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

K. Hiro, Y. Imai, M. Tanji, H. Deguchi, K. Hatari

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.

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.

![Diagram](image1.png)

**Fig. 1** Four stages of the Berthelot tube

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).

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

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.

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REFERENCES


