International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:10, No:5, 2016

Negative Pressures of Ca. -20 MPA for Water Enclosed into a Metal Berthelot Tube under a Vacuum Condition

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Abstract**—**Negative pressures of liquids have been expected to contribute many kinds of technology. Nevertheless, experiments for subjecting liquids which have not too small volumes to negative pressures are difficult even now. The reason of the difficulties is because the liquids tend to generate cavities easily. In order to remove cavitation nuclei, an apparatus for enclosing water into a metal Berthelot tube under vacuum conditions was developed. By using the apparatus, negative pressures for water rose to ca. -20 MPa. This is the highest value for water in metal Berthelot tubes. Results were explained by a traditional crevice model.

Keywords**—**Berthelot method, negative pressure, cavitation

I. Introduction

When a liquid is over-expanded at a temperature, pressure of the liquid becomes negative absolutely unless vapor phase appears. Since negative pressure is in metastable state thermodynamically, tiny bubbles are seen suddenly in the liquid, and the liquid coexists with its vapor. This phenomenon is called cavitation [1].

Negative pressure is an interesting and important object in science and technologies. For example, phase diagrams of proteins in negative pressure regions will give useful information to avoid aggregations of proteins in human bodies which may occur under negative pressure generated with medical ultrasounds [2].

There have been few experimental reports to measure liquids' properties under negative pressures except for their tensile strengths because cavitation occurs easily before negative pressured become high [2]-[4]. A suitable means for such measurements is the Berthelot method. This method uses difference of thermal expansion between a liquid and a container, and it generate static negative pressures.

In previous studies about the Berthelot method, containers were made of glasses [5], [6], metals [7] and minerals [8] exclusively. Metal tubes had merits of high strengths as pressure vessels and of experiments for various densities of liquids, though they had been said to be notorious materials for negative pressures lower than other containers. Therefore, studies of metal Berthelot tubes were carried out. Negative pressures for water of ca. -18 MPa [9] and some organic liquids of ca. -20 MPa [10] could be attained by repeating a few thousands of temperature cycles. These results were obtained on a basis of a gas-trapping crevice model with a gas supply assumption about cavitation nuclei [11]. In addition, properties under negative pressure regions to ca. -15 MPa were reported for two kinds of thermotropic liquid crystals [12], [13] and water [14]. However, negative pressures were too low to give useful information; techniques for higher negative pressures were requested.

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The crevice model insists that 1) gases trapped within tiny crevices in dust particles and on the container wall serve as heterogeneous nuclei when negative pressure builds up, and 2) negative pressure is limited by the supply of gas from sources in the metal bulk to the crevices [11].

In the previous studies of metal tubes, sample liquids were sealed into metal containers with softer metal plugs [9]-[14]. The operation was as follows; 1) the plugs were located on opening edges of the containers, and 2) they were forced to the edges with screws and were deformed there plastically. The operation was carried out under atmospheric pressure. If even the first of the operation had been done under vacuum conditions, the gases trapped within the crevices would have been reduced in amount; higher negative pressures would have been generated. Thus, in this study, an apparatus by which the sample liquid is poured into the container and is enclosed with the plug under a vacuum condition is made, and negative pressures with temperature cycles are measured. Negative pressures of ca. -20 MPa for water were obtained after a few thousands of temperature cycles at characteristic temperatures less than ca. 65 °C, at which pressures became zero. On the other hand, negative pressures for higher temperatures deteriorated. The results were explained by a gas trapping crevice model.

II. Experiment

The experimental procedure employed here is similar to that reported before [14]. So, we describe some specific to this study in detail and the others briefly.

Fig. 1 shows the Berthelot method schematically [15]. A Berthelot tube contains liquid and a small volume of air and liquid vapor at a temperature Ta as shown in Fig. 1 (a). When the tube is heated, the liquid fills the tube at a temperature as shown in Fig. 1 (b) because the liquid tends to expand more than the tube. At the temperature, liquid volume is equal to tube one, and pressure of the liquid becomes zero. The temperature is called T0. Then the tube is cooled, pressure decreases and, instead, negative pressure increases to a temperature Tc just before cavitation as shown in Fig. 1 (c) because the liquid tends to shrink more than the tube. Fig. 1 (d) shows the tube and contents at a temperature just after cavitation. When the tube at Fig. 1 (d) is heated, the liquid fills the tube again as shown in Fig. 1 (b). By subsequent cooling the tube, negative pressure builds up again. This series of stages (b) (c) (d) is called temperature cycles [11]. In metal Berthelot tubes, negative pressures increase with temperature cycles.

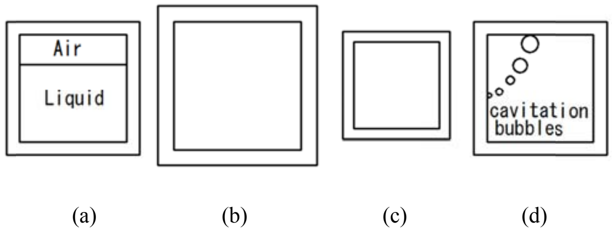

Fig. 1 Four stages of the Berthelot tube

Fig. 2 shows an apparatus for pouring a sample liquid (distilled water) into a container and covering the liquid with a plug under a vacuum condition. The apparatus consists of a vacuum pump, a cold trap for avoiding penetration of vapor to the pump, a bourdon vacuum gauge, the container into which the sample liquid was poured, Y shaped tubes, two glass tubes for the sample water and a metal ball which played a role of the plug, and vacuum hoses. The detail of the container, as shown in Fig. 2, consisted of a pressure transducer having a specimen chamber of type 630 stainless steel in its upper part, a socket for connecting the container with the hose and filling the sample water inside, a cup for a pool of hot water to adjust a temperature called T0 at which pressure became zero.

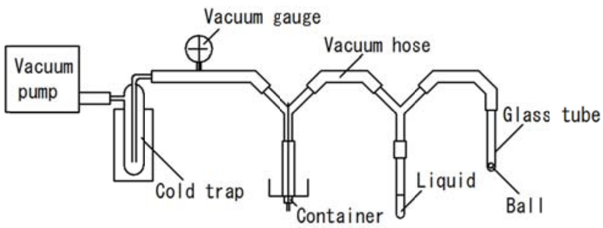

Fig. 2 An apparatus for enclosing a sample water into a container with a ball

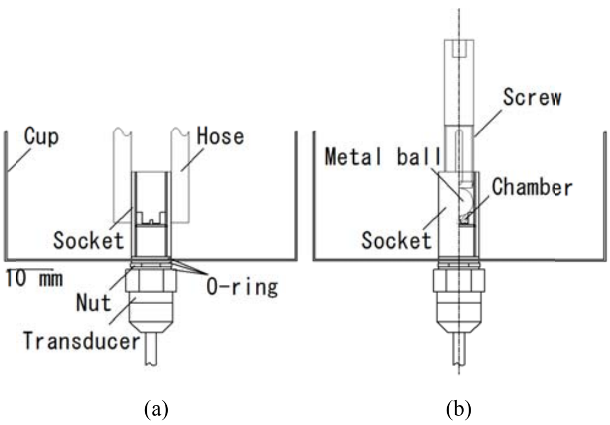

Fig. 3 A container part before and after filling water

The sample water was pre-boiled in the glass tube and was irradiated intermittently by ultrasonic waves, while the ball was heated in boiling water and was irradiated similarly. These pretreatments were efficient in removing weak cavitation nuclei [11].

In this study, two vacuum pumps, namely a rotary pump and a dry one, were used to examine an effect of degrees of vacuum on negative pressures. They had capabilities of evaporating to pressures less than ca. 0.2 Pa or equal to ca. 95 kPa.

A procedure for enclosing the sample water in the container with the ball under a vacuum condition using a rotary pump is as follows. Firstly, the vacuum pump was turned on, air inside the hoses and other parts of the apparatus was de-gassed, and the sample water boiled as pressure of air equaled to a pressure saturated with vapor. The boiling did not occur under another condition using a dry pump.

After a few minutes, the boiling was stopped because heat of vaporization was taken away. Secondly, by handling the hoses and the tubes carefully, the sample water was poured inside the socket as shown in Fig. 3 (a). Finally, the ball was moved from the glass tube onto the container similarly. Surface areas of the ball and the chamber which contacted with the sample water were not exposed to air through the procedure.

After the procedure was finished, the water was sealed as described below. The hose in Fig. 3 (a) was removed from the socket. At this time, the ball had been submerged in the sample water and been located on opening edge of the chamber. Then, a screw, as shown in Fig. 3 (b), was fit inside the socket. In the cup in the figure, hot water was poured and was measured with a Pt resistance thermometer to decide T0. When the temperature of the hot water was less than ca. 70 °C, the screw was fastened so that the ball was deformed plastically. For a temperature of the hot water, the severer an amount of sealing distortion was, the lower T0 was. In this study, the T0s were exclusively set around 65 °C within ± 2 °C.

After sealing the water, the Berthelot tube underwent temperature cycles with an automatic temperature cycle repeater (ATCR) with two baths to fully utilize the cavitation history effect that the greater the number of temperature cycles repeated, the higher the negative pressure attained [11]. The ATCR could repeat the cycle by alternate submersions of the tube in either of baths, hot and cool.

III. Results and Discussion

Trends in negative pressures with ca. 100 cycles for three different conditions under which amounts of the sample water were enclosed in the Berthelot tubes were shown in Fig. 4. Negative pressures for enclosure under an atmospheric pressure (1 atm) were levelled off from ca. -8 MPa to ca. -10 MPa with wide scatter, while those under low vacuum of ca. 95 kPa were from ca. -9 MPa to ca. -12 MPa with less scatter. Negative pressures for that under high vacuum of ca. 0.1 Pa increased from ca. -6 MPa to ca. -18 MPa with wide scatter.

The wide scatter for that under high vacuum was attributed to a severe experimental condition of ATCR. The tube was immersed into the cool bath to generate negative pressures. According to previous studies, a too high temperature at which the tube was immersed tended to cause a troublesome thermal shock, and a too low temperature caused cavitation just after the immersion [11].

In this study, the tube had no sensor to monitor the immersion temperature, that is, the sample water's temperature on the immersion. After trials, authors found intermediate temperatures of the cool bath regardless of negative pressures. The scatter of negative pressures for that under high vacuum was yielded as a result of the trials. Fig. 4 insists that enclosure of water under a higher vacuum condition was an excellent means to generate high negative pressures.

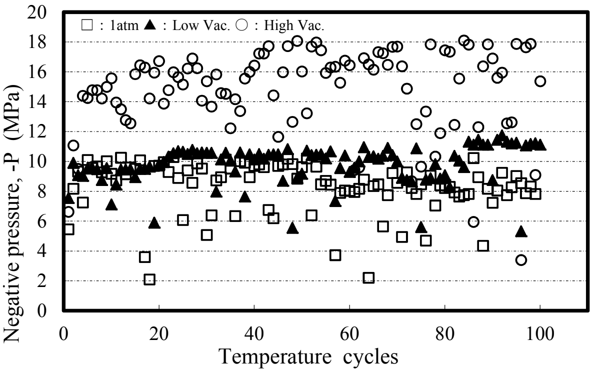

Fig. 4 Trends in negative pressures for three conditions; the brass ball was located on the container under atmospheric pressure (□), low vacuum (▲), and high vacuum (○)

Fig. 5 shows scatters in negative pressures with temperature cycles for the initial 3000 cycles for two kinds of ball under a high vacuum condition, namely tough pitch copper (TPC) and oxygen free copper (OFC).

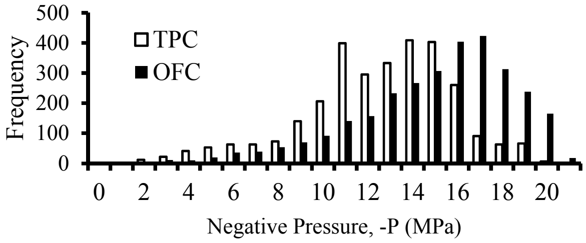

Fig. 5 Scatters in negative pressures with temperature cycles for the initial 3000 cycles for two kinds of ball; TPC (□), and OFC (■)

Negative pressures for OFC were higher than those for TPC, and frequencies of negative pressures in a range from -20 MPa to -21 MPa were 18 times. The highest negative pressure was ca. -20.7 MPa for OFC and ca. -19 MPa for TPC which were higher than ca. -18.5 MPa for an all-stainless steel tube [9].

Fig. 6 shows scatters in negative pressures with temperature cycles for the initial 2500 cycles for brass balls undergoing different surface treatments, namely non- and plasma treatments. Wettability was improved by the plasma treatment [16]. Negative pressures for the plasma treatment were higher than those for non-treatment. Negative pressures of ca. -19 MPa were obtained with the plasma treatment.

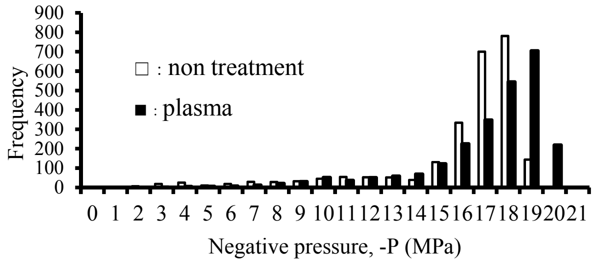

Fig. 6 Scatters in negative pressures with temperature cycles for the initial 2500 cycles for brass balls having different surface treatments; non (□), and plasma treatments (■)

Fig. 6 insists that negative pressures were restricted by gases trapped within crevices on the ball surfaces because negative pressures depended on surface conditions of the balls. Improvement of wettability was to reduce amounts of gases in the crevices and caused higher negative pressure.

The ball of OFC which underwent the plasma treatment was expected to generate high negative pressures. Fig. 7 shows scatters in negative pressures with temperature cycles for the initial 2352 cycles for the ball. The T0 for this experiment was adjusted at ca. 74 °C. The higher T0 was expected to lead higher negative pressures on a basis of principle of the Berthelot method.

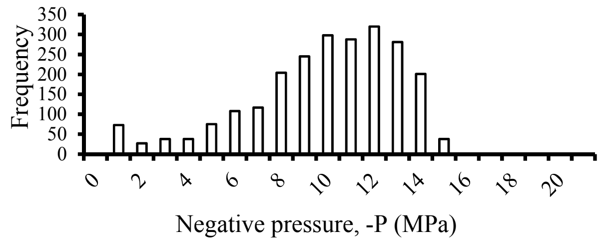

Fig. 7 Scatters in negative pressures with temperature cycles for the initial 2352 cycles for the ball of OFC having plasma treatment

Contrary to the expectation, negative pressures were low. The highest was only ca. 15.5 MPa. This was attributed to the high T0. Similar deterioration was observed in cases of acetone and water sealed with the balls of OFC.

According to the gas trapping crevice model as described in Section I, a pressure difference between gas in a crevice and a liquid contacting with the gas through gas-liquid interface depends on the interfacial tension [11]. It is known generally that interfacial tension decreases with temperature. Therefore, the higher T0 was, the pressure difference was smaller. The small difference indicates that cavitation occurred easily, causing low negative pressures. Here, we gave an interpretation on a basis of the gas trapping crevice model. Another interpretation is possible; gas in metal bulk was supplied into the crevice through grain boundaries connecting with the crevice. Generally, the supply rate depends on temperature; the rate increases with temperatures. Thus, a higher T0 caused lower negative pressures because gases were supplied faster. Regrettably, authors could not identify either of the two factors in this experiment.

IV. Conclusions

In order to generate high negative pressures by the metal Berthelot method, an apparatus for enclosing a sample liquid into a container with a ball was tested. Negative pressures of ca. -20 MPa was obtained for distilled water. The values are the highest for water in the metal Berthelot tube. The deterioration of negative pressures with high T0s was observed. The results were explained by a gas trapping crevice model.

Acknowledgment

Authors deeply thank Mr. Shigemoto and Mr. Ogawa for their help, and all staff in our department for their support.

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