~~SECRET~~

~~CONFIDENTIAL~~

This document consists of 38 pages.
No. 107 of 123 copies, Series TA

UNITED STATES ATOMIC ENERGY COMMISSION

SEP-168

PREPARATION AND CONSOLIDATION OF THORIUM AND THORIUM HYDRIDE POWDERS

By
R. B. Wagner
S. Storchheim

CLASSIFICATION CANCELLED
DATE 1-20-56
For The Atomic Energy Commission
H. F. Carroll
Chief, Declassification Branch

August 9, 1954

Atomic Energy Division
Sylvania Electric Products, Inc.
Bayside, New York

This document contains Confidential-Restricted Data relating to civilian application of atomic energy.

Technical Information Service, Oak Ridge, Tennessee

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

~~CONFIDENTIAL~~

~~SECRET~~

246-001

DISCLAIMER

~~-SECRET-~~

~~CONFIDENTIAL~~

Other issues of this report may bear the number DCF-4896.
Work performed under Contract No. AT-30-1-gen-366.

~~-SECRET-~~

246-002

CONFIDENTIAL

~~SECRET~~

TABLE OF CONTENTS

~~SECRET~~

~~CONFIDENTIAL~~

~~SECRET~~

SEP-168
Metallurgy & Ceramics

ABSTRACT

A study was made of powder characteristics and cold compacting properties of metallic thorium, Th_2 and Th_4 powders produced from Ames billet lathe turnings. In addition a preliminary study was made of the influence of various powder processing and sintering variables on some physical properties of cold compacted bodies. The cold compacting and sintering characteristics of metallic thorium powder were generally superior to those of the hydride powders. The thorium powder could be cold compacted at 75 tsi to 96% of theoretical Ames billet density and sintered to 99% of the billet density when heated to above 1250°C for one-half hour. A test bar made from cold compacted and sintered thorium powder was found to have an ultimate tensile strength of 45,200 psi and an area reduction of 38.5%

~~CONFIDENTIAL~~

Classification cancelled (or changed to ______)

by authority of Ltr frm Decl Br, 6/55

by Carl Spradle TISOR, date 6/22/55

~~SECRET~~

I. INTRODUCTION

Because of the ability to obtain fissionable U^{233} from thorium, thorium is now receiving steadily increasing attention. The main interest at present centers on its use as blanket material in breeder piles. The fabrication techniques used at present for thorium are the conventional types, including melting, casting and working. The successful application of powder metallurgy methods to thorium or its hydrides, ThH_2 and ThH_4, could involve a considerable saving in money. Preliminary work has indicated, SEP-138, that thorium hydride can be produced to a high degree of purity. In addition, thorium powder made from this hydride can be applied to powder metallurgy processes. Because of this, a detailed study of the preparation and subsequent densification of thorium powder was made.

It was recognized early in the program that it was of prime importance to understand the production and characteristics of the starting powders. This was especially true with regard to subsequent powder compacting and sintering. The following report contains the results of such an investigation in which the methods of producing thorium, ThH_4 and ThH_2 powders was varied. The resultant powders were then cold pressed and sintered. At all stages of the work the powders and specimens obtained were characterized and evaluated.

The data regarding the powders obtained include the effect of hydriding and decomposition, as well as of rehydriding and recomposition. In addition, hydriding was conducted for different lengths of time to ascertain what effect this had on the resultant powders. The powders obtained were characterized according to mesh fraction distribution, particle size, apparent density and flow rate. Cold compacting studies were also carried out on the different powders, and green densities were determined. Finally, sintering experiments were conducted to determine the effect of temperature and time-at-temperature, as well as green briquette cold compacting pressure, powder particle size and processing history. Sintered densities, hardnesses and electrical resistivities were measured. In addition, several specimens were checked for tensile strength and microstructure.

II. MATERIALS AND PROCEDURES

A. Materials

The raw material exclusively used in this study were lathe turnings from Ames thorium billets. Table I shows the composition of this material as analyzed by spectroscopic and chemical methods.

TABLE I

Composition* of Ames Thorium Chips "As Received"

	% by Weight
Be	0.1 - 1.0
Ca	0.0001 - 0.001
Cr	0.001 - 0.01
Cu	0.0001 - 0.001
Fe	0.01 - 0.1
Mg	0.0001 - 0.001
Mn	0.0001 - 0.001
Na	0.0001 - 0.001
Si	0.01 - 0.1
Th	balance
N	<0.017
O	0.11
C	0.05 - 0.06

* N, O, and C were determined chemically, while the rest of the elements were spectrographically determined.

B. Procedures

1. Hydriding of Ames Thorium Chips

The Ames thorium chips, as-received, were hydrided, according to a standardized procedure, to the dihydride or the tetrahydride form as limit and, if required, subsequently dehydrided to metallic thorium powder.

The hydriding procedure described below was designated as "singly hydrided". Several "doubly hydrided" charges were also made. These latter charges were first "singly hydrided", then dehydrided in vacuum at 700°C to approximately 20 microns and subsequently rehydrided. The equipment used for the hydriding and dehydriding of the material investigated consisted of a 4" i.d. inconel reactor chamber, externally heated, connected to a vacuum train and an argon and hydrogen gas purification system which produced gas at a dew point of approximately -80°C.

The procedure consisted of the following steps:

a. The chips were pickled in 30% HCl for five minutes and subsequently washed chloride-free and dried in air.

b. The chips were loaded into the reactor chamber which was then alternately evacuated to 20 microns and filled with purified argon. The reactor was then heated to 450 to 500°C under vacuum.

c. Purified hydrogen was then admitted and the exothermic reaction

$$Th + H_2 \longrightarrow ThH_2$$

was allowed to proceed to the formation of ThH_2 to about 650°C. The hydrogen pressure throughout the cycle was maintained at approximately 20" Hg. The time consumed for a 2500 g charge was generally 1 to 2 hours.

d. After reaction of hydrogen ceased, as indicated by a flowmeter, the product was cooled in hydrogen to room temperature and removed under an argon atmosphere if the desired product was ThH_2.

In the production of the ThH_4 type of material, the cooling cycle was arrested at 230°C and the charge maintained at that temperature until the visible absorption for the reaction,

$$ThH_2 + H_2 \longrightarrow ThH_4$$

producing ThH_4, ceased. The product, 2500 gms, was then allowed to remain at that temperature under hydrogen for specific lengths of time, 4.5 to 85 hours, in order to obtain products of varying hydrogen contents. At the end of this period the charge was cooled under hydrogen or argon and removed for further processing under tank argon.

e. In the case of the production of metallic thorium powder, the tetrahydride was pulverized to -100 mesh, as described below, and heated to 700°C under purified hydrogen at atmospheric pressure to enable the reaction

$$ThH_4 \longrightarrow ThH_2 + H_2$$

to take place. After evolution of hydrogen ceased, the chamber was exhausted at 700°C. The reaction

$$ThH_2 \longrightarrow Th + H_2$$

proceeded until only a minimal amount of hydrogen corresponding to an equilibrium pressure of approximately 20 microns remained. The charge was then cooled under vacuum and further processed. Fig. 1 shows a flow sheet of the process.

2. Intermediate Processing and Testing of the Powder

The hydrided thorium chips or the loosely sintered cake of metallic thorium powder were removed from the reactor chamber and further processed under a protective atmosphere of tank argon as follows:

a. The batch was sampled for analysis.

b. 100 g of the hydride powder in "as hydrided" condition were screened for fifteen minutes in a nest of standard 3" diameter sieves on a vibratory screening table to determine the relative friability of the material.

c. The remainder of the batch was crushed and pulverized to the desired mesh sizes by hand with a steel mortar and pestle.

d. The apparent densities and flow rates at the various fractions were determined by means of a Hall Flow Tester.

The bulk of the investigation was carried on with the mesh fractions, U.S. Standard sieve size,

-100 mesh
-20 +80 "
-100 +200 "
-325 "

Other mesh fractions and powder in "as hydrided" and "as sieved" condition were, however, also used in some phases of the work.

3. Cold Compacting of the Powder

The powder, both hydride and metallic, was pressed in a 0.500" diameter steel die in 5.00 g charges. The die was, in all cases, loaded and unloaded under a protective atmosphere of tank argon. Compacts were pressed at 28 tsi under argon while those compacted at higher pressures were pressed without protective atmosphere because of limitations of press equipment.

4. Sintering of Cold-Pressed Compacts

10 g specimens, 1-1/2" x 1/4" x approximately 1/4" were cold pressed in a V-block steel die and sintered in a high-frequency induction or electrical resistance tube furnace. The powder was loaded into the die and the compact removed from it under an argon atmosphere.

All cold-compacted thorium and thorium hydride compacts, with the exception of a few specimens sintered in hydrogen and vacuum, were sintered in a tank argon atmosphere. The dew point of the tank argon was -60 to -70°C.

Two types of sintering furnaces were used in this work. One type consisted of a 2" i.d. quartz tube surrounded by a graphite sleeve heated by a high-frequency induction coil. The space between quartz and graphite contained Norblack insulation. This furnace was used for sintering temperatures up to 1550°C. The other sintering furnace, used for temperatures up to 1350°C, consisted of a 2" i.d. mullite tube heated externally by a Kanthal electric heating element. In both cases the specimens rested on a vacuum degassed graphite slab in a slow flowing argon atmosphere during sintering. A few specimens were also sintered in a hydrogen atmosphere in a molybdenum-wire-wound electric resistance furnace and, under a vacuum of approximately 200 microns, in a graphite sleeve high-frequency induction furnace.

III. EXPERIMENTAL WORK AND RESULTS

A. Production of Powder

The Ames billet lathe turnings used as raw material were hydrided in lots up to 2500 g and dehydrided in 5000 g lots in the standardized manner described above. No operational difficulties were encountered. The strongly exothermic reaction of the hydriding of thorium to the dihydride caused local temperatures considerably above the theoretical reaction temperature of 650°C, but this condition did not seem to have any noticeable influence upon the product.

The batches of dihydride and tetrahydride produced were allowed to remain under hydrogen at reaction temperature for various lengths of time. The pressing properties of the resultant product, as well as the actual indications of hydrogen reaction and chemical analysis, showed that it was possible to accomplish further hydriding after the bulk of the reactable hydrogen, as indicated by the flow indicators used, had combined with the thorium. The major portion of the hydriding reaction, as indicated by the cessation of visible gas flow, consumed approximately one hour for the formation of the dihydride and three to four hours for the tetrahydride. Chemical analysis for hydrogen content of the product did not yield consistently reliable results, but did give an indication of continuous, if decreasing, hydrogen absorption over a period of eighty-five hours in producing the tetrahydride. Analysis showed the product to contain 1.68% H_2, $ThH_{3.9}$, and 1.53% H_2, $ThH_{3.6}$, for eighty-five and four-and-one-half hours of hydriding from ThH_2 to ThH_4, respectively. All batches of the dihydride analyzed showed a hydrogen content slightly in excess of the formula ThH_2, e.g., approximately 0.90%. The dehydriding of the tetrahydride in a vacuum of approximately 20 microns at 700°C resulted in a friable sinter cake.

B. Intermediary Processing and Testing of the Powder

The tetrahydride type of powder, dark blue in color, was easily crushed, and was considerably more friable than the light gray dihydride type. Table II shows the results of typical standard sieve analyses conducted on the "as hydrided" product for both the dihydride and tetrahydride. It can be seen that the sieving resulted in considerable comminution of the tetrahydride, but only in an insignificant amount in the case of the dihydride. All comminution was done with a steel mortar and pestle. The sinter cake of thorium resulting from the dehydriding of the tetrahydride was easily crushed to the -100 mesh particle size of the original hydride.

Table III shows typical flow rates and apparent densities of the various types and mesh fractions of powder investigated. The hydride powder particles were found, by microscopic examination, to be relatively more angular and sharp cornered than the particles of the thorium powder. The particles of the former powders are undoubtedly also harder and less ductile than those of the latter, thus resulting in more irregular shaped particles after comminution. These physical properties probably explain the poor flow properties of the hydride powders relative to the metallic thorium powder. The average particle size of a powder fraction was taken as the 50% intercept of a plot of log sieve mesh size in microns versus probability weight percent of powder passing through the indicated sieve.

The material when processed as described above, under a protective atmosphere of tank argon, and pressed in the manner outlined, was found not to be noticeably contaminated with oxygen, nitrogen or iron after processing as substantiated by spectroscopic and chemical analyses. The tetrahydride was pyrophoric in most mesh fractions including the "as-hydrided" fraction. The dihydride oxidized slowly upon exposure to air, while the metallic thorium exhibited the least tendency to surface oxidize.

No visible deterioration of pressed compacts stored under a protective atmosphere of argon for a period of one month could be ascertained in the case of both the higher hydride and the metallic thorium, but compacts pressed from the dihydride commenced to disintegrate after one or two days storage.

C. Cold Compacting of the Powder

The 5.00 g, 0.500" diameter specimens pressed from the powders, in the manner described above, showed a volumetric expansion of 2 to 3% upon ejection from the die. The compacts pressed from the tetrahydride and metallic thorium powders were sufficiently strong for handling when pressed at 7 tsi. The dihydride did not, however, give compacts that could be handled when pressed below 14 tsi.

Fig. 2 shows, for various mesh fractions, the green density versus cold compacting pressure relationship of a "doubly hydrided" tetrahydride type of powder. The average increase in the green density of the densest, "as hydrided", fraction over the least dense, -325 mesh, fraction over the pressure range of 25 to 75 tsi was found to be approximately 4%. The superior green densities of the "as hydrided" and "as sieved"

TABLE II

Standard Sieve Analysis of "As Hydrided" Product Sieved for 15 Minutes 100 g, 3" Diameter U.S. Standard Sieves

U.S. Std. Sieve Number	Opening Microns	ThH4 Type Product Weight On Sieve g	ThH4 Type Product Weight Passing Through Sieve	ThH2 Type Product Weight On Sieve g	ThH2 Type Product Weight % Less Than Stated Sieve
10	1651	0	100.0	2.60	97.8
20	833	23.22	76.6	95.50	2.28
80	175	67.66	8.37	1.65	0.63
100	147	4.09	4.25	0.27	0.36
200	74	2.93	1.29	0.13	0.23
230	62	0.60	0.68	0.13	0.10
325	44	0.37	0.31	0.10	--
-325	<44	0.31	--	--	--
Av. Particle Size*		470 microns		1150 microns	
Particle size before sieving, approximately		94% +20 mesh		98% +20 mesh	

* 50% intercept of plot of log sieve mesh size (microns) versus probability scale weight percent passing through sieve.

TABLE III

Average Apparent Densities and Flow Rates of Thorium Hydride Powder (Hall Flow Tester Used)

Type of Hydride	Mesh Fraction Microns	Av. Apparent Density g/cc	Av. Flow Rate g/cc
ThH_4	-20 +80	3.29	nil
	-100 +200	3.35	1.41
	-325	2.88	nil
	-100	3.50	nil
ThH_2	-20 +80	5.62	nil
	-100 +200	4.43	2.61
	-325	3.76	nil
	-100	4.46	nil
Th	-20 +80	3.61	nil
	-100 +200	4.04	2.38
	-325	3.95	2.03
	-100	4.68	3.03

(powder resulting from the standard sieve analysis) fractions is probably due to comminution of the particles to an effective size distribution during pressing. It can be seen that here, as in the case of all other powders investigated, a small, but definite, increase in green density results with increase of average particle size for fractions with narrow limits of particle size, e.g., -80 +100 mesh, etc.

The density variations, at various pressures, with mesh fraction of powder and length of hydriding time, e.g., hydrogen content, for a typical tetrahydride type of powder are shown in Figs. 3 and 4 respectively. It can be seen that the least dense, finest, powder (average particle size = 4.6 microns) exhibits a density approximately 4 to 5% lower than that of the densest, coarsest, powder over most of the pressure range investigated. The density varied with hydrogen content to only a small extent (approximately 1-1/2%), increasing with the length of hydriding time, e.g., hydrogen content. The latter relationship was found to hold true for the three mesh fractions, -20 +80, -100 +200, and -325 mesh investigated.

The less friable hydride, e.g., the ThH_2 type, shows similar relationships between green density and cold compacting pressure for varying mesh fractions and lengths of hydriding time. The only exception to these relationships is the reversal of the trend established by the -100 +200 mesh and -325 mesh fractions, in that the powder hydrided for the longer time shows lower green densities than that hydrided for the shorter time in the case of the -20 +80 mesh fraction. The actual difference is small but consistent. Fig. 5 summarizes the data.

In cold compacting the metallic thorium powder produced by dehydriding -100 mesh tetrahydride type powder, a maximum difference in green density of 1.5% was found between the three fractions, -20 +80, -100 +200, and -325 mesh, tested. Fig. 6 shows, however, that contrary to the behavior of the hydride powders, the coarsest fraction, -20 +80 mesh, exhibits the lowest green density above 30 tsi compacting pressure.

The various types of powder, as classified in accordance with their chemical structure, e.g., tetrahydride, dihydride and metallic thorium, exhibit marked differences in their green densities as shown in Fig. 7 for the -100 mesh fraction. The ThH_4 type of powder shows the poorest density, ranging from 5.6 g/cc at 10 tsi to 6.35 g/cc at 75 tsi. The medium dense compacts of the ThH_2 type range from 7.2 g/cc at 10 tsi to 8.6 g/cc at 75 tsi. The metallic thorium powder compacts show consistently a markedly higher green density ranging from 8.5 g/cc at 10 tsi to 11.15 g/cc at 75 tsi compacting pressure.

All green density versus cold compacting pressure curves show typical trends, mostly having a relatively flat slope in the vicinity of 75 tsi compacting pressure. The curves for the -100 mesh ThH_4 and ThH_2 type powder compacts show a marked flattening above 50 tsi.

The errors incurred in this study, aside from possible variations due to deterioration of the powder, consisted primarily of errors in measuring during the pressing operation. The pressing of a number of theoretically identical compacts showed this error to be ± 1.5%

D. Sintering of Cold Pressed Compacts

1. Sintering in Argon Atmosphere

The cold compacted specimens of thorium, thorium dihydride and thorium tetrahydride powder were sintered under various conditions in order to determine the effect of processing variables on the sintered density and other physical properties. The following is a breakdown of the results of this investigation.

a. Effect on Sintered Density of-

(1) Sintering Temperature

The sintering temperature was varied from 900°C to 1550°C for specimens of each type of powder, cold-pressed at 75 tsi and sintered in a tank argon atmosphere for 0.5 hours. Fig. 8 shows the variation of sintered density with sintering temperature for this sintering series. The most dense material, e.g., metallic thorium powder, while exhibiting a density not greater than green density when sintered at 900°C and 1000°C resulted in a compact having a sintered density of 11.53 g/cc at 1350°C. This density is within 99% of the attainable Ames billet bulk density, ranging generally between 11.57 and 11.63 g/cc. The material exhibited this high density when cold pressed at 75 tsi and argon atmosphere-sintered between 1250°C to 1550°C. Sintering this powder at temperatures above 1250°C did not result in a further increase in density.

The ThH_4 type of powder compact, consisting of thorium resulting from the decomposition of the ThH during sintering, attained a maximum density of 11.37 g/cc at 1550°C while the ThH_4 type powder compact, consisting of ThH_2 decomposed to thorium during sintering, attained a maximum density of 11.16 g/cc at 1550°C. All types of compacts showed a pronounced leveling off of the sintered density at temperatures above 1250°C. The ThH_2 and ThH_4 type of powder compacts, probably due to their low green densities, in spite of favorable sintering conditions brought about by the dehydriding of the powder during sintering, did not show any tendency to reach sintered densities comparable to those of the thorium powder compacts in the temperature range investigated.

(2) Sintering Time

Fig. 9 shows the influence of sintering time upon each type of powder compact as sintered in an argon atmosphere at 1000°C. The data represent the average of two specimens. While the thorium type of powder compacts showed no significant increase in density in the range of 1/4 hour to 8 hours sintering time, the other types of powder compacts did show increased densities for longer sintering periods. The ThH_4 type of powder compact reached maximum density after 1/2 hour of sintering while the ThH_2 type of powder compact reached maximum density only after 3 hours of sintering. It is interesting to note that this latter type of compact, while exhibiting a lower sintered density than the ThH_4 type below approximately 2 hours sintering time, attained higher densities for longer periods of sintering time.

(3) Cold Compacting Pressure

A series of compacts, including all three types of powder, were pressed one each, at 10, 25, 50 and 75 tsi and subsequently sintered in argon for 0.5 hr. at 1150°C. Fig. 10 shows the variation of sintered density with cold compacting pressure. The most pronounced effect of cold compacting pressure on sintered density was found in the case of the thorium powder compacts. The sintered density of the thorium powder compacts surpassed those of the ThH_2 powder compacts only beyond approximately 25 tsi and those of the ThH_4 powder compacts beyond approximately 45 tsi cold compacting pressure. The sintered density of the ThH_4 type powder compacts varied only within experimental error over the pressure range investigated; the thorium powder compacts, however, increased in sintered density from 9.6 g/cc for 10 tsi to 11.3 g/cc for 75 tsi cold compacting pressure. The rate of increase of density with compacting pressure did, however, substantially diminish toward 75 tsi. The ThH_2 type of powder compacts exhibited, over the entire pressure range, a sintered density markedly inferior to that of the ThH_4 type of powder, and above 25 tsi compacting pressure, inferior for that of the thorium powder compacts. While the sintered densities, in general, increased with compacting pressure, the rate of increase seemed to be very small for pressure above 50 tsi.

(4) Powder Particle Size

A series of ThH4 type powder compacts pressed at 75 tsi from various mesh fractions of powder within narrow ranges of particle size and sintered in argon at 1150°C for 0.5 hr. resulted in compacts exhibiting slightly increasing densities with decreasing average particle size of the powder.

The -100 mesh powder, representing a wider particle size distribution than the -20 +80, -100 +200, and -325 mesh powders showed, however, a lower density than the narrow range particle size powder of comparable average particle size. Fig. 11 summarizes the data graphically.

The "as hydrided" fraction (approximately 94% +20 mesh before pressing) is represented on Fig. 11 as a broken line indicating fair agreement with the tendency of the curve to flatten out in the direction of larger average particle size.

(5) Length of Hydriding Time

The length of hydriding time to which the powder was subjected was shown above to affect the powder characteristics and cold compacting properties of thorium hydride. This is probably caused by the fact that the powders held varying amounts of chemically bonded or adsorbed and absorbed hydrogen as well as by unknown effects of the length of hydriding time on the brittleness, particle structure and surface conditions of the powder. A series of test compacts of tetrahydride powder, hydrided for varying lengths of time from 4-1/2 to 85-1/2 hours did not, however, show any correlation between sintered density and length of hydriding time.

2. Sintering in Hydrogen Atmosphere and Vacuum

A few specimens of ThH_4 type powder cold compacted at 28 tsi, sintered in a purified hydrogen atmosphere in a molybdenum wound electrical resistance furnace at 1500°C for one hour, were considerably distorted after sintering. The densities of these compacts and those sintered in a vacuum of approximately 200 microns were 10.9 to 11.0 g/cc, considerably below the 11.3 g/cc density of the argon sintered specimens. A considerable amount of hydride, forming a layer on the surface of the specimen, was found to form during cooling in the case of the hydrogen sintered compacts. These sintering experiments were of an exploratory nature and do not preclude the possibility of satisfactory sintering of thorium compacts in a well purified hydrogen atmosphere or a vacuum.

E. Physical Testing of Sintered Compacts

1. Hardness of Sintered Compacts

All sintered specimens were hardness tested on a Rockwell Hardness Tester. No marked relationship between the hardness of the material and sintering conditions was found. In general all specimens above 11.0 g/cc density, regardless of powder and processing history fell between R_F80 and R_F90. Specimens of lesser density decreased rapidly in hardness to below R_F50 for approximately 10 g/cc.

2. Electrical Resistivity of Sintered Compacts

Electrical resistivity measurements made on a few specimens showed erratic results which could not be satisfactorily correlated with the sintered density of the material. Table IV summarizes the data. Even at the highest densities, all sintered specimens showed considerably higher electrical resistivities than a specimen machined from an Ames thorium wrought bar, e.g., 20 to 30 x 10^{-6} ohm-cm and 17.5 x 10^{-6} ohm-cm, respectively.

TABLE IV

Electrical Resistivity of Cold Compacted and Sintered Thorium and Thorium Hydride Compacts
(Current - 2 amps)

Type of Powder	Density g/cc	Electrical Resistivity, 10^{-6} ohm-cm
Th	11.18	24.0
Th	11.30	30.0
Th	11.52	24.0
Th	11.53	21.3
ThH_2*	10.19	29.5
ThH_4*	10.43	27.8
Ames Th Rod	11.59	17.5

* Decomposed to Th during sintering.

3. Tensile Strength of Sintered Compacts

The ultimate tensile strength of three sintered compacts tested are tabulated in Table V below:

TABLE V

Ultimate Tensile Strength of Cold Compacted and Sintered Thorium and Thorium Hydride Compacts

Specimen Type	Density g/cc	Ultimate Tensile Strength, psi	Reduction of Area, %
Th	11.53	45,200	38.5
ThH_4 *	11.13	36,300	12.5
ThH_2 *	11.00	33,900	15.0

* Decomposed to thorium during sintering.

4. Microstructure of Sintered Compacts

An examination of the microstructure of the specimens tested for ultimate tensile strength, as tabulated in Table V, showed all specimens to have equiaxed grains. The thorium and ThH_2 type of specimens contained grains 8-50 microns in size, while the ThH_4 type of specimen contained slightly larger grains, approximately 8-150 microns in diameter. All specimens contained considerable amounts of inclusions, probably thorium oxide. Figs. 12, 13 and 14 show the microstructures of these compacts.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

A. Production and Cold Compacting of Powder

Of the three types of thorium powder produced by hydriding and dehydriding Ames thorium chips, e.g., the thorium tetrahydride type, the thorium dihydride type, and metallic thorium, the latter powder exhibited markedly superior cold compacting properties as compared to the other two types.

The raw material, e.g., Ames thorium chips, hydrided easily to both types of hydride. The tetrahydride powder was considerably more friable than the dihydride type. In general, over the mesh fraction tested, the hydrides exhibited very poor flow properties while the metallic thorium powder fractions flowed satisfactorily with the exception of the coarse -20 +80 mesh fraction. The apparent densities of the powder types and sieve fraction tested did not show any significant trend or correlation with the process variables as investigated.

In obtaining the data for cold compacting these powders, the most significant variation of green density was found to be relative to the powder type. For example, the green densities for -100 mesh powder at 75 tsi compacting pressure were 6.35 g/cc for the ThH_4 type, 8.6 g/cc for the ThH_2 type, and 11.15 or 96% of theoretical Ames billet density, for metallic thorium powder. The metallic thorium powder also showed considerably superior compactability, relative to its theoretical bulk density, as compared to the hydride powders. The variation of green density with compacting pressure for varying mesh fractions of powder as well as for varying hydrogen contents of the hydride type powders was found to be not very significant, but generally showed a trend toward increasing green densities with higher hydrogen content (for an individual hydride powder type) and coarser particle size. Thus the variation of green density with particle size for metallic thorium powder was only 1.5% for the three mesh size fractions investigated, e.g., -20 +80, -100 +200, and -325 mesh. The data show that above 50 tsi, the increase in green density with cold compacting pressure is very small for the hydride powders while the thorium powder shows an appreciable rate of increase to 75 tsi.

B. Sintering and Testing of Cold-Pressed Compacts

Compacts, cold-pressed in a manner similar to that used in the investigation of the green properties of the powder, were sintered in a tank argon atmosphere at various temperatures, from 900 to 1550°C and for various lengths of time, from 15 minutes to 8 hours. The investigation of processing variables also included cold compacting pressure, powder particle size and hydrogen content of the powder.

It was found that the sintered density increased in a typical manner with temperature for all three types of powders used, e.g., metallic thorium, thorium dihydride, and thorium tetrahydride, for the sintering conditions to which they were subjected. The sintering curves flattened out above 1250°C to an extent which showed that higher sintering temperatures would not significantly increase the compact density. The metallic thorium compacts reached 99% of theoretical Ames billet density while the best densities obtained for the other types of powder were 97.8% and 96.1% for the ThH_4 and the ThH_2 type, decomposed to thorium during sintering, respectively. The latter two types of sintered compacts probably contained larger amounts of hydrogen than the thorium powder compacts resulting in a reduction of density. A study of sintered densities in relation to length of sintering period showed that, for the size specimens used, approximately 1/4" square in cross section, while the hydrides were considerably affected by the length of sintering time, the metallic thorium powder compacts were not so affected. Fig. 9 seems to indicate that the general trend in densities observed for the standard 0.5 hour sintering periods, e.g, thorium, ThH_4, ThH_2 in order of decreasing density, would show a reversal of the order of the last two types of powder in the case of sintering periods of several hours. However, even after a sintering period of 8 hours, the hydride type of powder compacts showed considerably lower densities than the metallic thorium type powder compacts.

The investigation of sintered density relative to cold compacting pressure showed, significantly, that while the hydride powders were not greatly sensitive to cold compacting pressure, metallic thorium powder specimens were so to a very considerable extent. The latter type of powder compacts exceeded the hydride types in sintered density only above approximately 45 psi cold compacting pressure. This behavior may be an indication of the cause of the relatively low sintered densities of the hydride types of powder compacts as compared to the metallic thorium powder compacts, particularly when considered in conjunction with the reversal of the order of sintered density on prolonged sintering described above. The compacts of thorium powder resulting from the dehydriding, during sintering, of the hydride powder compacts may be too loosely compacted to attain a high density during sintering, e.g., comparable to a metallic thorium powder compact cold-pressed at a pressure considerably below 75 tsi.

A significant superiority in sintered density of ThH_4 type powder of small average particle size over coarser powder was conclusively demonstrated by cold compacting and sintering ThH_4 type powder of various mesh fractions. Varying hydrogen content of this type of powder, as indicated by varying lengths of hydriding time, did not, however, result in noticeable changes in sintering characteristics. All specimens, regardless of powder type and processing history, exhibited a hardness of R_F80 to 90 for specimens having a sintered density of above 11.0 g/cc. It was not possible to correlate sintering conditions with the electrical resistivity of the material. The electrical resistivity of the pressed and sintered specimens was considerably higher than that of a wrought Ames bar, e.g., $20\text{-}30 \times 10^{-6}$ ohm-cm as compared to 17.5×10^{-6} ohm-cm. The higher resistivities of the powder metallurgical product are probably due to oxide inclusions as well as the presence of porosity. The ultimate tensile strengths and reduction of area of the metallic thorium powder specimens were markedly superior to those of hydride type of powder compacts due primarily to the inferior densities of the latter types of compacts. Table VI gives a general comparison of physical properties of wrought metal and compacts formed by cold-pressing and sintering.

Although relatively little, if any, contamination of the powder occurred during production and processing prior to sintering, the microstructure of the sintered compacts showed up to 3 volume % inclusions, probably consisting of oxide particles formed during sintering.

Compacts of ThH_4 type of powder sintered in purified hydrogen and a vacuum of approximately 200 microns showed densities inferior to those when sinte~~ring in argon.~~

TABLE VI

Comparison of Some Physical Properties of Wrought and Cold-Pressed and Sintered Thorium

Type of Specimen	U.T.S., 1000 psi	% Reduction in Area	Hardness R_F	Density g/cc
Cast, rolled and extruded Virgin Ames Metal, no heat-treatment.*	58.8	45.8	92.6	11.57-11.63
Powder Metallurgy	45.2	38.5	86	11.53

* The Fabrication of Thorium by Powder Metallurgy, J. G. Klein, K. G. Wikle, NYO-1115.

V. CONCLUSIONS

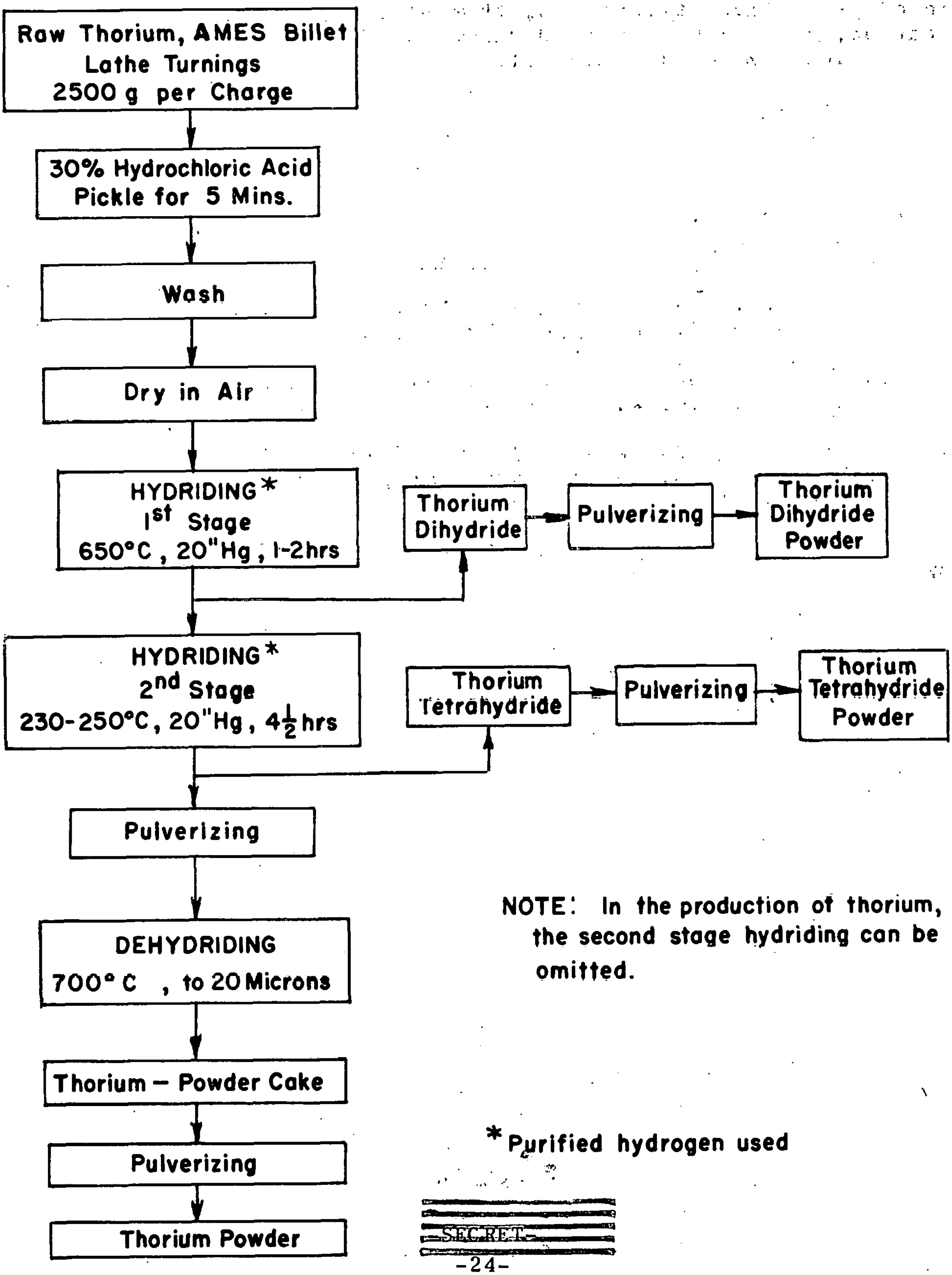
The present investigation of the production of thorium and thorium hydride powder, the powder characteristics and cold compacting properties of these powders, as well as the preliminary sintering study utilizing these powders, showed fabrication of thorium by the cold pressing and sintering techniques of powder metallurgy to be feasible. Metallic thorium powder exhibits the best fabrication characteristics. It can be fabricated into bodies having 96% of wrought metal density by cold compacting and 99% of the density of the wrought material by cold compacting and sintering in argon above 1250°C for short periods of time. Sintering in vacuum or careful control of atmosphere purity, reducing contamination during this processing operation, may be expected to result in bodies closer to the physical properties of the wrought material than the 77% of ultimate tensile strength and 84% of reduction of area of the wrought material achieved here. The comparatively low sintering temperatures relative to the melting point of thorium at which high density is achieved in this process points to the definite possibility of satisfactorily hot-pressing the material at temperatures considerably below half of its melting point, e.g., 900°C. This would make possible the hot-pressing of this material in the type of conventional high-speed steel or inconel dies used in the hot-pressing of uranium. Since the history of the production of thorium powder from wrought stock by hydriding and dehydriding does not seem to influence markedly the physical characteristics of the sintered product, a powder produced by a process not necessitating the production of the wrought material, and consequently perhaps less expensive, would seem to be very desirable for the more extensive development of thorium fabrication by powder metallurgical methods. The latter would be particularly advantageous if the resultant powders were non-pyrophoric and could be cold-processed without the use of protective atmospheres, thus allowing extensive simplification, resulting in considerable cost savings, in the handling and fabrication of the material.

BIBLIOGRAPHY

1. "Investigation of the Powder Metallurgy of Thorium (Part I)", W.G. Lidman, T. Weissman, SEP-138.
2. "The Fabrication of Thorium by Powder Metallurgy", J.G. Klein, K.G. Wikle, NYO-1115.
3. "Production of Powdered Uranium and Thorium" P. Chiotti, B.A. Barnes, Metal Progress 60, No. 3, September, 1951, pp. 60-65.

RBW:MS

PRODUCTION OF THORIUM AND THORIUM HYDRIDE POWDERS FROM AMES BILLET LATHE TURNINGS



NOTE: In the production of thorium, the second stage hydriding can be omitted.

*Purified hydrogen used

Fig. I Flow Sheet

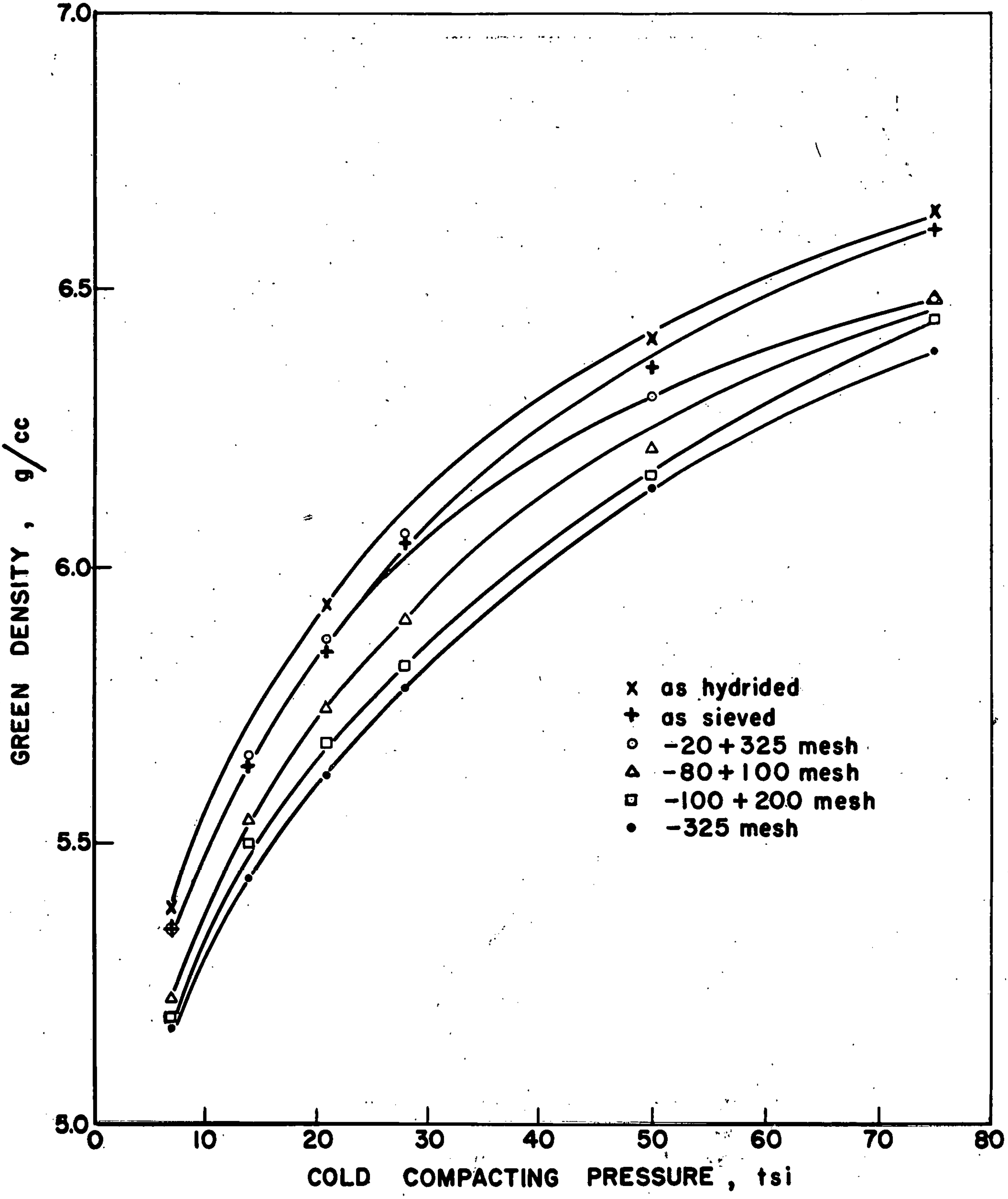


Fig. 2 - Green density vs. cold compacting pressure. Thorium Hydride ThH$_4$ type "doubly hydrided".

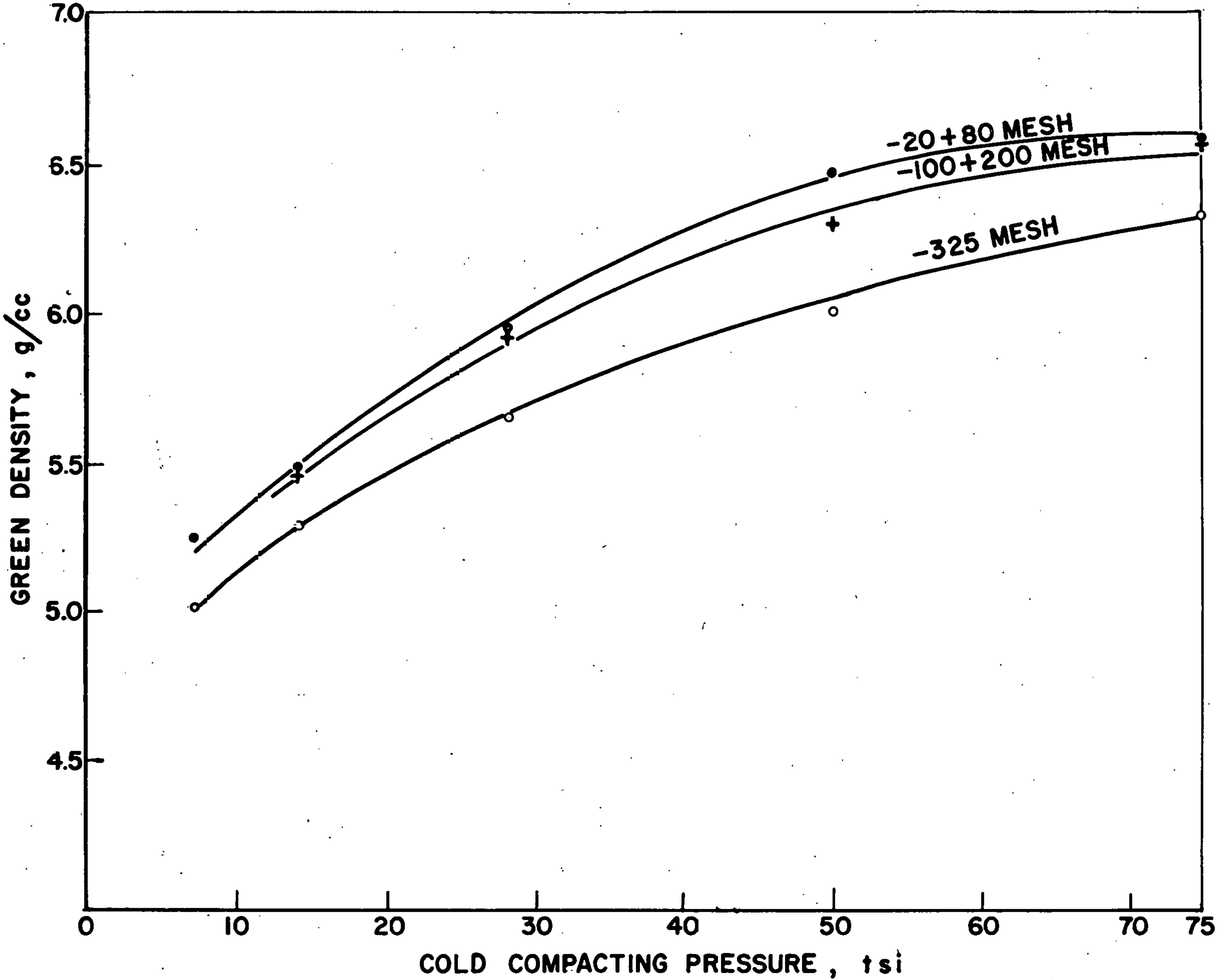


Fig. 3 - Green density vs. cold compacting pressure. Thorium Hydride ThH_4 type "singly-hydrided".

~~SECRET~~

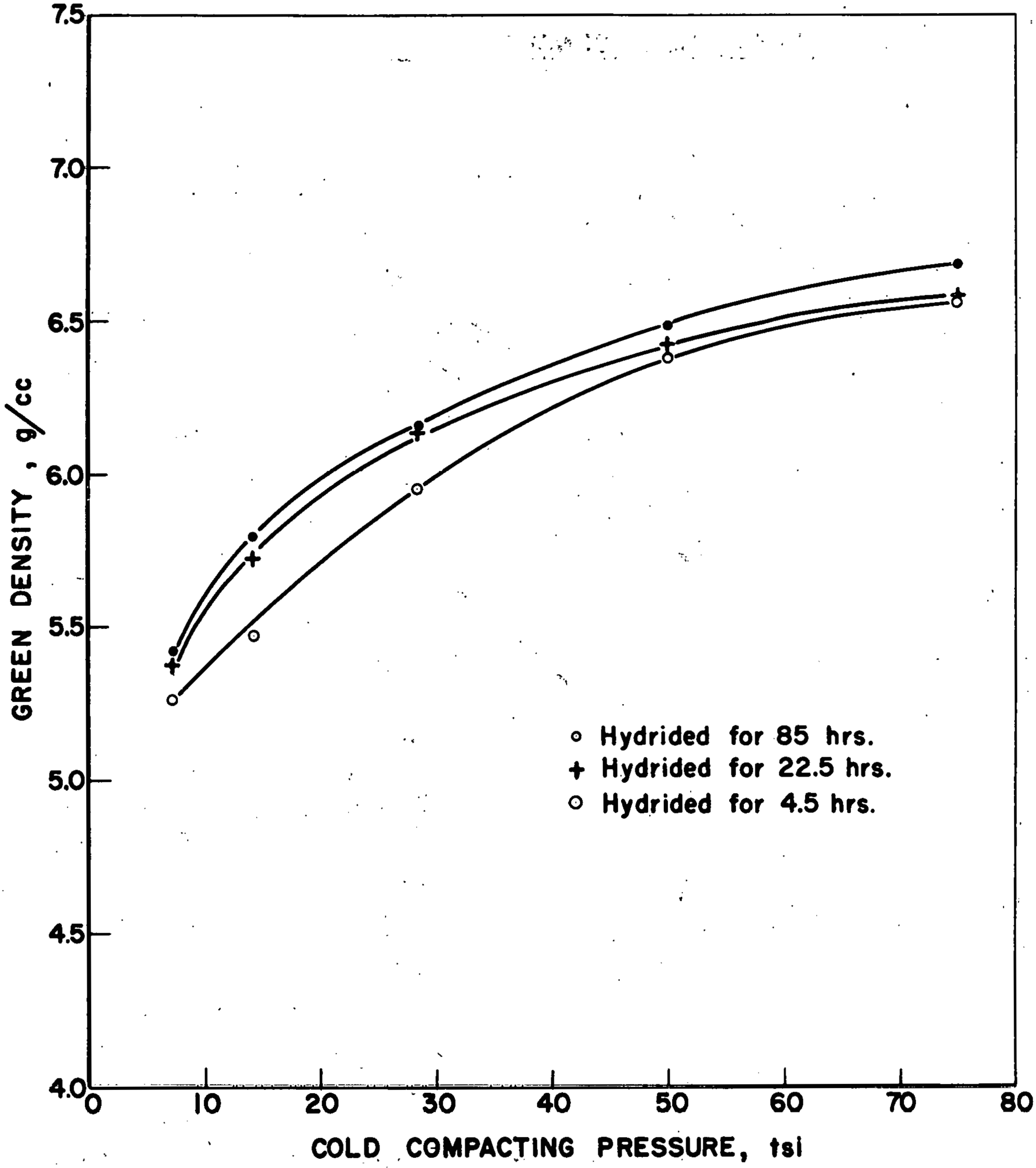


Fig. 4 - Green density vs. cold compacting pressure. Thorium Hydride ThH_4 type "singly hydrided" -20 +80 mesh.

~~SECRET~~

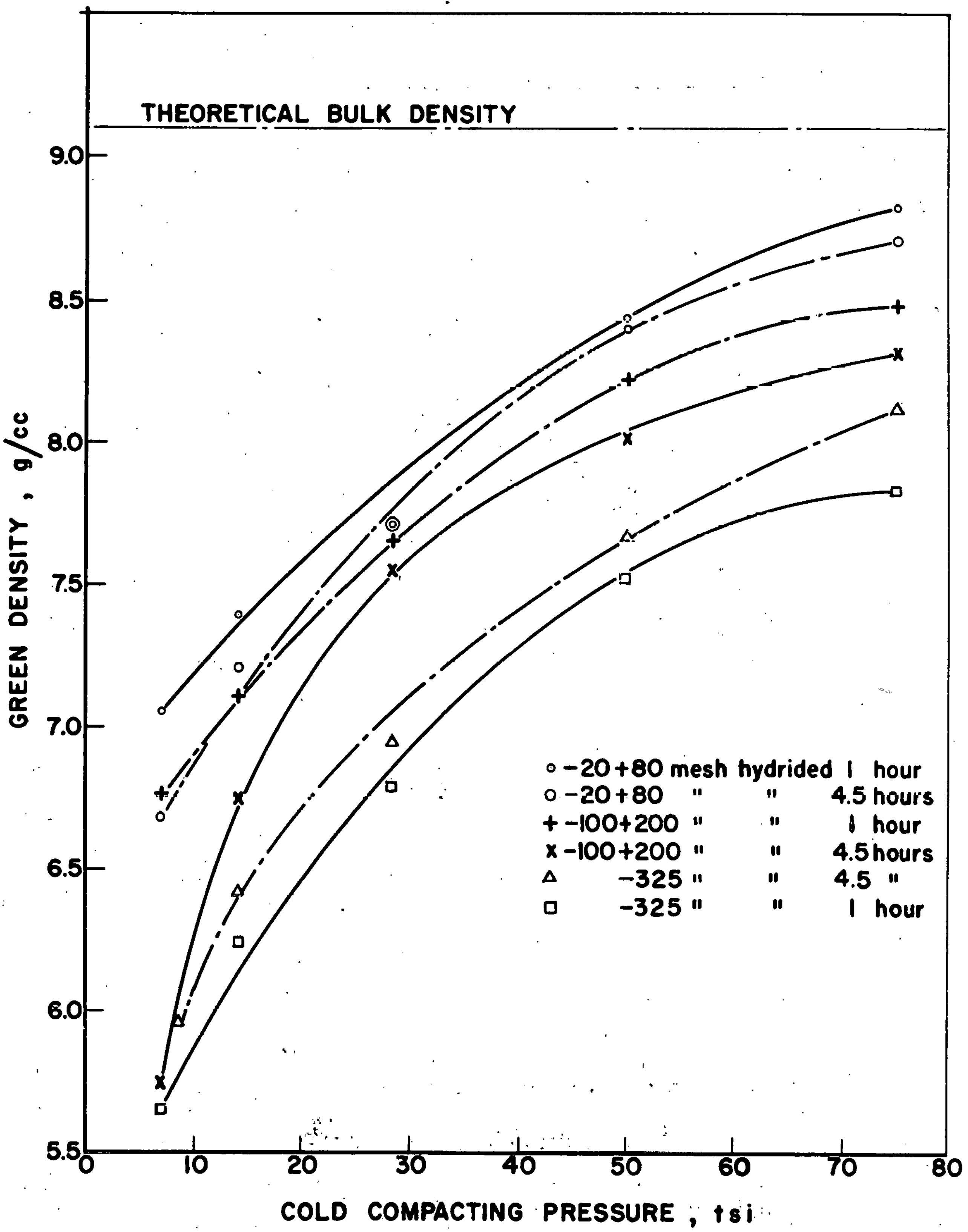


Fig. 5 - Green density vs. compacting pressure. Thorium Hydride ThH_2 type "singly hydrided".

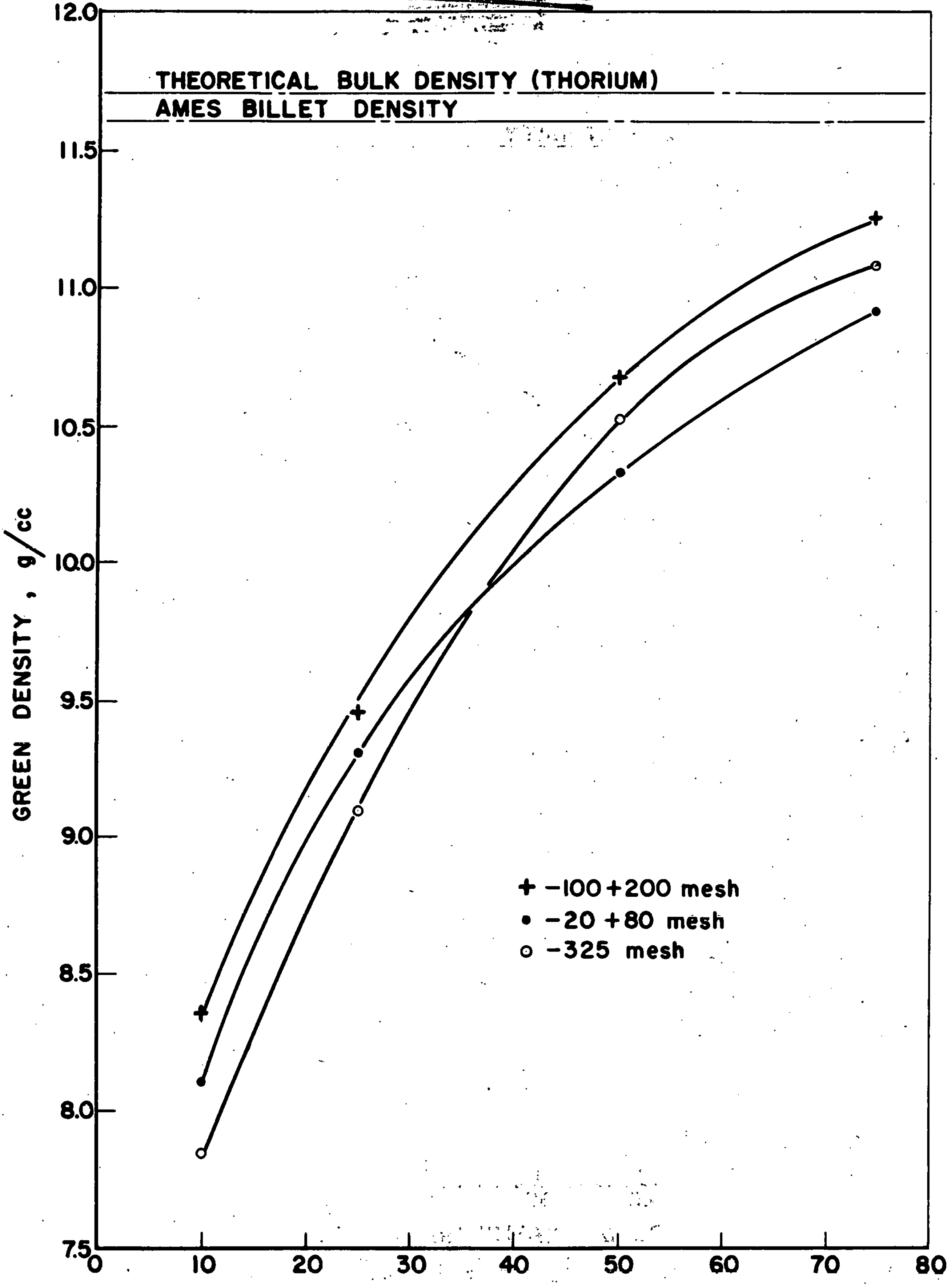


Fig. 6 - Green density vs. cold compacting pressure - Thorium.

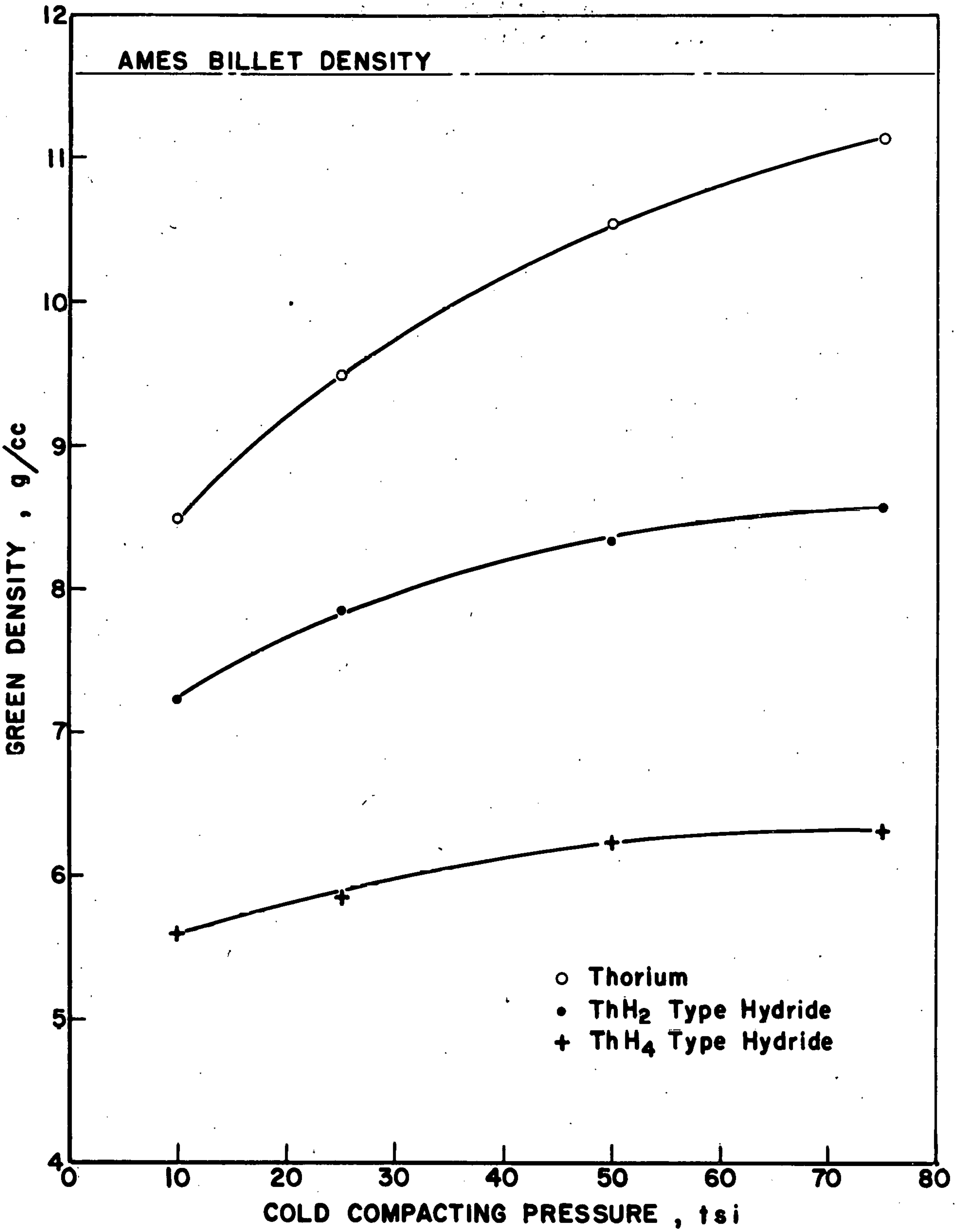


Fig. 7 - Green density vs. cold compacting pressure. Thorium and Thorium Hydrides, -100 mesh powder.

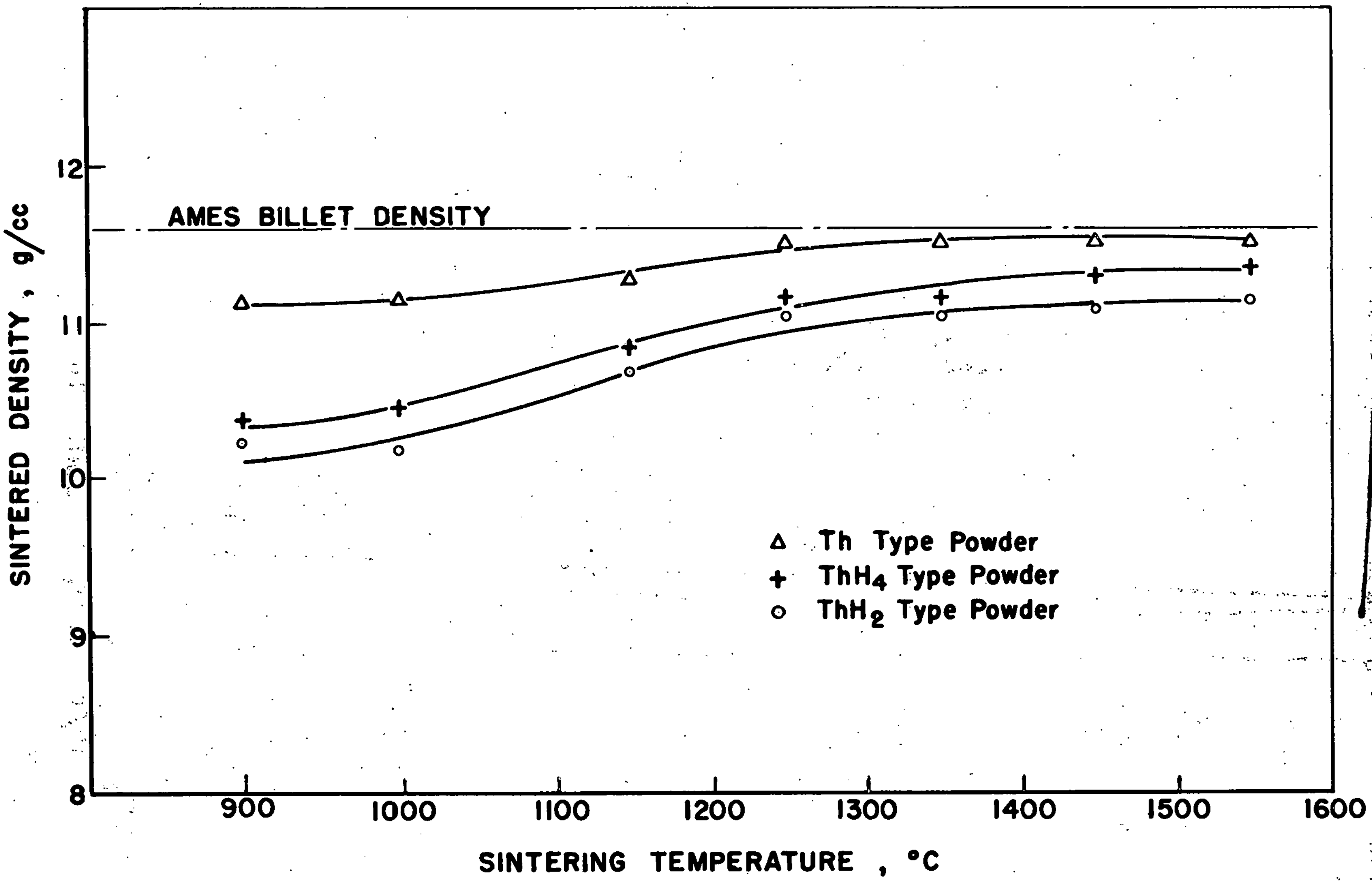


Fig. 8 - Sintered density vs. sintering temperature, thorium and thorium hydride cold pressed at 75 tsi sintered in argon for 0.5 hr.

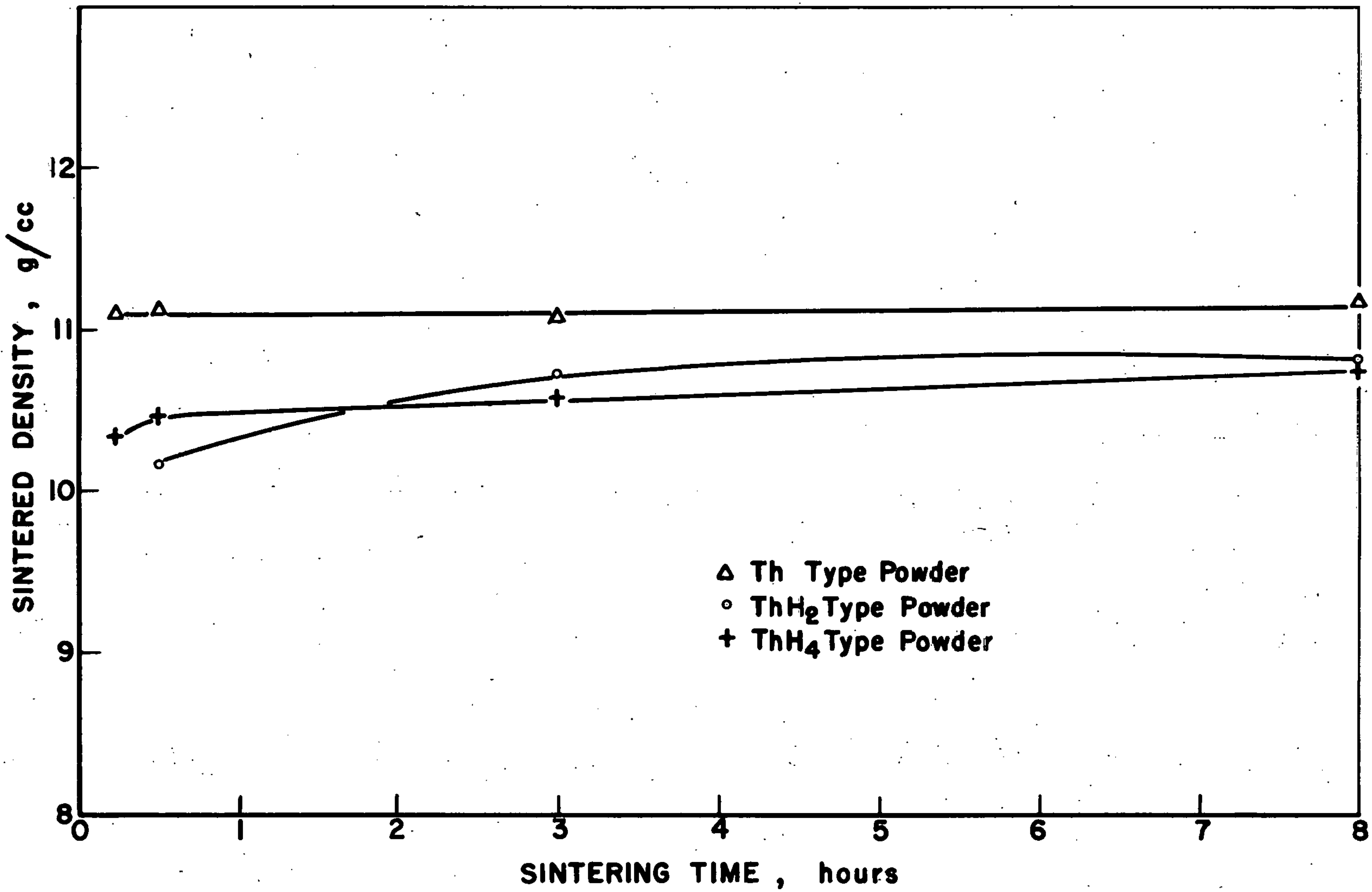


Fig. 9 - Sintered density vs. sintering time. Thorium and Thorium Hydride cold pressed at 75 tsi. Sintered in argon at 1000°C.

~~SECRET~~

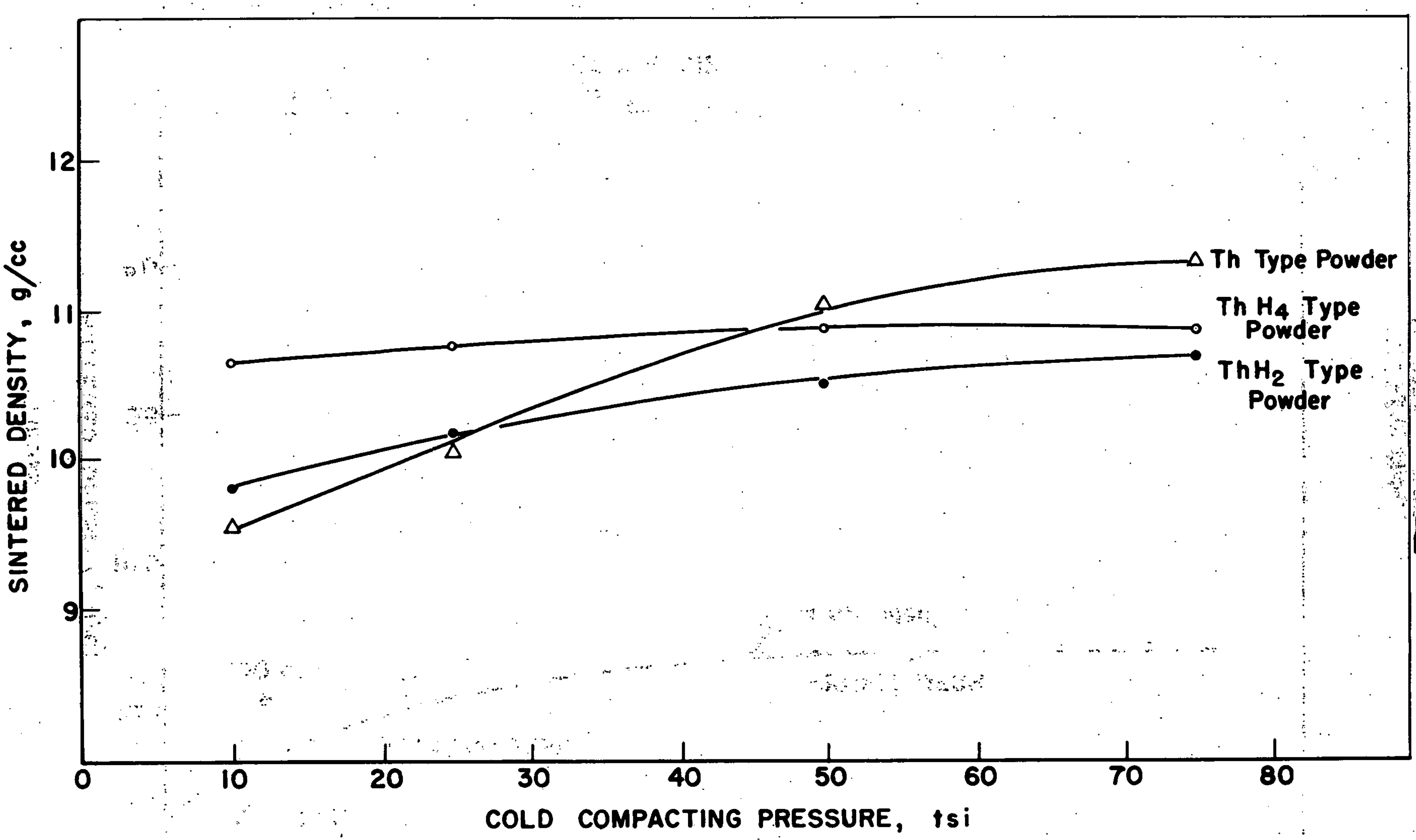


Fig. 10 - Sintered density vs. cold compacting pressure. Thorium and Thorium Hydride sintered in argon at 1150°C for 0.5 hr.

~~SECRET~~

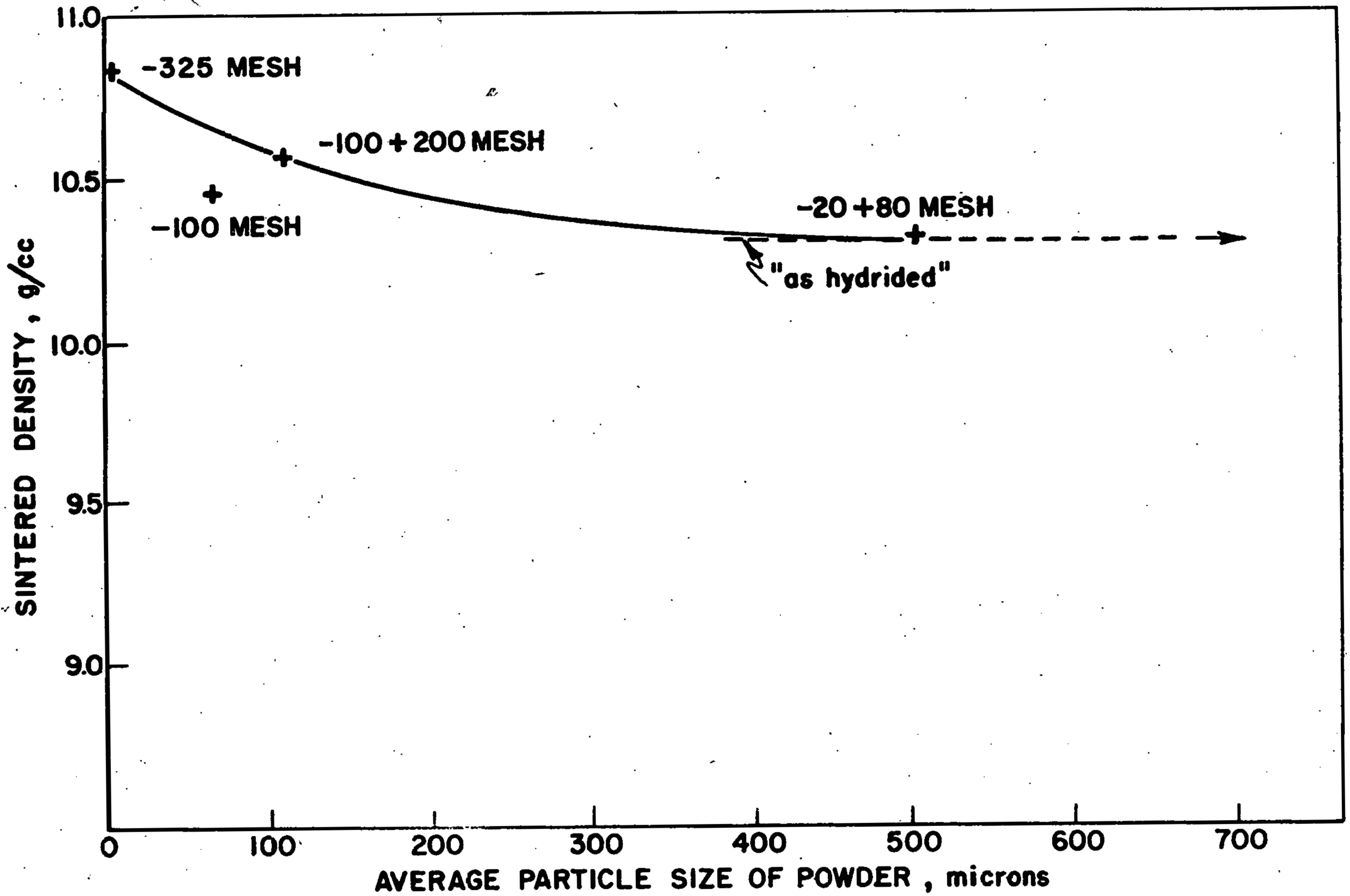


Fig. 11 - Sintered density vs. average particle size of powder. Thorium tetrahydride cold pressed at 75 tsi. Sintered in argon at 1150°C for 0.5 hr.

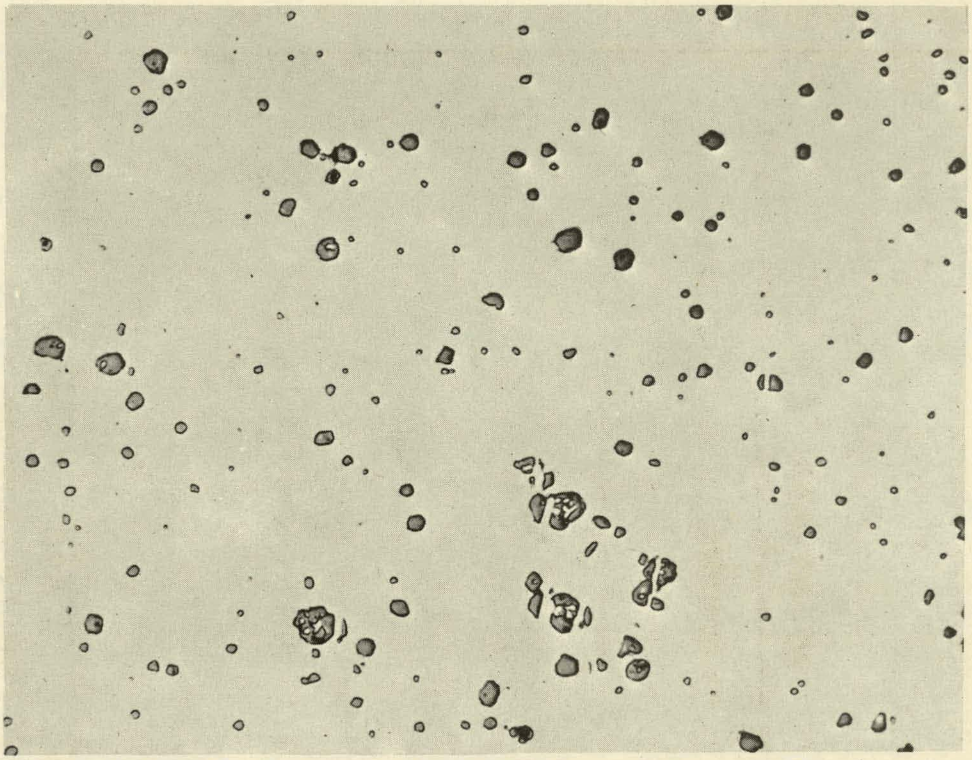


Fig. 12 - Thorium, -100 mesh, cold pressed at 75 tsi and sintered in argon at 1350°C for 1/2 hr. 500X

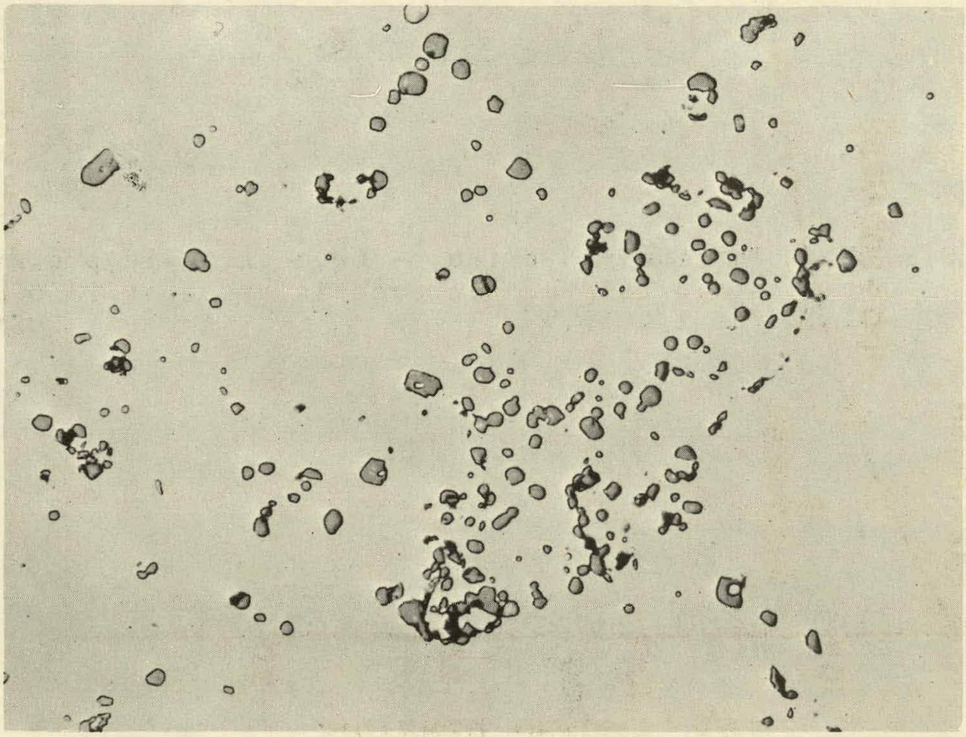


Fig. 13 - Thorium tetrahydride, -100 mesh, cold pressed at 75 tsi and sintered in argon at 1350°C for 1/2 hr. 500X

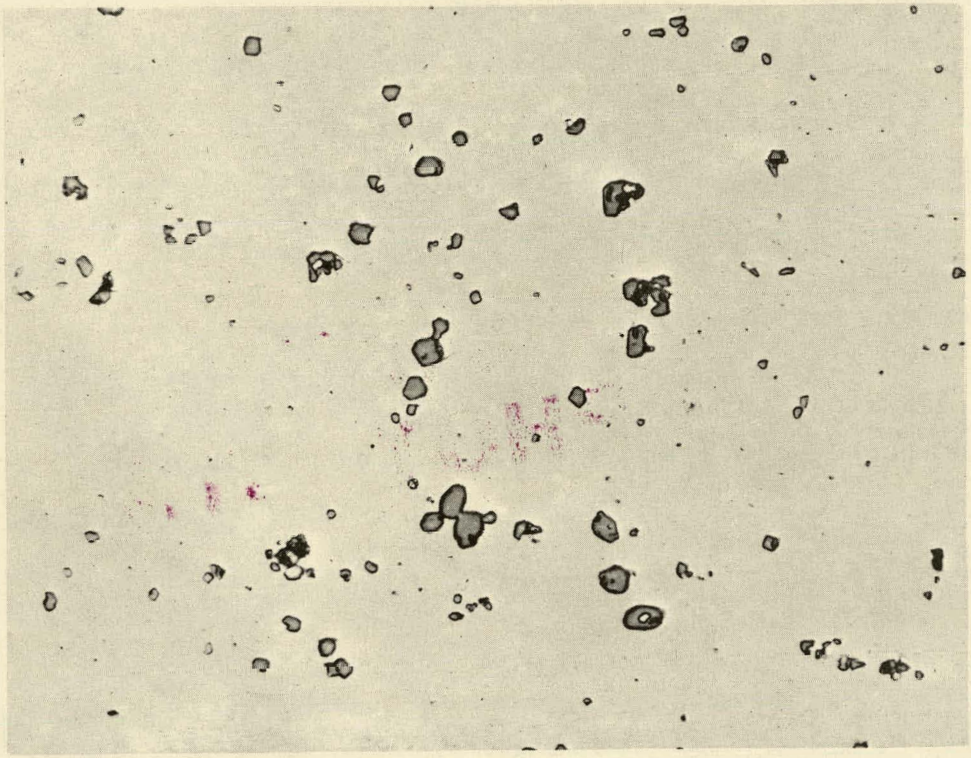


Fig. 14 - Thorium dihydride, -100 mesh, cold pressed at 75 tsi and sintered in argon at 1350°C for 1/2 hr. 500X

METALLURGY AND CERAMICS, M-3679 (14th Edition)

SEP-168 Series TA Copy No.	Standard Distribution
1	AF Plant Representative, Seattle
2	AF Plant Representative, Wood-Ridge
3	American Machine and Foundry Company
4-11	Argonne National Laboratory
12-16	Atomic Energy Commission, Washington
17	Babcock and Wilcox Company
18	Battelle Memorial Institute
19	Bendix Aviation Corporation
20-22	Brookhaven National Laboratory
23	Brush Beryllium Company
24	Bureau of Mines, Albany
25	Bureau of Ships
26-27	Carbide and Carbon Chemicals Company (K-25 Plant)
28-33	Carbide and Carbon Chemicals Company (ORNL)
34	Chicago Patent Group
35	Commonwealth Edison Company
36	Detroit Edison Company
37	Dow Chemical Company (Rocky Flats)
38-41	duPont Company, Augusta
42	duPont Company, Wilmington
43	Duquesne Light Company
44	Foster Wheeler Corporation
45-47	General Electric Company (ANPD)
48	General Electric Company (APS)
49-60	General Electric Company, Richland
61	Hanford Operations Office
62	Iowa State College
63-66	Knolls Atomic Power Laboratory
67-69	Los Alamos Scientific Laboratory
70	Mallinckrodt Chemical Works
71	Materials Laboratory (WADC)
72	Monsanto Chemical Company
73	Mound Laboratory
74	National Advisory Committee for Aeronautics, Cleveland
75	National Bureau of Standards
76	National Lead Company of Ohio
77	Naval Research Laboratory
78	New Brunswick Laboratory
79	Newport News Shipbuilding and Dry Dock Company
80	New York Operations Office
81-83	North American Aviation, Inc.
84	Nuclear Development Associates, Inc.

~~SECRET~~

METALLURGY AND CERAMICS, M-3679 (14th Edition) (Continued)

SEP-168 Series TA Copy No.	Standard Distribution
85	Nuclear Metals, Inc.
86	Pacific Northwest Power Group
87	Patent Branch, Washington
88-91	Phillips Petroleum Company (NRTS)
92	Power Plant Laboratory (WADC)
93-94	Pratt & Whitney Aircraft Division (Fox Project)
95	Sylvania Electric Products, Inc.
96	Tennessee Valley Authority (Dean)
97-98	University of California Radiation Laboratory, Berkeley
99-100	University of California Radiation Laboratory, Livermore
101	Vitro Laboratories
102	Walter Kidde Nuclear Laboratories, Inc.
103-106	Westinghouse Electric Corporation
107-123	Technical Information Service, Oak Ridge

DO NOT PHOTOSTAT

~~CONFIDENTIAL~~

~~SECRET~~