SHOCK-INDUCED DEFECTS IN HgO

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Powder compacts of HgO have been subjected to shock-loading and preserved for post-shock analysis to understand its reactivity and stability under transient temperature-pressure excursions. Recovered samples indicate several solid state reactions which are dependent on shock conditions. Metallic Hg is recovered in small amounts in the HgO compact as well as an as-yet unidentified ferromagnetic impurity not present in the as-received HgO powder. Further, there is evidence of reaction with the copper capsule at its interface with the HgO powder, forming an intermetallic alloy.

INTRODUCTION

Our synthesis experiments on Hg-containing superconductors showed HgO, known to decompose near 500° C, could be subjected, in the presence of other oxides, to rapid temperature excursions above 800° C without significant HgO decomposition (1). Prior to employing a shock-induced chemical synthesis route similar to our previous work (2,3) for the formation of Hg-containing superconductors (for which some phases are formed only under high static pressure environments), the properties of HgO under similar conditions were considered desirable. This note reports on powder compacts of HgO subjected to a variety of shock conditions appropriate for such synthesis.

EXPERIMENTAL

Commercially available HgO from Alfa/Aesar (reagent grade, stock #12276, lot #b15e10) was employed "as-received" in this study under careful conditions both in preparing and loading the powder compacts and in the subsequent analysis because of environmental concerns. This source of material was shown by x-ray

diffraction to be the usual orthorhombic form of HgO (Space group Pnma with cell edges 6.6121, 5.5201, and 3.5213 Å). Another form isomorphous with cinnabar, HgS, is of hexagonal symmetry with $a = 3.577$ and $c = 8.681$ Å. The orthorhombic form has infinitely long zigzag but planar chains of mercury and oxygen atoms extending along the a -axis while the hexagonal form is a distortion of the NaCl arrangement and is very slightly more dense with 32.06 Å³/molecule (verses 32.13 Å³/molecule for the orthorhombic form). The powder is orange in color. The X-ray line profiles of this powder were shown to be slightly broadened, consistent with a crystallite domain size near 1500 Å.

The pressed (to ~55% theoretical density) compacts were subjected to controlled shock compression conditions to peak pressures in the Sandia Bear recovery fixtures described and characterized previously (4). The shock conditions used in this study are given in Table 1. Each experiment yielded several samples, denoted as a "center" or "outer", corresponding to the location of the powder compact within the shock recovery fixture. Each sample experienced a different mean bulk temperature, as shown in the table.

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TABLE 1. Schedule of Shock Experiments (a)

Experiment		Compact Density	Peak Press.	Mean Bulk Temp. (b)
		Mg/m ³ (%)	GPa	°C
LE95-22	MBA-CB	5.95 (54)	22	400(650)
LE95-23	MB-B	6.03 (54)	7.5	225(300)
LE95-50	PB-B	5.90 (53)	5.0	150(75)

(a) For more detailed descriptions of pressure and temperature, see ref 4. MBA, MB, and PB indicate the Momma Bear A, Momma Bear, and Pappa Bear fixtures while -CB and -B the composition B and baratol explosives, respectively.

(b) The calculated mean bulk temperature in the center and in parenthesis, the outer ring of the samples are shown.

X-ray diffraction data were taken using a commercial Rigaku Θ - Θ automated powder diffractometer equipped with a monochromator on the detector set so both $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ radiation were obtained.

Transmission electron microscopy (TEM) specimens were prepared by dispersion of shock-loaded as well as the as-received HgO powders onto the holey carbon film of copper grids. A JEOL 1200EX TEM instrument at 120KV was employed. On most samples, both bright field imaging and dark field diffraction were carried out on selected grains.

The diamagnetism characteristic of mercury materials as well as that for superconductivity of trace amounts of metallic Hg were demonstrated by low temperature static magnetization data collected using our commercial SQUID magnetometer (Quantum Design model MPMS).

RESULTS

Experiment LE95-22 ruptured during shock-loading and did not yield any powder compact samples. The recovered sample-copper interface showed the same dull silver layer that the LE95-23 experiment also showed. The recovered

powder compacts of the other two shock experiments were separated into four samples, as described below, and together with parts of the interface layer, subjected to x-ray, TEM, and magnetization studies.

Sample Preparation

The recovered sample compact was removed essentially whole, but was somewhat fragile, particularly for the extreme edge of LE95-23 (resulting in a sample designated as "extreme edge") while a thin layer of powder adjacent to the top plug of LE95-50 stuck to the copper fixture plug and was hence separated from the compact, gently scraped from the plug, and designated as "top plug". The other samples resulted from separating the compact into the usual "center", "bulk", and "edge" samples. The edge samples appeared slightly more reddish-brown than the original orange color while the top plug sample appeared slightly more reddish. The center of the LE95-50 and the extreme edge of the LE95-23 samples were a bit more consolidated than the remainder of the samples and required more gentle grinding so as to pass through a 0.2 mm screen.

X-ray Diffraction Studies

X-ray diffraction measurements on a specimen of the dull silver interface cut from the lid of experiment LE95-23 showed that it was the intermetallic compound $\text{Cu}_{15}\text{Hg}_{11}$. This alloy crystallizes in space group R3m with $a = 13.351$ and $c = 16.175$ Å, a rhombohedrally distorted gamma brass structure type. Note that the corresponding rhombohedral cell would be $a = 9.4067$ Å, $\alpha = 90.413^\circ$ and, hence, this intermetallic has occasionally been reported as cubic. This intermetallic has also been confirmed by EDAX on SEM specimen.

X-ray diffraction showed only the orthorhombic form of HgO with no detectable traces of any other compound. The presence of well dispersed liquid Hg metal droplets, if present (see below) would not be detected at low concentration by the

usual x-ray diffraction experiment. There were no discernable differences between either the more reddish top plug or the reddish brown extreme edge and the other samples. The x-ray line profiles were all, but with the exception of the center LE95-50 sample, slightly narrower than the initial as-received or "standard" powder employed in the experiments. The line widths for most of the shock-loaded samples are consistent with those for a well annealed ~200 nm or larger crystalline domain-sized material, essentially those obtained for our Si powder previously run on our diffractometer. The single exception had line widths essentially the same as the standard and of the order of ~140 nm. This prevents any quantitative profile analysis using these samples. It was subsequently concluded that the gentle grinding on the LE95-50 "center" sample was sufficient to reduce the grains (crystallite domain size) because of the van der Waal interactions between the HgO zigzag chains of the crystal structure.

TEM Studies

TEM bright field imaging was used to determine the size and microstructure of the shock-loaded and as-received HgO grains. HgO proved to be very sensitive to the electron beam. All of the HgO grains observed break up into a fibrous morphology when exposed to a focused electron beam. Because of this sensitivity, detailed microstructural study is difficult; however, some changes in the shock-loaded samples were observed.

While the as-received grains were typically 100-300nm, 500-1500 nm grains for the edge sample of LE95-23, where the temperature is greatest, and 300-1000 nm for the center sample indicates grain growth, possibly occurring after the shock event. The lower temperature LE95-50 samples showed a smaller amount of grain growth. The edge sample consisted of 200-700 nm grains, with fine grains of fibrous-like clusters, less than 50nm in size found between the larger grains. The center of this sample showed a substantial amount of these fine

grained fibrous-like clusters; however, recall that this sample was ground a bit more than the other samples. Occasionally, a second phase was found among these clusters which under the electron beam appeared to move. These were subsequently believed to be small droplets of metallic Hg (see below).

Magnetic Properties Studies

The magnetic properties of the recovered HgO samples were examined at temperatures between 2 and 300K in applied magnetic fields up to 5 tesla. The as-received HgO powder employed in this study contains a significant paramagnetic impurity phase. Pure HgO has a small diamagnetic susceptibility at room temperature, $-2.03 \times 10^{-7} \text{ cm}^3/\text{g}$. In contrast, the as-received HgO is dominated by the impurity phase. Assuming the paramagnetism arises from a spin = 1/2, g-factor = 2 ion, approximately 0.4% impurity ions per Hg are present.

In contrast, the shock-loaded samples exhibit a large positive moment at 300 K which increases dramatically with peak shock temperature and pressure, reaching $+3.3 \times 10^{-3} \text{ emu/g}$ for the "outer extreme" LE95-23 sample. All four LE95-23 shock-loaded samples exhibit a roughly linear increase in moment with decreasing temperature, and the slopes are remarkably similar for the different shock conditions. The large positive moment at 300 K is attributed to an unknown ferromagnetic impurity introduced (formed) during shock loading. The nonlinear behavior of the magnetic moment verses applied field at 5 K, after the appropriate corrections for the plastic sample container and the reference as-received HgO powder, is characteristic of "hard" ferromagnetic materials where the moment "saturates" in large applied magnetic fields. The extreme outer LE95-23 has a ferromagnetic "saturation" value of $1.2(1) \times 10^{-2} \text{ emu/g}$. If the unknown ferromagnetic impurity were magnetite, Fe_3O_4 , with a saturation moment of 97 emu/g at low temperatures, this sample response would arise from an impurity level of 0.01% by weight. It is conceivable that shock

loading transforms about 3% of the paramagnetic impurity in the as-received HgO to a ferromagnetic phase.

The magnetic measurements also showed evidence for a small superconducting component in the shock-loaded HgO powders. In a magnetic field of 0.5 millitesla, sufficiently small so that the contribution for the just mentioned ferromagnetic impurity is negligible, data measured with decreasing temperatures from 5 to 2 K indicated the appearance of a substantial negative magnetic moment below a transition temperature, i.e., the onset of superconductivity. This negative moment arises from the Meissner effect (expulsion of the applied field from the superconducting grains.) All of the four LE95-23 samples show a superconducting transition just below 4.2K, consistent with metallic Hg. Since the as-received HgO powder showed no evidence for superconductivity, the shock-loading converts a small quantity of the HgO to Hg. These data suggest that the amount of metallic Hg increases going from the center, bulk, edge and extreme edge samples, -2.4, -4.0, -5.0 and -31. (all $\times 10^{-4}$ emu/g), respectively, at 2 K.

CONCLUDING REMARKS

There is strong evidence that metallic Hg is formed for samples subjected to the shock conditions of experiment LE95-23. This suggests that even under pressure of 7.5 GPa, with a mean bulk temperature rise to $\sim 225^\circ\text{C}$, HgO is decomposing into metallic Hg and that the Hg adjacent to the Cu fixture is sufficiently reactive to form the intermetallic compound $\text{Cu}_{15}\text{Hg}_{11}$. At locations away from the Cu interface, this Hg coalesces into microdroplets.

These microdroplets reside between the grains and were disturbed by the heating effect of the TEM electron beam. The beam also frayed and defoliated the HgO grains, showing the weak van der Waal interaction between the zigzag chains in the crystal structure of this orthorhombic form.

Further, at these low mean bulk shock-induced

temperatures, the HgO is able to significantly ($\times 5$) enlarge its grain size as evidenced by TEM bright field imaging. The lack of breadth of the x-ray lines beyond that resulting from the usual experimental diffraction optics is additional evidence for annealing at these low temperatures. Together, these results rule out the possibility of a pressure induced reversible phase transition consistent with the small reported density difference of the two forms.

Also of significance were the magnetic measurements of the as-yet unidentified impurity formed from the shock environment and possibly involving the metallic Hg present. Such low level detection of phases may prove useful in other shock studies.

On a more general vein, the present materials study contributes towards resolving several shock issues concerning our Bear fixtures and TiO_2 model calculations. Although there remains ambiguities whether events occur at pressure or result from post-shock effects, the major shock effects are consistent with previous studies. That is, there is no radial focusing in the LE95-50 experiment, leading to a more uniform pressure over the entire sample in contrast to LE95-23..

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