journal

J. Am. Ceram. Soc., **91** [8] 2730–2731 (2008)
DOI: 10.1111/j.1551-2916.2008.02480.x

Breath Figure Patterns in the Oxidation of Boron Nitride

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Liquids condensing on solids can form a pattern known as "breath figures." Here we report similar patterns for liquid boron oxide droplets formed by high temperature oxidation reaction of boron nitride. Boron oxide does not wet boron nitride, so the liquid B_2O_3 oxide forms small droplets. As oxidation proceeds at 1200°C, the oxide created by reaction on the surface migrates to existing droplets or forms new droplets. The average diameter and maximum diameter of the boron oxide droplets increase with time following the kinetics of breath figures, similar to water condensation breath figures for dew drops.

I. Introduction

Vapor can condense on cold surfaces in a self-similar pattern of liquid droplets known as "breath figures". Rayleigh described how droplets size increases during condensation by a combination of growth and coalescence.[1] Beysens and Knopler[2] showed that, as condensation deposits additional liquid, the average droplet size $\langle D \rangle$ increases with time according to scaling laws $\langle D \rangle \sim t^{\alpha}$, where the scale parameter depends on area fraction coverage, wetting angle, and other factors. The maximum droplet size D_{max} increases in a characteristic stepwise fashion,[3] with the steps associated with coalescence events. Breath figures have received a great deal of attention in a variety of areas, including self-assembled bubble arrays,[4] dew drops,[5] lithography masks,[6] and templated films.[7] We find similar droplet patterns in liquid boron oxide formed on the surface of boron nitride by high temperature oxidation. In this case, the liquid forms not by condensation from a vapor, but by reaction of the substrate with oxygen. This could be relevant to the oxidation of BN or other boria-formers, because it shows that the boria may not be a continuous film, but rather a pattern of isolated droplets.

Boron oxide is a liquid above 460°C, with a significant volatility at temperatures above 800°C, where boron nitride oxidation is rapid.[8] Boron nitride is poorly wetted by B_2O_3. As oxidation proceeds, the BN surface becomes decorated by droplets of liquid oxide. Figure 1 shows the surface of a hot-pressed BN coupon exposed to dry air for 8 h at 1200°C. The droplet features are glassy B_2O_3 at room temperature. These glassy B_2O_3 droplets can only be observed if the sample is carefully isolated from humidity, which otherwise would quickly create artifacts by hydration. The hydrated oxide observed after exposure to moist air is quite different and does not represent the actual oxide formed at high temperature. Our samples were reacted and stored in a special apparatus to assure a water-free environment,[9] which preserved the pristine B_2O_3 droplets.

At the oxidation temperature, the reaction forms a now-wetting B_2O_3 liquid. Breath figures are seen when non-wetting liquids form by condensation, so it is interesting to determine if reaction-formed liquids might also display breath figure kinetics. We examined B_2O_3 droplet growth to determine if it could be represented with breath figure growth kinetics. We measured the size of the all the visible droplets on micrographs from on BN samples oxidized for 0.5–30 h. The average droplet size vs. oxidation time is shown as a log-log plot in Fig. 2 (the size of the symbols are larger than the approximately 10% variation of the average droplet size for each oxidation time). A linear regression line drawn through the average diameters was fit to $\langle D \rangle > \sim t^{\alpha}$, with a scaling exponent $\alpha = 0.90+/-0.06$. A scaling exponent of $\alpha = 1$ is expected for the coalescence-dominated stage of liquid droplets on a liquid substrate.[10] During coalescence growth, droplets grow by flow of liquid from nearby droplets, forming a new larger droplet. This is quite different from Ostwald Ripening, because it does not involve by transport of species from small droplets to large droplets.

During the coalescence stage one expects stepwise growth for the *maximum* droplet size D_{max}. We measured the size of the largest droplet on several micrographs for different BN samples oxidized for 17 time periods ranging from 0.5–30 h. The D_{max} values are also shown in Fig. 2, for the largest droplet that was observed in the field of view of each micrograph (about 15 mm²). These have considerable scatter, but can be plausibly represented as stepwise growth with two prominent steps. The lines fit to through these points were drawn with the same scaling exponent as the $\langle D \rangle$, following Beysens and Knobler.[2] The first step represents about a doubling of the maximum droplet size, but the second step larger by a factor of about 4.5.

Unlike continuous condensation, the oxidation of BN at this temperature involves a combination of the formation of fresh liquid B_2O_3 by reaction with BN, and the loss of B_2O_3 by evaporation, as the overall process results in a weight loss. At 1200°C, weight loss is roughly linear with time at about 0.4%/h, so the liquid droplet pattern develops under a dynamic balance between formation of fresh liquid oxide and evaporation of existing liquid. It appears that throughout this process, the distribution of average and maximum liquid droplet size is governed by breath figure kinetics.

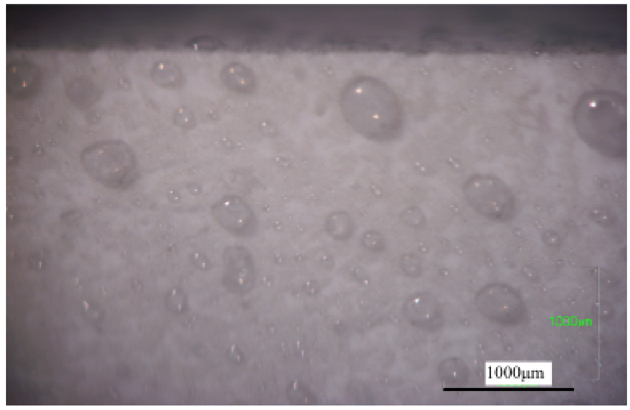

Fig. 1. Glassy B_2O_3 droplets on the surface of boron nitride oxidized in dry air for 30 h at 1200°C.

D. Butt—contributing editor

Manuscript No. 24436. Received March 18, 2008; approved March 25, 2008.
The authors thank the Vietnam Educational Foundation and the Office of Naval Research for financial support under the grant N00014-02-1-0034.
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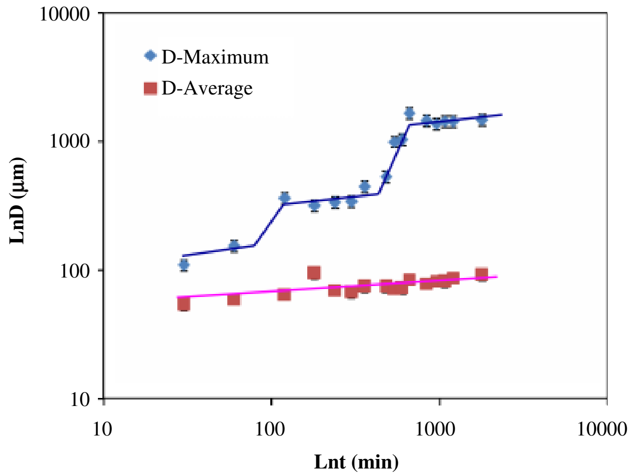

Fig. 2. Average droplet diameter $\langle D \rangle$ with regression line $t^{0.9}$ and maximum droplet diameter with two steps D_{max}.

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