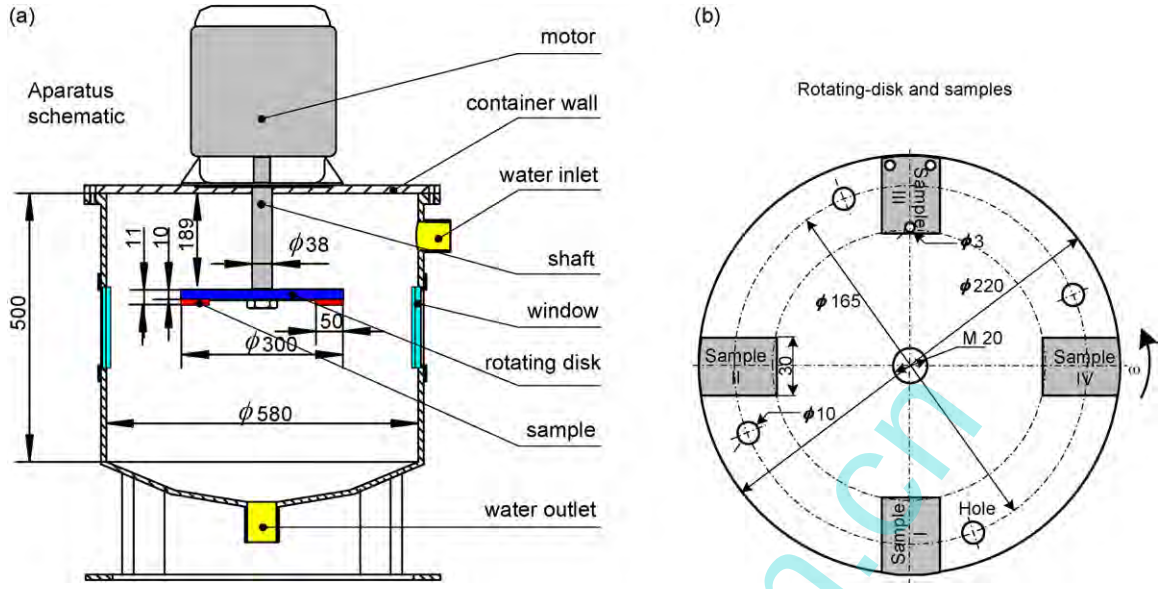


Fig. 1. (a) Schematics of the cavitation experimental apparatus and (b) the installment of the samples.

itation, a hole with 10 mm diameter is made on the rotating-disk in front of each sample. The rotating speed is 2800 round/min, and the corresponding velocity of the samples is near 30 m/s. In this experiment, the sample is made of Q235 steel without heat treatment, and its size is 40 mm × 30 mm × 6 mm. The chemical composition of Q235 steel is shown in Table 1. The depth of the sample installation site is 5 mm, and the up surface of the sample is 1 mm higher than the rotating disk surface. The fluid used in the experiment is tap water, and the temperature of the water is kept at 25 ± 1 °C using the low temperature water circulation system during the experiments.

### 2.2. Sample surface treatment

Hydrophilic and hydrophobic surfaces are prepared on the samples. The surfaces are prepared as follows. Firstly, diamond films are prepared on silicon disk surface. The diamond films are

Table 1
Chemical composition of the Q235 steel (%)

| C | Si | Mn | P | S | Fe |
|---|---|---|---|---|---|
| 0.22 | <0.05 | 0.48 | 0.012 | 0.022 | Remains |

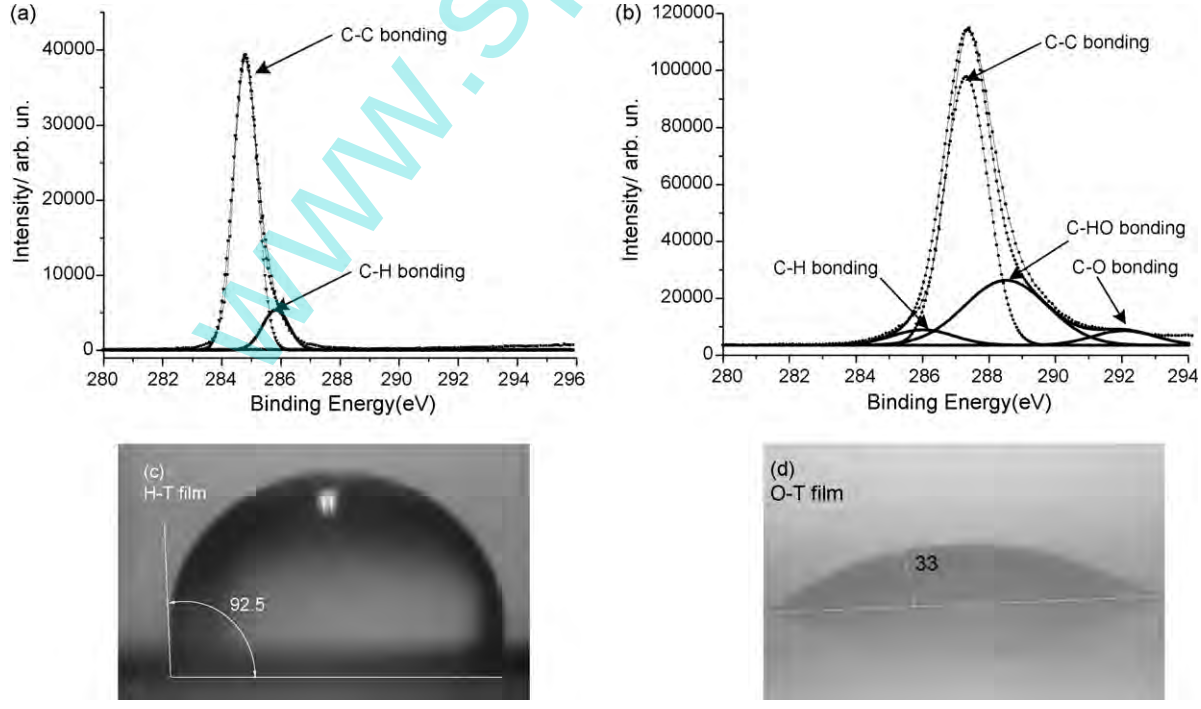


Fig. 2. C 1s core-level spectra of (a) hydrogen-terminated diamond film (b) oxygen-terminated diamond film; water contact angles of (c) hydrogen-terminated diamond film and (d) oxygen-terminated diamond film.

deposited onto low resistivity silicon (p-type) substrates from a hot-filament activated methane hydrogen gas mixture with the pressure of 50 Torr. The filament temperature is 2500 °C and that of substrates is 830 °C. The mixture flows at the rate of 5 L/min, and the growth rate is 0.24 μm/h. A continuous film of diamond is obtained after 15 h of growth.

Secondly, two different surface terminations, oxygenation and hydrogenation, are made on the diamond film. For oxygenation, the as-deposited diamond film is boiled for 1 h in a solution of conc. $HNO_3/H_2SO_4$ (1:3) at 350 °C. For hydrogenation, the acid treated diamond surface is exposed to microwave hydrogen plasma at about 800 °C for 10 min after a preceding annealing step in UHV at 1100 °C. As a result, a hydrogen-terminated diamond film and an oxygen-terminated diamond film are prepared, and the surface material tested by XPS is shown in Fig. 2.

The plots of Fig. 2(a) and (b) correspond to C 1s core-level spectra of hydrogen-terminated and oxygen-terminated diamond films, respectively. The peak fitting has been carried out in Fig. 2(a) and (b) to identify the different chemical states. For the hydrogen-terminated diamond film, the peak at 285.8 eV can be attributed to C–$H_x$ bond. For the oxygen-terminated BDD film, it also possesses some C–$H_x$ bond, which is low in intensity. The peak at 288.5 eV, however, has a strong intensity, which could be assigned to hydroxyl group. In addition, a peak at 292.1 eV, low intensity but broad, can be attributed to either carbonyl or carboxyl group [9]. The surface wetting properties are believed to be affected by the C–$H_x$ bond [10–15]. After hydrogen-plasma treatment, the diamond surface is covered by hydrogen atoms and the reconstruction occurs [10–12]. Aleshin et al. [13] proposed C=C binary bonds form and the atomic valence state changes to an $sp^2$ state as a result of the carbon atom shift parallel to the surface. Thus, the surface energy of the diamond film decreases after hydrogenation, and the water wetting angle increases [14,15].

The oxidation process for the diamond films desorbs the bonded hydrogen and removes the $sp^2$ phase bonds, recovering the $sp^3$. This process increases the surface energy and results in a more hydrophilic surface [14,15]. The water contact angles of the two different surfaces are measured before the cavitation test using JC200A contact angle tester. The photos of water droplet on silicon surface are shown in Fig. 2a. The water contact angles on hydrogen-terminated and oxygen-terminated diamond films are 92.5° and 33°, respectively. The hydrogen-terminated diamond film is hydrophobic, while the oxygen-terminated diamond film is hydrophilic. These results cope with the experiment results given by [16].

Table 2
Film hardness testing

| | Tested data (GPa) | Average value (GPa) |
|---|---|---|
| Hydrogen-terminated diamond film | 30.5, 32.0, 41.5 | 34.7 ± 5.9 |
| Oxygen-terminated diamond film | 35.5, 28.5, 30.5 | 31.5 ± 3.6 |

Thirdly, the silicon disk covered by terminated film is adhered on the sample's surface using epoxide resin glue. Samples I is covered by the hydrogen-terminated diamond film, while sample III is covered by the oxygen-terminated diamond film. The other two samples are used as the balance. The surface roughness of the two film surfaces measured by Scanning Probe Microscope (SPM, CSPM-4000) are shown in Fig. 3, five points with size of 2 μm × 2 μm on each sample surface are measured by SPM. The average value of the root mean square (RMS) for the 5 tested points on the hydrogen-terminated surface is 53.15 ± 8.02 nm, and the average value on oxygen-terminated surface is 58.14 ± 9.58 nm. The roughness of the two kinds of surfaces is almost the same. Except for the same roughness, the hardness of the two films is also same. The hardness of the film is tested using MML Nanotester, 3 points on each kind of film with the surface interval of 10 mm are tested and the data are shown in Table 2. The average hardness values of the two films are both near 30 GPa. So, through the surface treatment, the experimental conditions for the two samples are same except for the surface termination, whose effect on cavitation damage is focused in the experiment.

## 3. Results and discussions

### 3.1. Cavitation damages

The cavitation damage experiment lasts 4 h. After the experiment, the sample surfaces are cleaned and observed by scanning

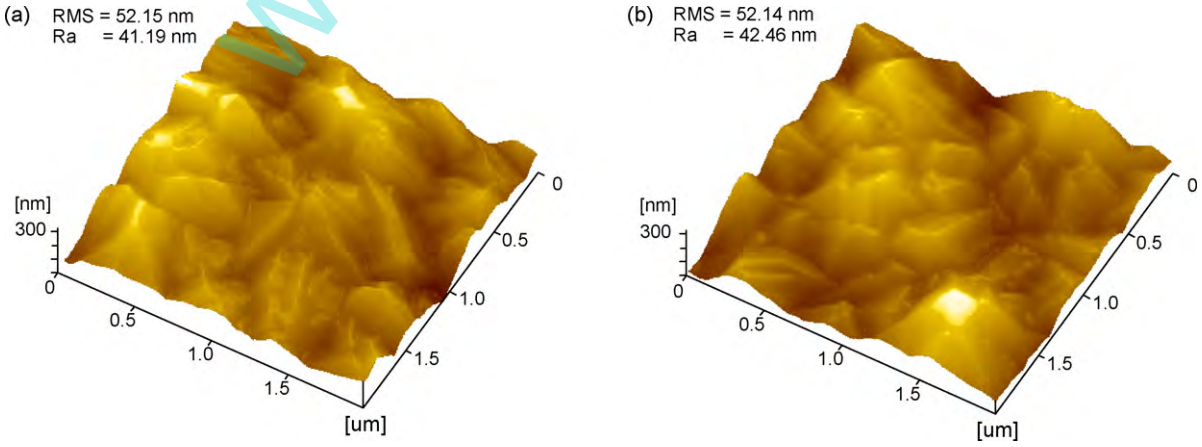


Fig. 3. Measured surface roughness of (a) the hydrogen-terminated film, and (b) the oxygen-terminated film.

electron microscope (SEM, Quanta 200 FEG). To allocate the position of the place to be observed, a scratch with the shape of 'Γ' is made on the sample surface using glasscutter. Here, the film surface before and after the experiment is shown in the following figures. Fig. 4(H-I) and (O-I) show the two original surfaces before experiments. The first letter 'H' indicates that the surface is a hydrogen-terminated surface, while the first letter 'O' indicates that the surface is an oxygen-terminated surface. Fig. 4(H-II) shows the area 100 μm in front of the corner point of the scratch in case that the scratch may have effect on the

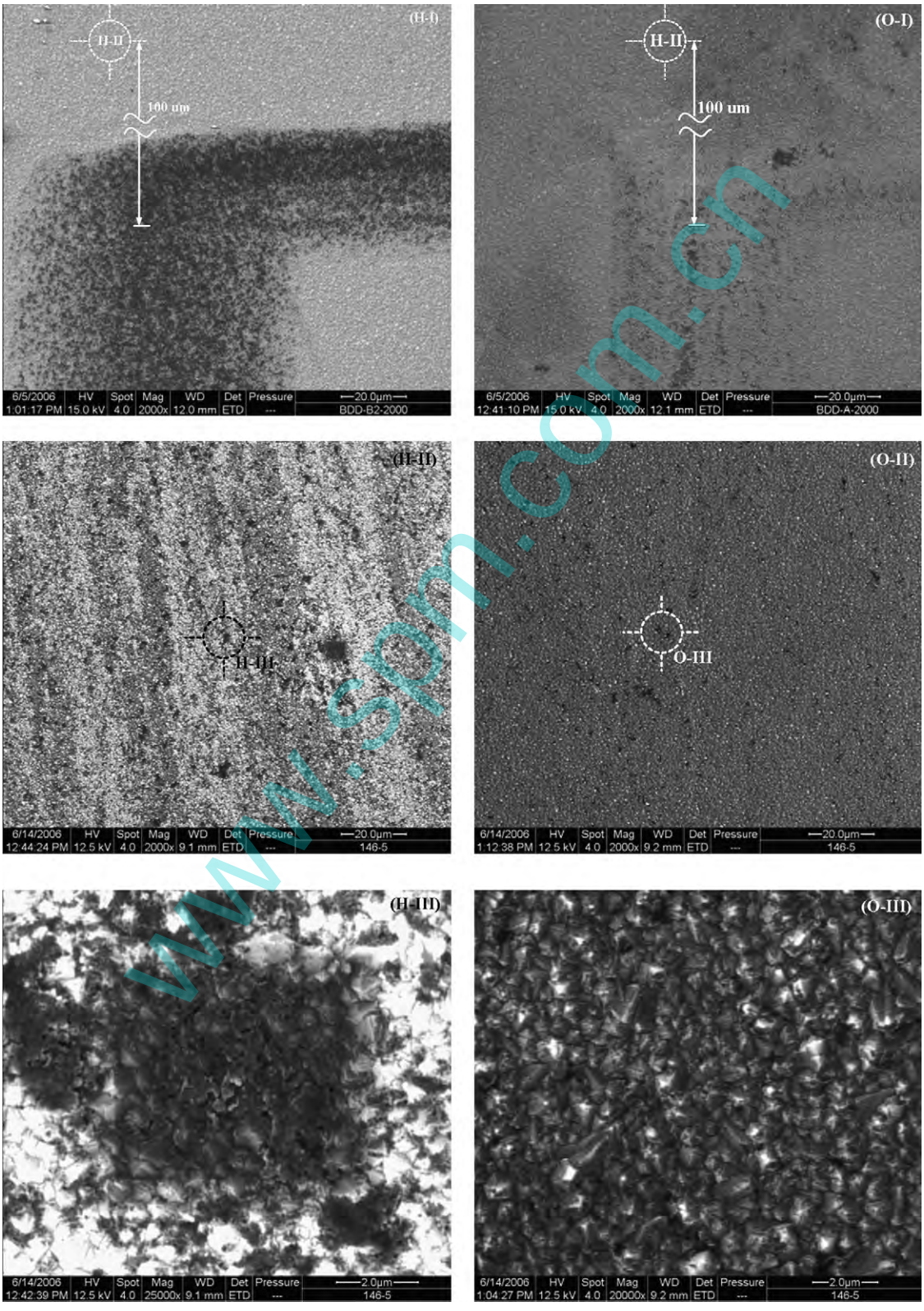


Fig. 4. Surfaces of samples observed by SEM. (H-I)–(H-III) are the hydrogen-terminated film; (O–I)–(O-III) are the oxygen-terminated film.

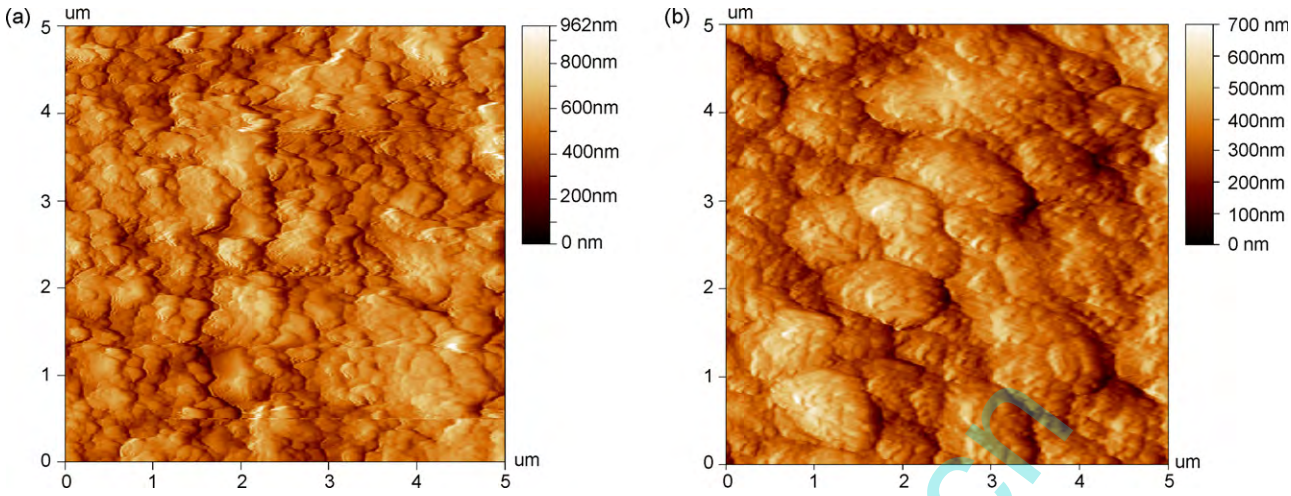


Fig. 5. Surface roughness measured by SPM. (a) hydrogen-terminated surface and (b) oxygen-terminated surface. Measuring area is 5 μm × 5 μm.

cavitation damage results. Fig. 4(H-III) is the enlarged view of the area marked in Fig. 4(H-II). Same treatment is also applied to the figures of oxygen-terminated surfaces. The magnitude, scale and other testing parameters are shown at the bottom of each figure.

It is found from the figures that both of the two original surfaces are smooth besides the scratches. But after the experiment, there is a great difference between the two surfaces. For hydrogen-terminated surface (H-II), there are some obvious pits on the surface (shown as the dark points on the film surface). While for oxygen-terminated surface (O-II), no such obvious pits are found (the smaller dark points are mostly the shadow of the grains, later disappeared in Fig. 4(O-III)). To show the pit on the film clearly, an enlarged view of the marked area including a dark point is provided as Fig. 4(H-III) and (O-III). In Fig. 4(H-III), the center part is obviously darker than the round part. Because some crystal grains of diamond are also observed in the center part, the color difference should not be caused by the conductivity of the material, but the height of the surface. So the center part is lower than the other place and the dark point is a pit. Moreover, the diamond film is very hard; it is difficult for the particles in the water to cause scratches and collision pits on the film. On the other hand, numerical results [2–4] suggest that bubble collapse may provide enough energy. So it is considered that the pits on hydrogen-terminated surface are the trace of cavitation damage.

Besides, the crystal grains on hydrogen-terminated surface (H-III) are not as continuous and well faceted as those on oxygen-terminated surface (O-III). It seems that some grains in the pits on hydrogen-terminated surface are removed from their original place. Because such surface damage will result in the increment of the surface roughness, the surface damage can also be verified by the surface roughness measurement. The surface roughness of the hydrogen-terminated and the oxygen-terminated surfaces are measured by the SPM, and the results are shown in Fig. 5 (a) and (b), respectively. Five points on each kind of surface are measured. RMS of the hydrogen-terminated surface is $106.5 \pm 5.5$ nm, and the value on oxygen-terminated surface is $82.3 \pm 5.6$ nm. The hydrogen-terminated surface becomes rougher than the oxygen-terminated surface, the reason is thought to be the more serious surface damage generated on the hydrogen-terminated surface. Also, the results in Fig. 5 prove that the crystal grains on hydrogen-terminated surface are not as complete as those on oxygen-terminated surface, which is also found in the SEM pictures.

It can be concluded that more obvious cavitation damage pits are found on the hydrogen-terminated surface than on the oxygen-terminated surface. Because other conditions are same, it is considered that cavitation damage more easily occurs on hydrogen-terminated surface than on oxygen-terminated surface, and the surface termination is proved to have effect on generating cavitation damage on solid surface.

### 3.2. Discussion

According to Harvey's [17] theory, nucleation on solid surface is a necessary step for the bubble formation in liquid, while homogeneous nucleation within the bulk water is not expected to be observed according to the condition given by Harvey. Bubbles can form within preexisting gas pockets located in surface cracks and imperfections of solids in a process known as heterogeneous nucleation, and this process is shown in Fig. 6 [8]: supersaturated gas diffuses into the gas pockets, causing bubble growth and eventual detachment from the solid support. Unlike homogeneous nucleation, heterogeneous bubble nucleation can occur whenever water is supersaturated [18]. Usually, there are two sources of solid surface to provide the locations for nuclei. One is the surface of particles in the water; the other is the solid wall to be damaged. In the experiment, both of the two diamond film surfaces are not ideal smooth, and the nuclei may exist in the crevices on the two solid surfaces. The cavitation damage on hydrogen-terminated film proves that the surface roughness condition for nucleation is satisfied.

However, the cavitation damage seems to occur more easily on the hydrogen-terminated film surface, it indicates that other conditions should be considered besides the surface roughness. As Harvey [10] suggested, the crevice attaching the nuclei should also have a hydrophobic surface. In the experiment,

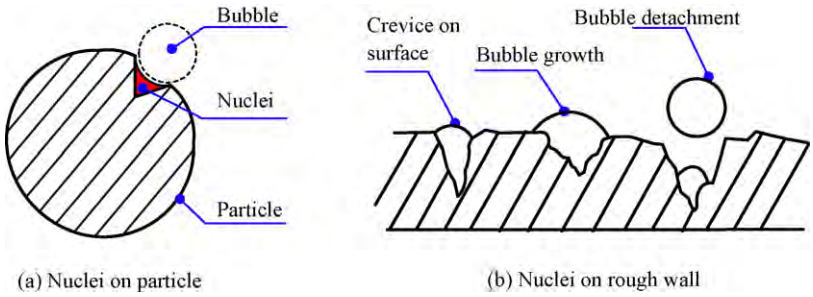


Fig. 6. Nucleation on particle and wall surfaces.

contact angles of the two diamond surfaces are measured. The hydrogen-terminated diamond film shows a water contact angle of 92.5°, as expected for a surface terminated with the C–H groups. A significant decrease of the water contact angle is observed for the oxygen-terminated diamond film. This value is comparable to the previous report [16]. For hydrogen-terminated film, the bubbles are more easily to form on the solid wall. Then the bubbles collapse and cause the cavitation damage on the wall. In contrast to the hydrophobic surface, heterogeneous nucleation is difficult to complete on hydrophilic surface, and the cavitation damage is consequently not so easily generated on such surface. It is suggested from the results that the bubble growing from the wall, not the particle surface, has more probability to damage the wall surface.

## 4. Conclusions

Cavitation damage experiment has been performed on hydrogen-terminated diamond film surface and oxygen-terminated diamond film surface. From the experimental results and analyses, some conclusions are drawn as follows.

Firstly, experimental results show that both diamond films underwent cavitation damages. Moreover, the damage on hydrogen-terminated surface is more severe than that on oxygen-terminated surface. The reason is that the oxygen-terminated film has a hydrophilic surface, one of the necessary conditions for heterogeneous nucleation is lacked and bubbles are difficult to form on the surface. As a result, the cavitation damage more easily occurs on the hydrogen-terminated film surface.

Secondly, the effect of the nucleation on the hydrophobic surface, on the other hand, indicates that the collapse of the bubble growing on the wall plays important role in generating the cavitation damage.

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