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Dynamics of gas micronuclei formed on a flat hydrophobic surface, the predecessors of decompression bubbles

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ABSTRACT

It is a long-standing hypothesis that the bubbles which evolve as a result of decompression have their origin in stable gas micronuclei. In a previous study (Arieli and Marmur, 2011), we used hydrophilic and monolayer-covered hydrophobic smooth silicon wafers to show that nanobubbles formed on a flat hydrophobic surface may be the gas micronuclei responsible for the bubbles that evolve to cause decompression sickness. On decompression, bubbles appeared only on the hydrophobic wafers. The purpose of the present study was to examine the dynamics of bubble evolution. The numbers of bubbles after decompression were greater with increasing hydrophobicity. Bubbles appeared after decompression from 150 kPa, and their density increased with elevation of the exposure pressure (and supersaturation), up to 400 kPa. The normal force of attraction between the hydrophobic surface and the bubble, as determined from the volume of bubbles leaving the surface of the wafer, was 38×10^{-5} N and the tangential force was 20×10^{-5} N. We discuss the correlation of these results with previous reports of experimental decompression and bubble formation, and suggest to consider appropriate modification of decompression models.

1. Introduction

One of the main limitations on diving is decompression sickness (DCS), which is caused by the evolution of bubbles in tissue supersaturated with inert gases following decompression from high pressure. For a bubble to evolve, a critical (minimal) size is required to start the process. Bubbles smaller than this critical size redissolve, due to the high pressure caused by surface tension. Thus, as is now widely known, nuclei having a critical radius of curvature must be present before or during decompression for bubbles to evolve in a diver (Hennessy, 1989).

Over the last half a century, it was proposed, for example, that gas micronuclei are formed by cavitation, when two solid surfaces in a liquid are separated (Craig, 1996; Hayward, 1967). It has been suggested that these nuclei are stable gas micronuclei that are present in hydrophobic crevices (Harvey et al., 1944; Liebermann, 1957), or that they are enclosed in micelles of surface-active molecules (Fox and Herzfeld, 1954; Yount et al., 1977). We recently argued that gas micronuclei might be formed in the human body on flat hydrophobic surface that do not have crevices (Arieli and Marmur, 2011). This is so, since it has been shown, using atomic force microscopy, that tiny, flat gas nanobubbles, measuring 5–30 nm, form spontaneously when a smooth (almost uni-molecular) hydrophobic surface is submerged in water containing dissolved gas (Meyer et al., 2005; Singh et al., 2006; Stevens et al., 2005; Switkes and Ruberti, 2004; Tyrrell and Attard, 2001; Yang et al., 2007). While the existence of nanobubbles on hydrophobic surfaces is generally accepted, the mechanism responsible for their stability is yet under discussion (Seddon et al., 2011; Weijs et al., 2012).

In our previous study (Arieli and Marmur, 2011), these nanobubbles were assumed to be the source of gas micronuclei from which bubbles evolved during decompression on smooth hydrophobic wafers. Indeed, bubbles evolved on hydrophobic but not hydrophilic, silicon wafers. This publication also dealt extensively with a possible critique of the method, to the effect that air cavities may have been produced on insertion of the wafer into the water. The main arguments against this were that (a) large numbers of studies had failed to observe any bubbles or nanobubbles on hydrophobic wafers placed in water, following degassing at low pressures (below 10 kPa, which is above our degassing pressure); and (b) no nanobubbles were present when wafers were placed in ethanol, while they appeared after anaerobic replacement of the ethanol with water (Considine et al., 1999; Meyer et al., 2005; Stevens et al., 2005; Switkes and Ruberti, 2004, among others).

There are numerous hydrophobic surfaces in the living body, such as subcutaneous fat, visceral fat, and part of the inner surface of

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blood cavities: the umbilical vein, right ventricle, pulmonary vein, and left ventricle (Hills, 1992). Hills (1992) also demonstrated an oligolamellar lining of phospholipids on the luminal aspect of many blood vessels: venules and capillaries in the cerebral cortex and the aortic endothelium. These surfaces may be the sites where gas micronuclei form spontaneously, even in the absence of crevices.

To further the understanding of decompression-induced bubble evolution, the present paper focuses on the following essential questions: (1) Do the effective gas micronuclei depend on the level of gas supersaturation? Effective gas micronuclei are the subpopulation of nanobubbles that were transformed to growing bubbles. (2) What is the force required to detach a bubble from the surface at which it originated? (3) What is the time scale for the evolution of gas micronuclei? These questions were experimentally studied, using well-defined, hydrophilic and hydrophobized silicon wafers.

2. Methods

2.1. Wafer preparation

Silicon wafers are almost molecularly flat with no crevices on their surface. Circular silicon wafers from two sources, 100 mm P/B(100) 1–10 Ω cm 500 μm (SSP Prime, University Wafer, Boston, MA), henceforth designated UW-wafers, and 100 mm P/B/Cz 10–20 Ω cm 500 μm (Semiconductor Processing Co., Boston, MA), designated SP-wafers. In our previous study (Arieli and Marmur, 2011) we used UW wafers. Report from the experience in the laboratory pointed that hydrophobicity of UW wafers was lower than that of SP wafers. This led us to choose both for the study of the effect of the level of hydrophobicity. Wafers were cut into squares with sides measuring 4.5–5.0 cm. Wafers were cleaned, coated with a hydrophobic layer and the advancing and receding contact angles (as a measure of hydrophobicity) were done as described in our previous paper (Arieli and Marmur, 2011). The hydrophobic molecules bind covalently to the wafer and therefore produce uni-molecular coating. After a few hyperbaric exposures the wafers lost some of their hydrophobicity, probably due to their becoming contaminated or oxidized. This was suspected when bubble density in a used set of wafers was lower than in freshly added wafer, and was later confirmed by measurement of the contact angle. We therefore used more than one batch of wafers, designated UW-I and UW-II, and SP-I, SP-II and SP-III. The contact angles of the hydrophobic UW-I-wafers with a drop of water were $109.8 \pm 2.1^\circ$ for advancing angle, $78.7 \pm 4.5^\circ$ for receding angle, and hysteresis (advancing minus receding angle) $31.1 \pm 4.7^\circ$; contact angles of UW-II-wafers were $115.3 \pm 1.1^\circ$ for advancing angle, $95.4 \pm 2.1^\circ$ for receding angle, and hysteresis $19.9 \pm 1.6^\circ$. Advancing angle of UW-II was greater than UW-I (*t*-test, $P < 0.002$), and hysteresis of UW-II was lower than UW-I (*t*-test, $P < 0.005$). There was no significant difference in advancing contact angle between the three hydrophobic SP batches ($113.8 \pm 1.5^\circ$, $114.0 \pm 1.4^\circ$, and $115.1 \pm 1.7^\circ$ for SP-I, SP-II and SP-III, respectively). Hysteresis was $13.4 \pm 1.5^\circ$, $13.0 \pm 1.2^\circ$, and $17.6 \pm 1.6^\circ$ for SP-I, SP-II and SP-III, respectively; hysteresis of SP-III was significantly higher than SP-II and SP-I (ANOVA, $P < 0.009$). An overall comparison of SP- and UW-wafers yielded no significant difference in advancing angle, but higher hysteresis for UW-wafers (*t*-test, $P < 0.0001$). Each batch consisted of 6–7 wafers, with a total area of 145 ± 7 cm^2. A few clean wafers were left without the coating to serve as a hydrophilic reference (contact angle $\sim 30^\circ$).

2.2. Degassing and hyperbaric exposure

A Pyrex bowl (diameter 26 cm, height 5 cm) was filled with double distilled water (18 MΩ) to a level of 3 cm, and placed for a day in a desiccator (Vacuum pump XDS 5, Edwards, Crawley, West Sussex, UK) at a low pressure of 3.2–3.8 kPa, about 1 kPa above water vapor pressure, for washout of dissolved gases and any tiny bubbles. Ambient (room) pressure was restored, and the silicon wafers (6–7 hydrophobic and 1 hydrophilic) were rinsed with double distilled water and placed under the water with the shiny, almost molecularly flat surface facing upward. Low pressure was resumed for another 1 h, after which ambient pressure was again restored. The few bubbles which appeared on the hydrophobic wafers during the low pressure phase were released by tapping on the desiccator. The wafers were left underwater in the desiccator at ambient pressure and exposed to the surrounding air for 2 h (unless as specified in Protocol III). This time was allowed for the assumed formation of nanobubbles on the hydrophobic surfaces from the dissolved air.

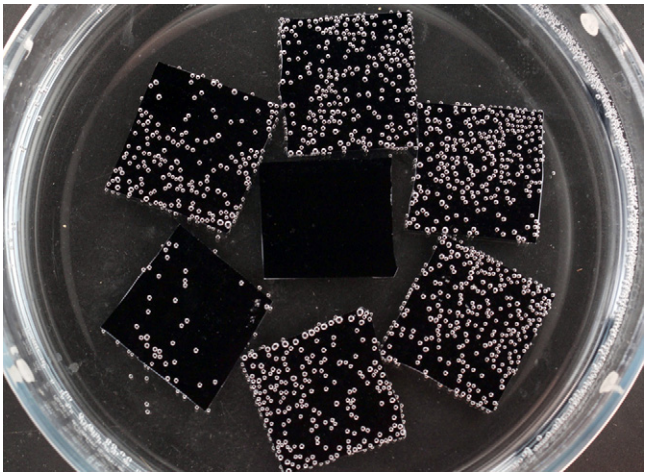

Fig. 1. Six hydrophobic UW-I-wafers on the periphery and one hydrophilic UW-I-wafer in the center, photographed 2.5 h after decompression from 300 kPa (20 msw).

The bowl was then transferred from the desiccator to a 150-l hyperbaric chamber (Roberto Galeazzi, La Spezia, Italy), a ribbon of chromatographic paper was pasted around the rim, and it was covered with another glass bowl to prevent dust contamination. The bowl containing the wafers was kept at the scheduled pressure for 20 h, at room temperature. The pressure was then reduced at 100 kPa/min to that of the surface (the ambient pressure in the room). The bowl was carefully removed from the hyperbaric chamber for photography. At the end of the photographic session, the wafers were rinsed with double distilled water and left out to dry under cover on filter paper before storage for the next experiment. The glass bowls were dried and then rinsed, first with propanol and then acetone; the desiccator was also rinsed, first with propanol and then ethanol. A photograph of one batch of UW-wafers is shown in Fig. 1. These wafers were photographed 2.5 h after decompression, when the bubbles had reached a volume that enabled us to see a clear contrast. As has already been shown in our previous report (Arieli and Marmur, 2011), no bubbles evolved on the hydrophilic wafer in the center of the bowl, but only on the hydrophobic wafers in the periphery. Hydrophilic wafers were therefore of no further concern. All procedures were conducted at a room temperature of 19–24 °C.

2.3. Experimental protocols

2.3.1. Protocol I: effect of hyperbaric pressure (gas supersaturation) on the density of gas micronuclei

Hyperbaric pressures at 50 kPa (5 msw) intervals between 150 kPa (5 msw) and 400 kPa (30 msw) were selected in random order. The bubbles which formed on each wafer were photographed immediately (1–5 min) after decompression. Bubbles were counted using an image processing program (Image-Pro-Plus, Media