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Reactor Technology Division

URANIUM HYDRIDE: A SURVEY

A. S. Kitzes

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URANIUM HYDRIDE: A SURVEY

1.0 Abstract

The results of a survey to determine the feasibility of producing non-pyrophoric uranium hydride in tonnage quantities are presented. It is debatable whether or not uranium hydride can be made non-pyrophoric. A great deal of research and development work is necessary on the subject. UH_3 compacts with a density of 9 g/cc can probably be made and the compacts "canned". Temperature stability data are given but no radiation stability data are available. UH_3 cannot be mixed with molten lead, bismuth, tin or cadmium since the U-metal alloy is formed releasing hydrogen. Compressing UH_3 and powdered lead gives low density compacts. No cost data available; Metal Hydrides Incorporated, the only commercial producers of hydrides will not commit themselves on cost or production of non-pyrophoric material until a sample is made under plant conditions.

2.0 Introduction

Preliminary calculations by the ORNL theoretical physics group on shielding have shown that a weight-savings can be effected in the total shield weight for the reactor of a nuclear powered aircraft if uranium hydride can be used as a shielding component. These calculations are based on the condition that either:

> UH_3, as a dry powder, can be pressed to a density of 9 g/cc or uranium hydride with a hydrogen content equivalent to UH_2 and a pressed density of 11 g/cc is available.

A survey, therefore, was initiated upon the request by E. P. Blizard (Memo dated December 19, 1949) to ascertain the availability of uranium hydride, etc. production, physical properties, alloying characteristics and its stability to radiation and temperature.

This report is a result of this survey. The information and data which are presented in this paper have been gathered from a number of sources. The project literature, mainly Rabinowitz and Katz (1) was reviewed. NEPA, Y-12 personnel, and the Metal Hydrides Incorporated, the only commercial producers of hydrides, were contacted for whatever information they may have had at their disposal.

3.0 Preparation and Production of Uranium Hydride

The preparation of uranium hydride is easily effected by heating lumps, turnings, or other forms of uranium metal to 225°-260°C

3.0 Preparation and Production of Uranium Hydride (Cont'd)

in an atmosphere of hydrogen (1,2). It has been reported that the reaction is most rapid at 225°C. There is some incubation period before the reaction starts at temperatures below 300°C and the incubation period has been found to depend upon the purity of the hydrogen.

The Metal Hydrides Incorporated have prepared ton quantities of uranium containing hydrogen during the early development of the Manhattan District work (3). Most lots were pyrophoric. Some material, however, was prepared in such a state as to lead them to believe that the compound may exist in a non-pyrophoric state. No uranium hydride is being produced today.

4.0 Physical Properties of UH_3

4.1 Physical State

Uranium hydride (UH_3) is a black to brownish gray powder. It is a very fine powder. Most of it easily passing through a 400 mesh sieve. The hydride gives fibrous pseudo-crystals 2-3 mm in length when prepared by hydriding at high hydrogen pressures (1,3). Dr. V. P. Calkins, (4) NEPA, has suggested another method in which the particle size of UH_3 may be increased, and that is by hydriding uranium slugs, allowing the hydrogen to penetrate into the solid uranium.

4.2 Density of UH_3

The bulk density of this material is 3.4 g/cc. The true density is 10.9 g/cc as calculated from X-ray diffraction measurements and by helium displacement measurements. The density of pressed blocks of UH_3 has been investigated. The data are shown in Table I and plotted in Figure 1, where the density has been plotted as a function of pressure.

TABLE I

DENSITY OF PRESSED BLOCKS OF UH_3

Pressure (tons/in^2)	Density (g/cc)
28	7.3
60	7.5
100	7.9
160	8.4 - 8.7

4.2 Density of UH_3 (Cont'd)

Dr. T. R. P. Gibb, Jr., Metal Hydrides (3), reports that Spedding has prepared uranium hydride which had a bulk density approaching the theoretical density by using 130 atmospheres of hydrogen at 600°-700°C in a special bomb. Dr. Gibb also states that the coarse fibrous hydride (pseudo-crystals) should be compressible to a density higher than 8.7 g/cc. Perlman and Weissman (5) have succeeded in preparing uranium hydride having a density of 10 g/cc or more by treating uranium in the cavity of a steel cylinder so that the expanding hydride was compressed by its own expansion. The data of Perlman and Weissman indicate that the product they obtained is probably a mixture of uranium and uranium hydride since unreacted uranium was always found in the compacts. Burke et al (6) report that it is possible to produce compacts which have densities as high as 9.0 g/cc by bonding uranium hydride with synthetic resins. The product is readily handleable, and almost any desired shape can be made. The technique which Burke et al used is as follows: The hydride is mixed with the plastic dissolved in a suitable solvent. Mixing is done in an inert atmosphere (CO_2 or N_2). The solvent is then evaporated and the mix tray dried. The dry mix which is now non-pyrophoric is pressed at 100°-150°C under a pressure of 100,000 psi. The maximum true density of the compact is about 7.8 g/cc. Higher UH_3 densities can be obtained by adding uranium metal powder since the mixture of hydrogenous plastic with pure UH_3 has a higher hydrogen to uranium ratio than 3. Pure uranium metal is added to bring the H/U ratio back to 3. Polystyrene, polyethylene, and reduced polystyrene were used as the binders. Higher densities than 9 g/cc can probably be attained but experience has shown (6) that the compacts are not very stable and often crack when removed from the dies.

4.3 Pyrophoricity of UH_3

Most of the men who have worked with UH_3 claim that it is pyrophoric, igniting below 170°C in air. However, Gibb states that Metal Hydrides has made some UH_3 which was non-pyrophoric and so did Calkins (4) while he was at Ames. The pyrophoricity of UH_3, according to these men and other workers in the field, is a complex problem. The chief source of its hazard is probably attributable to the fine state of subdivision. Finely divided metals such as lead are spontaneously inflammable in air. Uranium hydride tarnishes in air even after brief exposure. This would tend to indicate extremely rapid formation of an oxide film. Gibb believes that UO_2 is the reason for the pyrophoricity of UH_3. On the other hand, Calkins believes that the finely divided unreacted uranium metal is the reason for the pyrophoric character of UH_3. He further contends that

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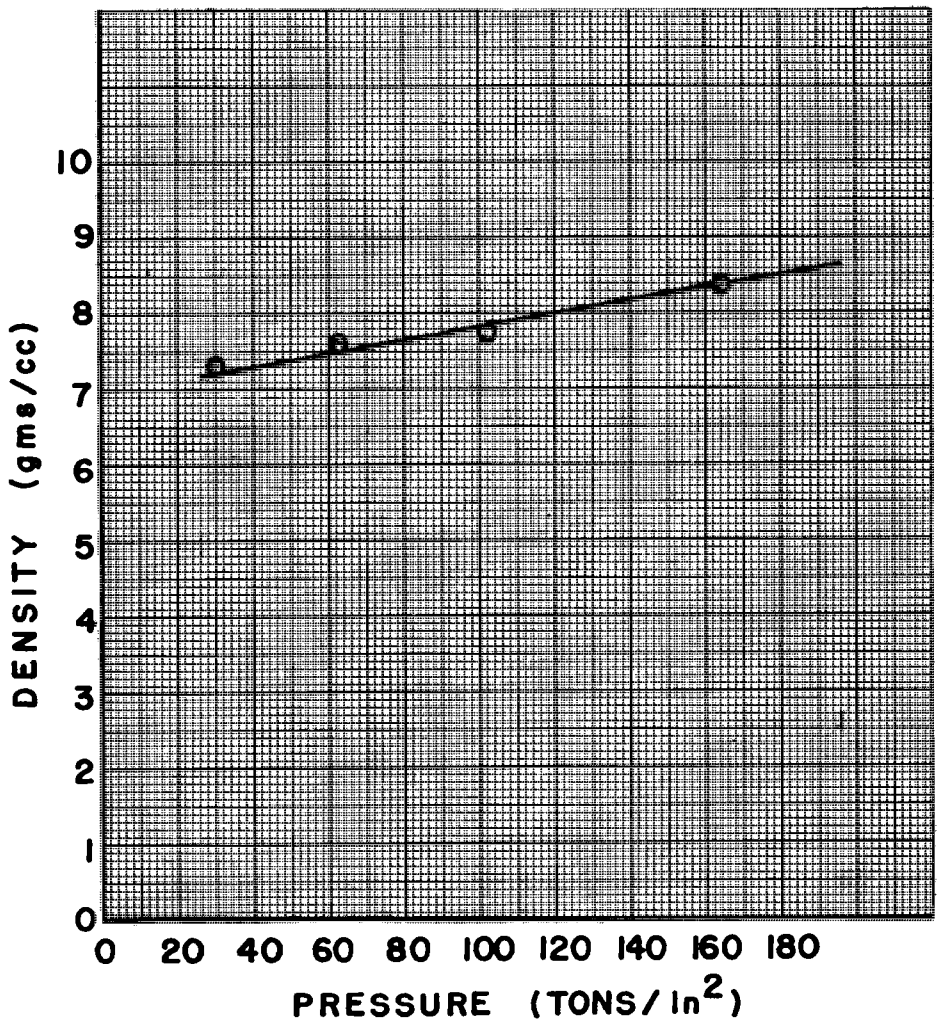

FIGURE I. DENSITY OF PRESSED BLOCKS OF URANIUM HYDRIDE

4.3 Pyrophoricity of UH_3

if the uranium metal is exceedingly clean before hydriding, and if either the uranium is completely hydrided or the unreacted uranium removed from the hydrided material, the resulting UH_3 will be easily handled.

It was previously pointed out that UH_3 coated with a synthetic resin in an inert atmosphere is non-pyrophoric. The difficulty with this technique of producing non-inflammable UH_3, however, is that the resin will probably be the weak link under intense neutron radiation.

4.4 Ratio of Hydrogen to Uranium

The data in Table II which are plotted in Figure 2 are presented through the courtesy of Dr. Gibb, Metal Hydrides Incorporated. The relationship of N_H, the density, and number of atoms of hydrogen per atom of uranium, is shown. N_H is the number of hydrogen atoms per cubic centimeter multiplied by the factor 10^{-22}. It should be noted that there is a relatively slight increase in N_H as the number of hydrogen atoms increase from 2.7 to 3. It seems reasonable, therefore, to assume that partially hydrided material might be more easily compressed and might also be less pyrophoric so that the most dense compact prepared from it might have properties more desirable than UH_3. These last statements are highly problematical since there are no data available to support them. However, they are presented here for consideration.

4.5 Temperature and Radiation Stability

The equilibrium pressure of H_2 over UH_3 at about 430°C is one atmosphere. Hydrogen can be completely removed from the hydride in vacuum at about 430-440°C. The equation relating the decomposition pressure in mm of Hg and absolute temperature is:

$$\log P_{(mm)} = 9.28 - \frac{4500}{T} \qquad (1)$$

and shown in Figure 3.

4.5 Temperature and Radiation Stability (Cont'd)

TABLE II (a)

EFFECT OF H CONTENT ON N_H

Formula	Density (g/cc)	N_H
U	19.05	0
$UH_{.345}$	17.35	1.52
$UH_{1.06}$	15.16	4.07
$UH_{1.96}$	12.88	6.37
$UH_{2.7}$	11.48	7.80
UH_3	10.86	8.18

TABLE II (b)

EFFECT OF DENSITY ON N_H

d_{25^oC}	N_H	
10.9	8.25	Stoichiometric, massive
8.8*	6.66	Coarse powder, dry pressed
8.7	6.58	Powder dry pressed at 160 TSI
3.4	2.57	Uncompressed powder

*Estimated

No data are available for the radiation stability of UH_3. Calkins (4) expressed the opinion, however, that UH_3 should have the same stability to pile radiations as Titanium hydride. Titanium hydride was found to be stable to pile irradiations for 1800 hrs at 160-340°C and an estimated thermal flux of 0.5×10^{12} neutrons/cm^2-sec (7). Collins of NEPA, in cooperation with O. Sisman's Group, ORNL, is planning to study the radiation stability of UH_3. Samples will soon be put into the pile for observation.

5.0 Chemical Properties

5.1 Reaction of Gases with UH_3

It is safe to handle UH_3 under atmospheres of CO_2 and N_2 if the temperature of the gases are below 200°-225°C. There is a reaction

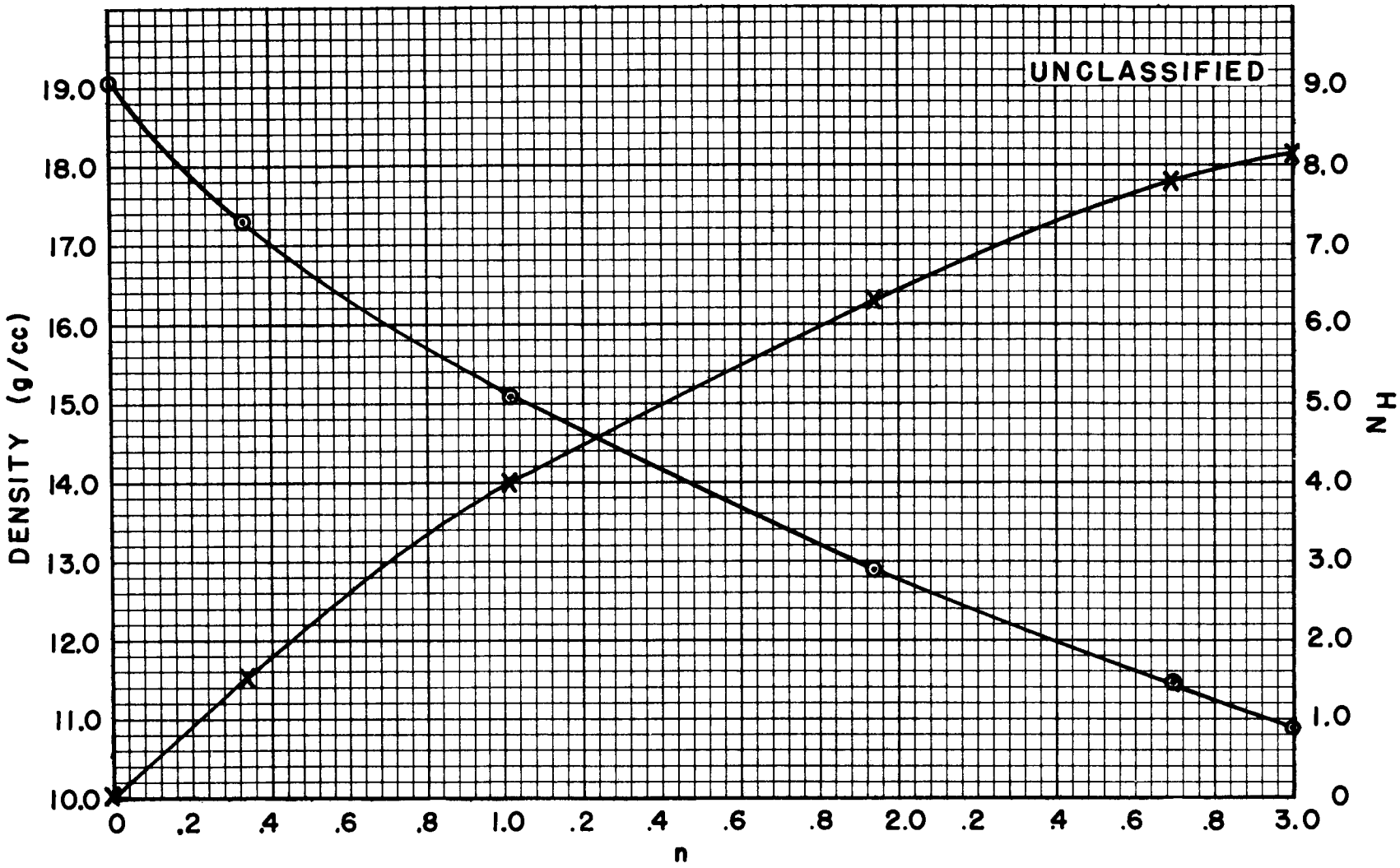

FIGURE 2. DENSITY AND N_H OF UH_3 AS A FUNCTION OF n

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5.1 Reaction of Gases with UH_3 (Cont'd)

between UH_3 and CO_2 and N_2 above 225°C probably with formation of carbides and nitrides. UH_3 reacts slowly with water vapor at 200-300°C.

5.2 Alloys of UH_3 with Other Metals

5.2.1 Uranium Hydride Amalgams

No hydrogen or heat is involved when mercury is poured onto the hydride. The solution, probably a colloidal suspension of UH_3 in mercury, is very fluid up to 10% UH_3, viscous at 20% UH_3, and a pasty mass at 30%. From 40-60% UH_3 the mass is semi-solid and above 60% UH_3, the mercury is absorbed in much the same manner as oil is taken up by sawdust. The mass becomes pyrophoric again above 90% UH_3. A material called "quasi-hydride" is formed when air is passed through a solution of hydride in mercury. The hydride ($UH_{2.8}$) is thrown out, which, upon analysis, contains 92.4% U, 1.2% H and probably 1.4% O. The quasi-hydride is ordinarily air stable but samples have ignited for unknown reasons.

5.2.2 Metal Bonding

Burke et al (6) report that fairly satisfactory bonding can be produced by ball-milling UH_3 with freshly reduced lead powder in an inert atmosphere, and cold pressing the finished mixtures in a steel die. The product did not have a satisfactory density since about 50 volume percent of lead was needed for bonding. The compact also oxidized in air. Several attempts were made to bond uranium hydride with molten lead, tin, and cadmium but they all resulted in the formation of alloys of the metal and uranium with the evolution of hydrogen.

No information is available on the reaction between molten bismuth and UH_3. In view of the data of Burke et al, molten bismuth would react similarly with UH_3. Hydrogen would be released with the formation of an uranium-bismuth alloy.

Uranium hydride can probably be safely clad with a number of metals. No data are available on the subject, but one might expect UH_3 to be non-corrosive.

5.3 Reaction with Organic Solvents

The reaction between UH_3 and chlorinated organic solvents is dangerous (1,2). Violent explosions usually occur. Hydrocarbon solvents, acetone, ether, ethyl acetate, and etc. have no effect on the hydride.

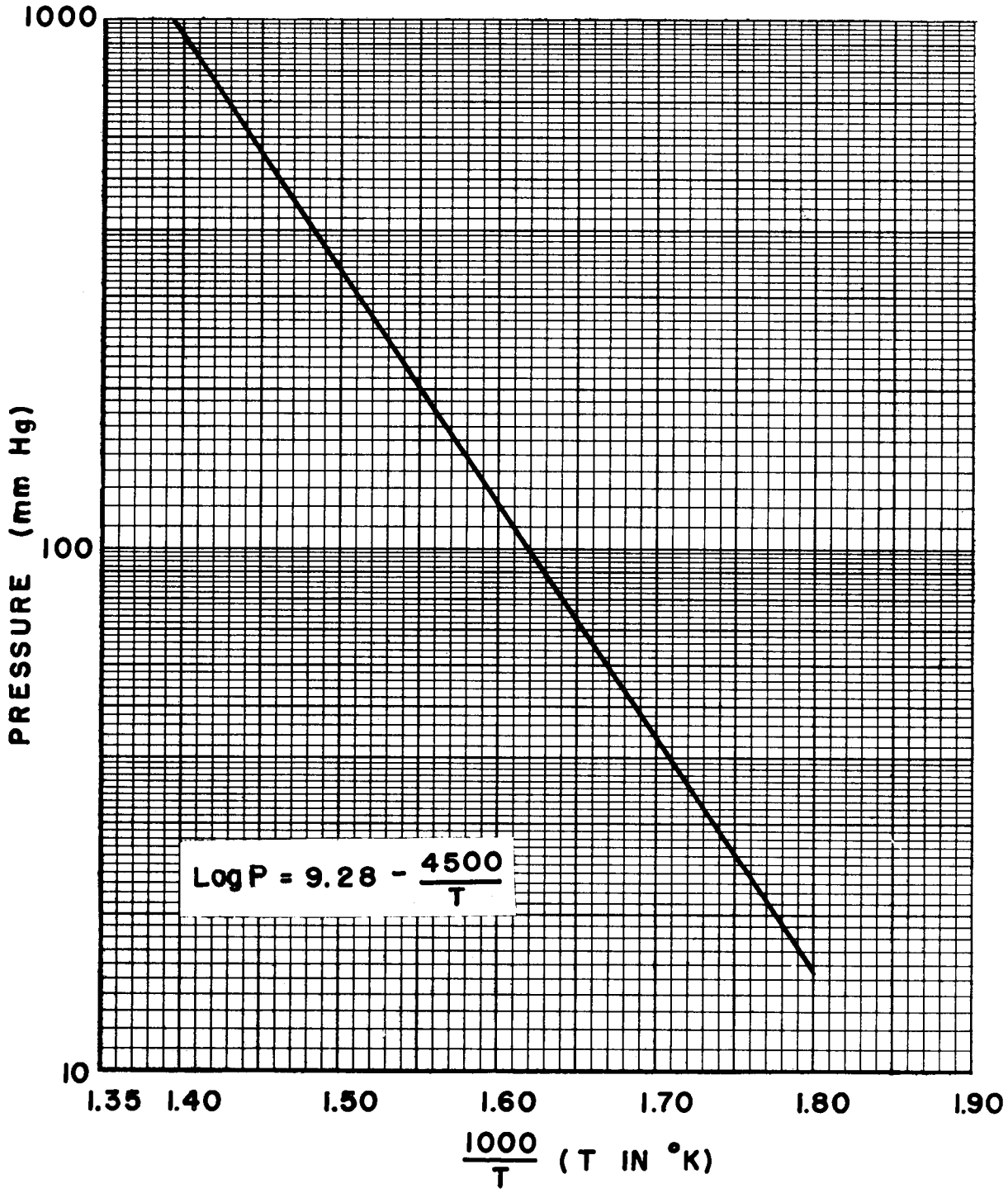

FIGURE 3. DECOMPOSITION PRESSURE VS TEMPERATURE FOR UH_3

6.0 Conclusions

1) Most lots of uranium hydride (UH_3) are pyrophoric, some have been made which are not. Non-pyrophoric uranium hydride can probably be made but a concentrated effort must be made on all phases of the problem. Titanium hydride (TiH_2) was once considered pyrophoric, but now non-pyrophoric material is made in tonnage quantities.

2) The density requirements can probably be met.

3) The material can easily be clad in a number of metals since UH_3 is non-corrosive.

4) UH_3 forms amalgams with mercury. Alloys of uranium and metal are formed releasing hydrogen when UH_3 is mixed with molten lead, tin, and cadmium. No information is available on bismuth-UH_3, but this combination should act similarly as the other metals and form U-Bi alloys.

5) UH_3 and powdered lead compacts have been made. The low density of the compact rules out this possibility of embedding UH_3 in lead.

6) Uranium hydride dissociates on heating. At 430°C the UH_3 is in equilibrium with hydrogen gas at one atmosphere pressure. The formation and decomposition of UH_3 is reversible and very sensitive to temperature.

7) The radiation stability of UH_3 is unknown. It can be assumed however that it is as stable as TiH_2 to pile radiation as a first approximation.

8) No cost on production data are available since no large quantities of material with the desired properties have been made. Metal Hydrides, Inc., the only commercial producers of hydrides, will not commit themselves until a lot of non-pyrophoric material has been produced under plant conditions. Once a sample is obtained, questions as to the stability, density, composition, etc. can be fully determined, as well as the cost of production on large scale.

7.0 Acknowledgements

The author wishes to express his appreciation to Mr. R. B. Gallaher for his assistance in compiling data on UH_3. Thanks are also due to Dr. V. P. Calkins, NEPA, Mr. G. H. Clewett, Y-12, for the information on properties and handling of UH_3, and to Dr. T. R. P. Gibb, Jr., Metal Hydrides, Inc. for the graph showing density relationships.

[redacted]

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