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UCID-19557

SCANNING-ELECTRON-MICROSCOPY STUDY OF CORROSION AND
SURFACE FEATURES IN GLASS MICROBALLOONS

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MASTER

September 15, 1982

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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ABSTRACT

Gaseous acid treatment (HBr) of surface-hardened binary glass microballons results in etching and the growth of salt nodules, tubes or whiskers, depending on moisture conditions. Temperatures from 400°C to 625°C for 24 h or more are required for the effects to be significant. Numerous imperfections, including craters, are documented on the unexposed interiors surfaces. The evident phase separation and nucleation sites suggest a need for better production controls and post-production annealing.

INTRODUCTION

The use of glass microballons (GMB) for laser inertial confinement fusion purposes requires both high surface smoothness and the ability to load gases through the GMB walls. To accomplish the latter by permeation generally requires temperatures in excess of 350°C for many hours or days. There is, therefore, reason to expect chemical activity, and possibly surface degradation at such temperatures. In the present study, the effect of bromine on surface treated GMB spheres is examined by scanning electron microscopy. Bromine is a candidate fill gas for neutron diagnostic purposes. In the course of these experiments, the interior surfaces of microballons were also examined for surface irregularities. The mechanism of corrosion, and plausible causes of irregularities are discussed.

EXPERIMENTAL

As the concern was posed, bromine could be assumed to be within the GMB, and the glass raised in temperature until DT permeation was adequate. We make the reasonable assertion that at the temperatures in question, a DT-Br₂ mixture is not only thermodynamically unstable, but the reaction is photolytically initiated. Therefore, only the product, HBr, was considered for its corrosive properties. In addition, there is some evidence for water within the GMB,¹ which is not surprising because the production source is

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Loudox, a sodium-silicate-water mix. The amount of water, however, is unknown, and accordingly we considered corrosion under both dry and wet conditions. Only the exterior surfaces were exposed to HBr. The exterior surface differs from the interior primarily because of a chemical treatment to retard weathering.² The chemical significance of the treatment is the creation of a thin hydrogen-glass surface layer, and the fluoridation of non-bridging oxygen sites on the surface. The latter reduces surface ion exchange by creating an electroneutral barrier. However, neither process is considered to be irreversible, particularly at elevated temperatures.

Glass microballons, 160 μm in diameter, with 6 μm walls, designated 93104-D2A, were obtained from the target fabrication facilities. The production of this batch has been documented, but the interiors have not previously been examined.

Gaseous electronic grade hydrogen bromide was obtained from Scientific Gas Products, specified as 99.99% (min). A reactor tube was prepared from 5 mm I.D. quartz, and short sections of a quartz capillary tube were employed to contain some small number of sample spheres, and to ease handling. The reactor was placed in a clamshell furnace, and a setpoint controller maintained the desired temperatures for the duration of the experiment. A stainless steel high vacuum manifold was employed to assure a base outgas pressure of 10^{-6} torr, and the fill gas pressure was measured with a 1000 torr MKS Baratron transducer. The room temperature pressure was 760 mm for every experiment.

The summary of the experimental conditions appears in Table I. Two samples (DRY400, DRY625) excluded water, and differ only in the temperature and duration. Sample WET560 included 10 μL of water in the reactor, which served to provide a vapor pressure of approximately 30 torr and effectively provided an unlimited supply of water for reactions at the GMB surface. The two controls provide baseline conditions for the room temperature environment and for a sample heated in dry argon.

Table 1. Experimental Conditions

<u>Text Reference</u>	<u>Original Sample No.</u>	<u>Fill Gas</u>	<u>Reaction Temperature, °C</u>	<u>Time, Hr.</u>
Control 1	1667-1	Ar	25	-
Control 2	1670	Ar	400	53
DRY400	1669	HBr	400	84
DRY625	1667-2	HBr	625	24
WET560	1668	HBr, H ₂ O	560	24

RESULTS AND DISCUSSION

Inasmuch as the scanning electron micrographs (Plates 1-5) present only morphological data, and the chemical data, obtained solely from electron diffraction spectroscopy, was supportive but not definitive, the interpretations must rely on inference, based on known processes, and on physical-chemical data. Where these are lacking, speculation is sometimes offered to suggest approaches to future work.

SURFACE ETCHING

A comparison of Plates 1A and 1B, the controls, to Plates 1C and 1D reveals a generalized surface attack. The 3.5-fold increased reaction duration was evidently more effective than an increase of 225°C, suggesting solid state diffusion limits the attack. Plate 1D reveals surface features ranging from 0.1 to 0.4 μm in size, but the depth of attack cannot be estimated. Plate 3A (sample DRY400) reveals etch-induced surface mottling. This strongly suggests inhomogeneity on the 1 to 5 μm (and larger) scale. Micro-inhomogeneity in sodium-silicate and sodium borosilicate glasses has been studied extensively.⁴ Aggregations of stoichiometric groupings have been

proposed to account for macrophase separations.⁴ The apparent absence of mottling features in sample DRY625 (Plate 3B) may be explained by 1) the temperature is sufficient for annealing, and the surface has been homogenized, or 2) there has been insufficient etching time for mottling patterns to become apparent. The latter is supported by the appearance of the interior, and is discussed below.

MICROPORES AND SODIUM MIGRATION

Plate 2 (Sample WET560) graphically demonstrates the effect of water in enhancing leaching of the GMB wall. The presence of long protuberances everywhere on the surface can best be explained by a model, illustrated in Fig. 1. Within the glass wall, sodium can move either as the oxide, or by ion exchange. Migration of the oxide is variously claimed to occur above 500°C or 700°C.³ The rate of ion exchange is unquestionably orders of magnitude faster at lower temperatures. Corrosion mechanisms are often described as limited by the sodium ion diffusivity in bulk glass.³ Water provides the essential hydrogen ions to release sodium hydroxide:

Plate 2C shows the protuberances to be hollow tubes. This suggests that at the base of the tubes, a gas forming reaction is important, for which water must be locally deficient. The thermodynamically favored reactions at 560°C which result in gas are:

1. $\text{Na}_2\text{O} (\text{s}) = \text{Na}(\text{g}) + \text{O}_2(\text{g})$
2. $\text{Na}(\text{g}) + \text{HBr} = \text{NaBr} + 1/2 \text{H}_2(\text{g})$
3. $\text{Na}(\text{g}) + \text{H}_2\text{O} = \text{NaOH}(\text{l}) + 1/2 \text{H}_2(\text{g})$

The NaOH is liquid at temperatures above 318°C. Further, the neutralization reaction

must produce a solid salt crust on the face of the liquid NaOH phase, thus limiting the diffusion of water to the interior. The composite model proposes tube growth to be driven by the arrival of gas-producing Na_2O at the glass surface at a rate in excess of ability of moisture to permeate through a salt crusted bubble of liquid NaOH. If the water access to the surface were not so limited, no gas, and only NaOH(l) and NaBr(s) would be expected. As a refinement in the dynamics of the model, the elongated shape of the tube may be attributed to the ease of breaking the crust at the point of greatest curvature, the end of the tube. Plate 2D is an electron diffraction spectroscopic confirmation that the tubes contain Na, K and Br. The large Si signal is attributed to electron scatter from the nearby surface, which prevents identification of sodium silicate, which may also be present in the tubes. The sample, when subsequently exposed to air, absorbed water in a fashion expected of a deliquescent surface.

The presence of tubes, therefore, suggests pores in the glass which are large compared to the norm. In Plate 2B, the tubes are surrounded by depletion circles, but outside these circles, many nodules of NaBr exist, whose sizes, compared to those of the tubes, suggest the relative distribution of pore sizes.

In the absence of water, Plate 3A (sample DRY400) shows a large number of nodules, spaced with approximately the same surface density as the larger tubes in sample WET560 (Plate 2A). This suggests large pores are again the sites for the formation of NaBr. It is probable that Na_2O migration is much reduced at 400°C , and that product water, from the reaction

provides the necessary ingredient for the ion exchange transport of sodium to the surface at the pores.

Plate 3B (Sample DRY625) shows whisker-like formations, again occurring with approximately the same surface density as the larger tubes in Sample

WET560 nodules in Sample DRY400. Plate 3C reveals the dimensions of individual whiskers. A diameter of 0.1 to 0.15 μm and a length of 1.3 μm is representative. Assuming these are solid NaBr ($\rho = 3.2 \text{ g/cc}$), a low estimate of 164 fmol sodium per whisker is obtained. Assuming Plate 3B is a representative sample of the surface, an estimate of 6500 whiskers is obtained for the entire surface. One can conclude that at least 12%, a significant fraction, of the original Na_2O (21.9%, Ref. 2) has extruded.

An examination of the interior of sample DRY625 (Plate 3D) (as well as the other samples) showed nothing which could be identified with the postulated pattern of large pores. Decomposition at the surface by means of reaction 1, and the absence of HBr or water precludes such evidence. A few rod-like particles were located, ca. 4 μm long, which may well be debris from the breaking of the GMB.

However, the examination of the interior surface in general shows that much more significant surface irregularities than those produced by corrosion exist.

INTERIOR FEATURES

Each of the individual samples were fractured while mounted. Plates 4 and 5 illustrate the types of features found. Plate 4A shows an overview of the interior of the control sample which had been heated in argon for 53 hrs. A large circular depression, measuring 32 μm across, is flanked on the left by a roughened area, which is enlarged in Plate 4B, revealing a cluster of granules. Plate 4C, taken from a chip from sample DRY400, shows a crater, and irregular surface and two protruberances suggesting shards not quite coalesced into the wall at the time of quenching. A small irregular fissure nearby is unique, and may represent a fold-back of walls from a more open structure. Whatever the dynamics of formation of these features, which suggest some type of frothing process, it is clear that neither the production annealing nor the present heat treatment was effective in smoothing the interior walls to the degree found on the exterior.

Depressions, or craters, occurred in the interior of all but one sample in varying numbers and sizes. Their maximum depth was less than 1 μm . The pattern of craters bore no relation to the mottling pattern observed on the exterior. Most rims were smooth. This fact and the continuity of linear features into craters (Plate 5D) suggest a fluid subsidence mechanism, as one might expect from the collapse of the network or voids within the GMB walls.

Plate 3D (sample DRY625) shows a relatively smooth surface, without detectable craters. Although this might well have been its original condition before heating, it seems fortuitous that this sample also experienced the highest temperature, and the exterior surface, while etched, exhibits no mottling, as described above. A tentative conclusion that annealing begins to be effective in a 24 hr period somewhere between 560°C and 625°C deserves further work.

In addition to craters, isolated instances of rills (Plate 5C), wrinkles (not shown), pits, and fibers (Plate 5B) were present, all on the scale of a micrometre or less in cross section. In Plate 4D, a very rough sample surface is shown, with apparent phase separation on the submicron scale, and large (3 μm) nodule- or shard-like embedded mounds. Plate 5C also shows a rough surface, and two of many instances of needle clusters, which are typically 2 μm long. Plate 5A reveals these to have a decidedly crystalline character, suggesting catalytic sites may be important.⁵

SUMMARY AND CONCLUSIONS

In summary, the exposure of GMB surfaces to HBr does result in surface etching, which in turn exposes evidence of relatively large scale subsurface chemical inhomogeneity. The presence of especially large pores has been inferred. These are important to the formation of nodules or whisker-like extrusions, whose shape and size depend on the dryness, duration and temperature of exposure. The latter provide some measure of control for maintaining surface smoothness, and suggest further quantitation.

This production GMB batch not only exhibits a pattern of general inhomogeneity but, on the interior walls, gross surface imperfections occur which are uncharacteristic of rapidly quenched glasses. It may be useful to speculate that some of the features, such as crystallization of needles, may be catalyzed by trace impurities. A frothing process also may result from impurities seeding vaporization at multiple sites. More homogeneous glass can be achieved by compositional changes, for example, by the addition of K_2O (or Cs_2O), which is known to lower the phase separation temperature of binary glass.⁴ Finally, the possibility that additional annealing will smooth the crater-like interior formations deserves attention.

ACKNOWLEDGEMENTS

The primary effort of the target fabrication measurements group under William Halsey was critical to this study. Helpful discussions with Richard Pearson (Chemistry) and John Weir (Lasers) were much appreciated.

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Fig. 1. Chemical processes at the glass surface exposed to HBr and H_2O .

The position of reaction nodes indicates the phase or phase surface where the reaction occurs. For example, Na_2O dissociation occurs at the glass/gas bubble boundary. Predominately species are bold-faced, transient or quickly dissipated species (i.e. H_2) are shown in light print.

Plate 1. Evidence for surface etching.

A. Control 1, not heated.

B. Control 2, heated in argon.

C. Sample DRY625, HBr etched.

D. Sample DRY400, HBr etched.

Plate 2. Sample WET560, severe weathering with water and HBr.

A. Overview of the GMB showing the number of tubular formations

B. Tubes and nodules.

C. Broken-off tubes; the arrow shows a stub in cross section.

D. EDS analysis of the tubes shown in the inset. NaBr and KBr are confirmed.

Plate 3. Formations obtained under dry conditions.

A. Sample DRY400, showing nodules.

B. Sample DRY625, showing "whiskers".

C. Sample DRY625. Closeup of "whiskers".

D. The interior of sample DRY625.
A smooth surface and near-absence
of whiskers are notable.

Plate 4. Interior features.

A. Large circular depression

B. Granular cluster

C. Shard-like features and a fissure.

D. Rough surface and nodules.

Plate 5. Interior features.

A. Crystalline growth

B. Fibers and submicron pits

C. Circular rill, surface roughness and needle clusters.

D. Craters suggesting subsidence.

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
535 Port Royal Road
Springfield, VA 22161

Price: Printed Copy \$: Microfiche \$1.50

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