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AUG 77 P D ZAVITSANOS, F N ALYEA, J A GOLDEN F30602-76-C-0131

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August 1977

REDEFINITION AND IMPROVEMENT OF METAL VAPOR RELEASE TECHNOLOGY

General Electric Company/RESD

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This research was sponsored by the Defense Nuclear Agency under Subtask L25BAXHX632, Work Unit 04, entitled "Improved Barium Releases".

ROME AIR DEVELOPMENT CENTER
Air Force Systems Command
Griffiss Air Force Base, New York 13441

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APPROVED: Joseph J. Simons

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Project Engineer

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(6) REDEFINITION AND IMPROVEMENT OF METAL VAPOR RELEASE TECHNOLOGY.

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report presents the results of laboratory investigations which involved optimization studies of advanced concepts in atmospheric release technology in terms of barium vapor yield (efficiency) and increased safety. One of the most promising reactions which was identified was the reaction between Titanium and boron (in the condensed phase) to form Titanium diboride, and heat. The heat from this reaction is used to vaporize barium.

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Laboratory tests of the Titanium/Boron/Barium system produced a maximum yield of Barium vapor in the amount of 41.2% of the total mixture chemical weight.

This research was sponsored by the Defense Nuclear Agency under subtask L25ABXHX632, subtask title: "IR Phenomenology and Optical Code Data Base", work unit 04, work unit title: "Improved Barium Releases". This effort was monitored by Rome Air Development Center, Joseph J. Simons, OCSA, Griffiss AFB NY 13441.

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I. INTRODUCTION

Atmospheric experiments involving the release of metal atoms have been a subject of interest for a number of years. The release of barium vapor and its subsequent photo-ionization has been used to provide partial simulation of nuclear detonations. Barium payloads can be utilized in Transionospheric Satellite Communication programs for the purpose of performing propagation experiments in an environment which simulates certain aspects of nuclear detonation.

The objective of this effort was to (a) pursue analytical studies, computations, and consultation for the Defense Nuclear Agency's (DNA) Ad Hoc Panel for Redefinition of Barium Metal Vapor Release Technology for Advanced Communications System Program, and (b) pursue laboratory investigations which involve optimization studies of advanced concepts in atmospheric release technology in terms of barium vapor yield (efficiency) and increased safety.

II. THERMOCHEMICAL CONSIDERATIONS

A. Prediction of Barium Vapor Yield Based on the Ti/B Reaction

The high exothermicity associated with some condensed phase intermetallic reactions was identified (1, 2) as a convenient and potentially effective means of generating metal vapors for atmospheric releases. The reaction between titanium and boron has been used as heat source for atmospheric releases involving aluminum (2) as well as barium (3).

In order for a given scheme to be of practical interest, the following criteria must be satisfied: 1) Reaction can be easily initiated; 2) once initiated the reaction must be self-sustained at a fast rate; 3) the realized temperatures must be high enough to vaporize the metal of interest; 4) the system must be scalable to large quantities, and 5) the reaction should not be explosive.

As previously stated, one of the most promising reactions which was identified was the reaction between titanium and boron (in the condensed phase) to form titanium diboride according to the following stoichiometry:

$$Ti(s) + 2B(s) \longrightarrow Ti\,B_2(c) + \text{heat.}$$

Due to favorable thermochemical properties, this is a "gasless" reaction, i.e., the only product in addition to heat is the condensed phase of $Ti\,B_2$; the calculated adiabatic temperature resulting from the above reaction is $4043^{o}K$.

In view of the fact that the boiling point of barium ($2100^{o}K$) is considerably less than the calculated adiabatic temperature, it is safe to assume that the system can be used as "barium vaporizer" by simply adding barium to the mixture. The vapor pressure of barium in comparison to the other two components of the system (Ti and B) is shown in Figure 1. Since the vapor pressure of barium is five to six, orders of magnitude higher than that of Ti and B respectively, it is expected that extremely small amounts of gaseous titanium and boron would be generated during the barium release. Using the thermochemical properties (Table I) which govern the yield of barium vapor, the Ti/B/Ba system was balanced near the boiling point of barium:

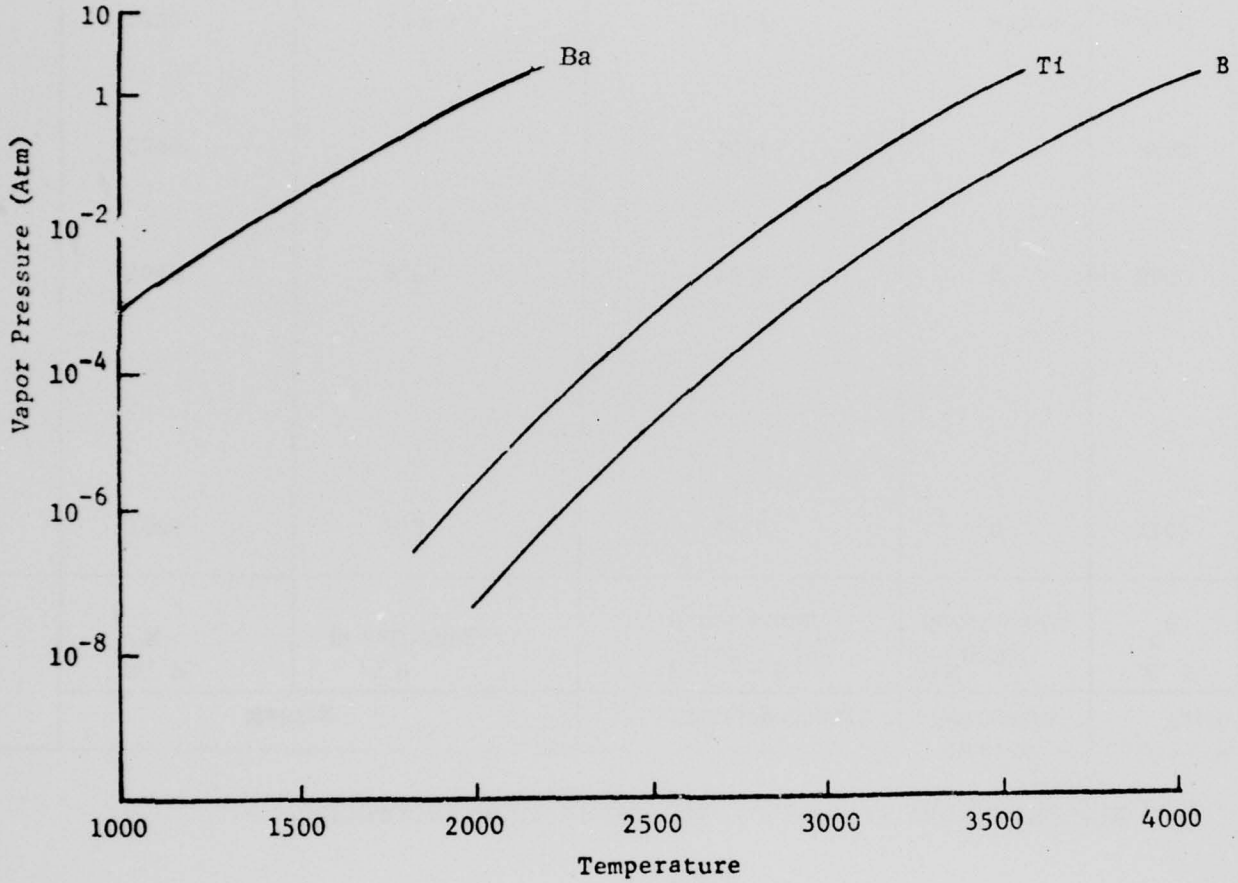

FIGURE 1. VAPORIZATION PROPERTIES

TABLE I

THERMOCHEMICAL PROPERTIES OF METALS AND COMPOUNDS (4-8)

Material	Melting		Enthalpy Change	Heat of Formation	Vaporization	
	M. P. ^{o}K	$\triangle H$ (k cal/mole)	$H_{2100} - H_{298}$ (k cal/mole)	$\triangle H_{f(298)}$ (k cal/mole)	B. P. ^{o}K	$\triangle H_{(298)}$ (k cal/mole)
Ba	1000	2.3	14.0	0	2100	43.9
Ti	1940	4.0	18.3	0	3575	112.7
B	2300	5.1	10.1	0	3950	129.2-137.9
TiB_2	3193	12 ± 3	31.7	-71.6	>4000	

TABLE II

THERMOCHEMICAL COMPARISONS

REACTION	Ba	+	CuO	=	BaO	+ Cu	$\sum$
mol. weight	137.36		79.57		153.26	63.57	216.93
$\triangle$ H 298 (k cal/mol)	0		-37.3		-132.3	0	-95.0
$\int_{298}^{2100} CpdT + H_{tr}$					23.2	15.0	38.2

NET AVAILABLE HEAT: - 56.5 kcal/mol
- 0.26 kcal/g

REACTION	2B	+	Ti	=	TiB_2		
mol. weight	2x10.82		47.90		69.59		69.59
$\triangle$ H (298)	0		0		-71.6		- 71.6
$\int_{298}^{2100} Cp\,dT + H_{tr}$					31.7		31.7

NET AVAILABLE HEAT: - 39.9 kcal/mol
- 0.57 kcal/g

$$Ti(s) \quad 2\,B(s) + (0.66\,Ba(s) = \quad Ti\,B_2(c) + 0.66\,Ba(g)$$

$$(298^{o}K) \qquad\qquad (2100^{o}K)$$

This suggests that as much as 0.66 gram-atoms (or 90.6g) of Ba could be vaporized by 1 - mole (69.59 g) of $Ti\,B_2$ which corresponds to a theoretical efficiency of 56% based on the total chemical weight.

B. Comparison of the Heat Production with Other Mixtures Used for Ion Cloud Generation

As a baseline comparison, the Ti/B/Ba system was compared with the most widely utilized reaction between Ba and CuO which forms BaO, Cu and Ba(g). The thermochemical properties of these two systems are shown in Table II.

The net available heat for barium vaporization was estimated for both cases as the difference between the exothermicity of the respective reaction minus the energy required to elevate the products to a temperature equal to the boiling point of barium ($2100^{o}K$).

$$\Delta H \text{ available} = \quad \Delta H_{(298)} - \int_{298}^{2100} CpdT + \quad H_{tr}$$

where H_{tr} represents the heat of transition.

For the comparison, the amount of heat which one gram of the initial mixtures evolves is crucial; as shown in Table II, the Ba/CuO reaction evolves $\frac{56.5}{216.9}$ 0.26kcal/g while the Ti/B reaction generates $\frac{39.9}{69.54}$ 0.57 kcal/g. Therefore, the Ti/B mixture is about 2.2 times more efficient than the Ba/CuO mixture.

C. Laboratory Results and Discussion

The Ti/B/Ba mixtures were prepared in a dry box under flowing nitrogen. The barium was in granules ranging in size from 0.1mm - 2mm and was supplied by Ventron (Beverly, Mass.). The mixtures were subsequently loaded into a graphite crucible and fired either in a vacuum tank or into a quartz tube in flowing nitrogen at one atmosphere. *

The reaction crucible shown in Figure 2 has a volume of about 70 cm^3 and an orifice 0.5 cm in diameter. It is made of zirconia lined with grafoil to minimize heat losses by conduction. The reaction was initiated with a hot wire ($800^{o}C$) and the vaporized barium was partly contained inside a quartz tube. Figure 3 shows the conclusion of one such run where the barium has been converted to BaO by atmospheric oxygen.

The vaporization yield was estimated by removing the residual barium from the reaction mixture by boiling in hot water. Subsequent vaporization of the water made it possible to reclaim the residual barium in the form of BaO.

Several concentrations ranging from 22-47% barium (by weight) were studied and the results are shown in Table III.

As expected from theoretical predictions, almost total removal of the available barium took place. The highest yield of 41.2% is indeed impressive. This preliminary study suggests that much higher yields, than previously possible, can now be achieved by this reaction with the additional advantage of increased safety.

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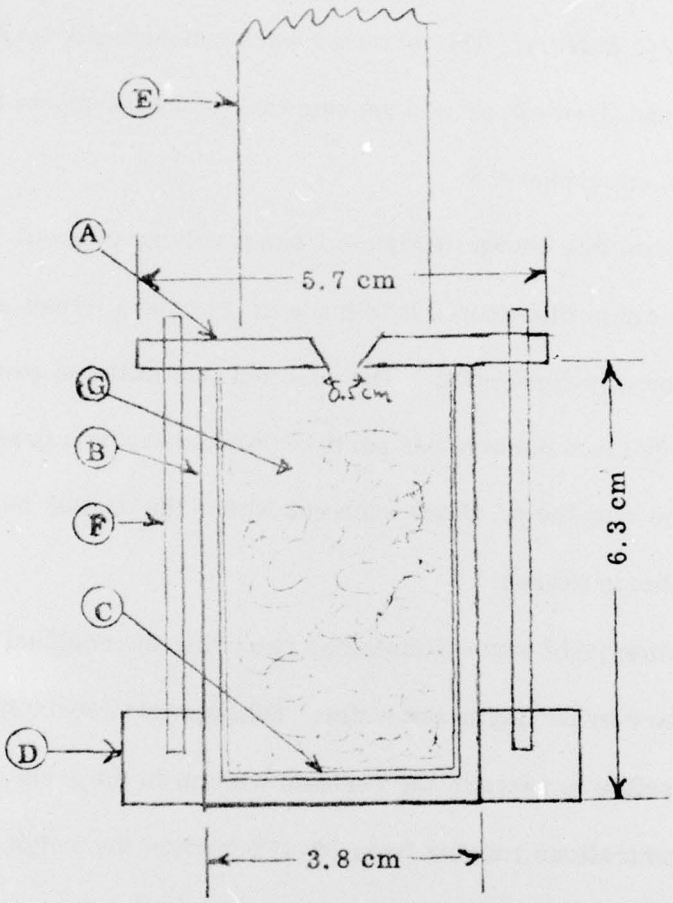
*A special pretreatment of the barium granules reduced drastically the oxidation rate and made it possible to carry out the firings in flowing nitrogen at one atmosphere.

FIGURE 2. REACTION CRUCIBLE



A = Graphite Lid

B = ZrO_2 crucible

C = Grafoil Liner

D = Base

E = Quartz Tube 1" Diameter

F = 6-32 Threaded Rod

G = Reaction Mixture

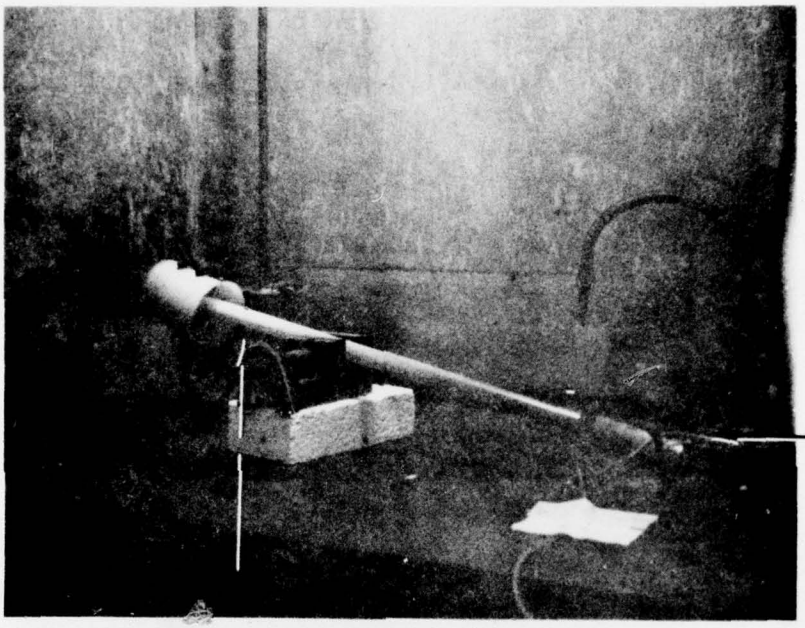


FIGURE 3. PHOTOGRAPH OF REACTION CRUCIBLE AND OXIDIZED BARIUM DEPOSIT

TABLE III

BARIUM VAPORIZATION EFFICIENCY

Mixture	% Ba (in Mixture by Wt.)	Ba - Recovered from Residue (g)	Ba - Vaporized (in g)	% Ba Vaporized (Based on Total Mixture Chemical Wt.)
Ti/B - 17 g Ba - 5 g	22	0.78	4.22	19.2
Ti/B - 17 g Ba - 5 g	22	0.18	4.82	21.9
Ti/B - 17 g Ba - 6.9 g	28.9	9.62	6.28	26.3
Ti/B - 17 g Ba - 8.5 g	33.3	0.96	7.54	29.6
Ti/B - 17 g Ba - 15 g	46.9	1.8	13.2	41.2

The safety aspect is based on the fact that the Ti/B reaction requires a sustained high local temperature of 800°C for initiation and is insensitive to shock or electrostatic charges.

III. ANALYSIS

Consultation to the DNA/RAAE Ad Hoc Panel No. 3, "Redefinition of Barium Metal Vapor Release Technology for Advanced Communications Systems", was provided by Dr. F. N. Alyea under support of the present contract. Specifically, this effort required consultation with Dr. E. Bauer of the Institute for Defense Analysis and emphasized preparation of the Panel report entitled, "Barium Releases for Communications Experiments."

The work involved writing Chapter V, "Barium Release Phenomenology", general report organization, and considerable text editing, particularly in the appendicies. The report has been submitted to DNA for approval.

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