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AN EVALUATION OF ZIRCONIUM AS A STRUCTURAL MATERIAL FOR HIGH TEMPERATURE THERMAL PILES

By

W. L. Sibbitt

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ABSTRACT

Interest in the chemical and physical properties of ductile zirconium has been revived primarily by the results of an investigation performed in the Physics Division at the Oak Ridge National Laboratories. In addition, as a result of the research and development work at the MIT Metallurgical Project and at the Bureau of Mines Laboratories, the application of zirconium appears to be feasible and the potentially available supply quite adequate at a rather moderate cost. Therefore, it was desirable to compile the existing data on the chemical and physical properties which were of interest in the various applications for which zirconium might be considered.

This paper presents an evaluation of zirconium as a structural material for high temperature thermal piles with additional notes on:

1. Various bases for comparison of pile materials.

2. Comparison of Zr, Cb, Fe, Al, Be, BeO and C.

3. Physical and chemical properties of zirconium and columbium with special emphasis on applications in water-cooled piles.

4. Occurrence, availability, and production of zirconium and columbium.

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I. INTRODUCTION

In general, the possible stable moderator materials for thermal piles may be limited to hydrogen, deuterium, beryllium, and carbon or compounds of those elements. In many cases the moderator will be used as a diluent for the fissionable material as well as a structural material. In many designs it may be desirable or necessary to use a structural material with superior physical properties; consequently, other elements may in those cases be used.

Table No. 1

Materials with Favorable Moderating Properties

1. Hydrogen	6. Beryllium Oxide
2. Helium	7. Water
3. Oxygen	8. Heavy Water
4. Fluorine	9. Graphite
5. Deuterium	10. Beryllium

Table No. 2

A Partial List of Structural Materials

1. Zirconium	5. Beryllium
2. Columbium	6. Iron
3. Aluminum	7. Graphite
4. Beryllium Oxide	

In cases where it might be desirable to introduce other materials (Coolant, alloys, etc.) it would be feasible to introduce large quantities of the following elements:

Table No. 3

Other Elements Which May Be Introduced Into Thermal Piles in Large Quantities

1. Magnesium	5. Bismuth
2. Silicon	6. Phosphorous
3. Tin	7. Sodium
4. Lead	8. Potassium

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2. EVALUATION OF MATERIALS

The rate at which a high power level pile can operate is limited almost entirely by the rate at which heat can be removed. Consequently, heat transfer considerations have a profound effect on the:

1. Design
2. Neutron utilization
3. Size

Therefore, the following three criteria are considered to be important in the design of the systems for heat removal and mechanical operations:

1. Low specific power requirements for heat removal.
2. Minimum interference with the nuclear reaction.
3. Engineering feasibility.
   a. Chemical and physical stability.
   b. Radiation and corrosion effects.
   c. Allowable working stresses.
      (1) Load stresses.
      (2) Residual stresses.
      (3) Thermal stresses.

If the unit is to function for a reasonable length of time, the requirement of engineering feasibility must be satisfied even though the size and neutron utilization of the pile are adversely affected. Some materials are unusually susceptible to damage by thermal stress, and thus the heat generation might be limited by the thermal stresses developed in the solid parts of the structure. However, other considerations could control, such as:

1. Maximum coolant temperature.
2. Maximum temperature at the solid surface.
3. Maximum temperature in solid interior.

A. Moderator Materials

All structural materials, to a degree, must be compatible with criteria two and three. Therefore, it is of interest to compare all of these materials as moderators as well as structural materials.

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The effects of atomic weight, absorption cross-section, and scattering cross-section must be considered when evaluating a moderator. The factor $X_1 = \frac{\sigma_s \xi}{\sigma_a}$ may be used as a criterion of the efficacy of a moderator where

σ_s = Scattering cross-section

σ_a = Absorption cross-section

M = Molecular weight

$$\xi = 1 - \frac{(M-1)^2}{2M} \ln \frac{M+1}{M-1}$$

$$\left(\xi \text{ ca. } \frac{2}{(M + 2/3)} \text{ for large values of M}\right)$$

Table No. 4

Comparison of Moderators[17]

Element or Material	Mass M	Cross-Sections σ_s	σ_a	Moderator Efficacy X_1 per atom
Hydrogen	1.0080	20	0.31	64.5
Helium	4.003	1.5	very small	very large
Oxygen	16.000	4	0.001	480.0
Fluorine	19.000	4	0.01	40.4
Deuterium	2.015	5.7	0.001	4100.
Water	18.008	44	0.62	65.1
Heavy Water	20.015	15.4	0.003	2903
Beryllium	9.02	4	0.01	82.8
Beryllium Oxide	25.02	8.1	0.011	126.5
Graphite	12.01	4.8	0.0045	168.5
Phosphorous	30.98	10	0.3	2.1
Sodium	22.997	3.5	0.45	0.654
Magnesium	24.32	4	0.35	0.915
Silicon	28.06	1.8	0.22	0.565

[redacted]

A number of these moderators would not be readily useable because they are normally gases -- hydrogen, helium, oxygen, fluorine and deuterium. The requisite high pressures and the concomitant high pressure differences would give serious handling problems for all of these gaseous moderators. If these elements were compounded into liquid or solid states then these objections would be mitigated.

B. Structural Elements

In the case of a substance used primarily as a structural material the strength per unit absorption may perhaps be used to estimate the relative degree of interference with the nuclear reaction. Figure No. 1A, "Efficacy of Structural Materials" shows the values of strength per unit absorption as a function of the temperature. The data given in Tables Nos. 5 and 6 were used to obtain the strength per unit absorption. This figure, No. 1A, would appear to indicate that beryllium oxide is far superior to the other materials; however, the fact that beryllium oxide is a brittle material places severe limitations on its engineering applications.

Table No. 5

Structural Material Evaluation for Thermal Piles[17,23]

Material	Symbol	Absorption Cross-Section (barns)	Absorption Mean Free Path (Inches)	Melting Point °F
Zirconium	Zr	0.4	24.40	3092 to 3870
Columbium	Cb	1.2	5.90	3542 to 4380
Iron	Fe	2.5	1.67	2795
Aluminum	Al	0.2	31.50	1220
Beryllium	Be	0.01	276.0	2462
Graphite	C	0.005	960	6740 (sublimes)
Beryllium Oxide	BeO	0.01	552	4616

[redacted]

Table No. 6

Ultimate Tensile Strength** (in psi) of Structural Materials[23,24]

Material	Temperature °F 100°F	500°F	1000°F	1500°F
Zr	38,000	27,000*	15,000*	5,000*
Cb	43,000	39,000*	32,000*	25,000*
Fe	43,000	40,000	18,800	6,000
Al	12,000	3,500	(1,500 at 700°F)	------
Be	27,000	23,000	19,000	15,000
C	1,200	1,200	1,200	1,200
BeO	14,000	14,000	14,000	14,000

* Estimated Values
** All materials fully annealed

In the previous section a factor X_1 was used as a measure of moderator efficacy. A more practical criterion is the value of X_2, per unit volume, instead of X_1 per atom. For materials having both desirable moderator and structural properties the value of (X_2 · tensile strength) could be used as a basis for comparison.

Table No. 7

Comparison of Combination Moderator and Structural Materials[17]

Element	Mass	Density	Cross-Sections		Moderator Efficacy		Moderator and Structure Efficacy
	M	ρ	σ_s	σ_a	X_1 Per Atom	X_2 Per Unit Volume	X_2 · tensile strength
Cb*	92.91	8.4	6	1.2	0.105	0.57	0.0256×10^6
Fe*	55.84	7.8	11	2.5	0.154	1.30	0.056×10^6
Zr*	91.22	6.4	8.2	0.4	0.450	1.90	0.072×10^6
Al*	26.97	2.7	1.33	0.24	0.399	2.42	0.029×10^6
Be	9.02	1.85	4	0.01	82.80	1.020	27.6×10^6
C	12.01	1.65	4.8	0.0045	168.5	1.390	1.55×10^6
BeO	25.02	2.85	8.1	0.011	126.5	1.760	24.7×10^6

* Structural materials which are shown for comparison purposes only.

[redacted]

[redacted]

Table No. 7 emphasizes the fact that beryllium, graphite, and beryllium oxide are, at present, the only moderating materials which are applicable to structural applications.

As previously mentioned, the requirements of engineering feasibility must be satisfied, at least to a degree, if the unit is to function. To recapitulate -- the materials must first be useable by virtue of their nuclear properties; then the question of engineering feasibility must be considered. The feasibility of the use of various materials for a given application is based on a great number of considerations -- chemical, physical, and mechanical properties, as well as fabrication characteristics, etc.

Some materials are unusually susceptible to damage by thermal stresses and thus the heat generation might be limited by the thermal stresses developed in the solid parts of the structure. Therefore, it is enlightening to estimate the order of thermal stresses developed in various materials for a uniform heat production per unit volume.

The quantity of uniform heat generations per unit volume which produces the critical thermal stress is proportional to a factor F, if we assume elastic materials and the validity of the stress-strain relationships of elasticity. Then: (See Figure No. 2A).

$$F = \frac{Su}{\frac{(E \cdot alpha)}{(1 - nu)} \frac{1}{k}}$$

Table No. 8

Mechanical Properties of Structural Materials
(nu = 0.3 estd.)

ZIRCONIUM

Temperature	Su psi	$E \times 10^{-6}$ psi	k (estd.) Btu/hr ft °F	Alpha x 10^6 °F^{-1}	F	$\frac{E \cdot alpha}{(1-nu)\ k}$
100	38,000	10.7	34	3.6	23,600	1.615
500	27,000	9.4*	32	4.2	15,300	1.76
1000	15,000	7.8*	30	5.0	8,060	1.86
1500	5,000	6.0*	28	6.0	2,720	1.84
			IRON (nu = 0.303)			
100	43,000	29	50	6.3	8,210	5.24
500	40,000	23	32	8.1	4,810	8.31
1000	18,800	15.5	24	8.9	2,300	8.20
1500	6,000	9.0	18	10.0	840	7.15

[redacted]

[redacted]

Table No. 8, Cont'd

Temperature	Su psi	$E \times 10^{-6}$ psi	k (estd.) Btu/hr ft °F	Alpha x 10^6 °F^{-1}	F	$\frac{E \cdot alpha}{(1-nu)\ k}$
			ALUMINUM (nu = 0.33)			
100	12,000	9	118	13	8,100	1.48
500	3,500	6.8	130	15.2	2,940	1.19
700	1,500	5.7	140	16.4	1,500	1.00
			BERYLLIUM (nu = 0.3)			
100	27,000	38	80	6.0	6,640	4.07
500	23,000	31.5*	70	7.1	5,050	4.56
1000	19,000	22.5*	56	8.5	3,900	4.87
1500	15,000	15*	42*	10.0	2,940	5.10
			GRAPHITE (nu = 0.2)			
100	1,200	1.5	60	2	19,200	0.0625
500	1,200	1.5*	35	2.2	16,200	0.074
1000	1,200	1.5*	25	2.4	9,500	0.126
1500	1,200	1.5*	20	2.6	6,750	0.178
			BERYLLIUM OXIDE (nu = 0.2)			
100	14,000	46	60	3.3	4,400	3.17
500	14,000	46	47	4.4	2,500	5.5
1000	14,000	46	27	5.3	1,270	11.0
1500	14,000	46	18	6.2	800	17.5
			COLUMBIUM (nu = 0.3 estd.) k (estd.)			
100	43,000	19	32	4	13,200	3.4
500	39,000	18	30	5.4*	8,410	4.64
1000	32,000	15.5	28	6.8*	5,950	5.38
1500	25,000	13	26	8.0*	4,350	5.74

*Estimated values

[redacted]

[redacted]

where:

Su = Ultimate tensile strength

nu = Poisson's ratio

E = Young's modulus

alpha = Linear coefficient of thermal expansion

k = Thermal conductivity

The values of the physical properties which were used in these evaluations are given in Table No. 8.

Experiments have proven that BeO and Be fail in tension due to thermally induced strains over the following temperature ranges:

BeO up to 2500°F

Be up to 300°F

It is possible that a somewhat more ductile beryllium may yet be produced. Since beryllium oxide is a perfectly elastic material these stress calculations should give truly representative values. It is very improbable that metals, including beryllium at temperatures above 300°F, would fail in tension due to thermally induced stresses, since metals exhibit plastic flow at these temperatures. However, this phenomena must be considered under engineering feasibility; that is, the resulting creep must normally be maintained within given limits. For these reasons the calculations for the metals cannot be related directly to performance. Because of somewhat analogous relations, the predicted conditions of failure for graphite are probably very conservative.*

In addition to all of these considerations, the specific application must be feasible; that is, the material must be chemically and physically stable and have sufficient resistance to corrosion and radiation damage. Some of the pertinent properties are shown in the following table.

---

*A recent report, AL-327, has proven that this statement is correct. The 0.435" diameter samples were used to measure the tensile strength up to the sublimation point. The tensile strength attained a maximum value at 4900°F of ca., twice the strength at room temperature. With internal heat generation the temperature drop through the sample was greater than 340°F when the surface temperature was 4900°F.

[redacted]

Table No. 9

Material Evaluation
(irradiation and corrosion)

Symbol	Melting Point °F	Damage by Fast Neutrons
Zr	3092 to 3870	Apparently none
Cb	3542 to 4380	Apparently none
Fe	2795	Apparently none
Al	1220	Apparently none
Be	2462	Apparently none
C	6740 (sublimes	Serious
BeO	4616	Slight (anneals out above 1500°F)

Corrosion Resistance

Zr	It forms a stable oxide film stable in pure water at 480°F -- stable in He at high temperatures. Absorption of other gases causes embrittlement.
Cb	Forms a stable oxide film -- the upper temperature limit is not known.
Fe	Forms a loose oxide film -- attack continues.
Al	Forms a stable oxide film which is retained in acid solutions.
Be	Forms a stable oxide film.
C	Readily oxidized.
BeO	Attacked by water vapor at high temperatures.

The limitations imposed by the corrodibility of the materials are known for BeO, C, Al, and to some extent for Be. However, only sufficient information is available on Zr and Cb to make them appear promising. Zirconium appears to have somewhat more resistant properties than columbium.

C. Conclusions

1. Zirconium

Figure No. 2A shows that zirconium is superior to all of the other metals as a structural material. These values are probably conservative for

use in helium. Macroscopic examinations have indicated the Zr may be used in pure water at least up to 480°F. Zirconium absorbs H_2, O_2, and N_2 with concomitant reduction in tensile strength; however, these relationships are not known in a quantative way. Investigations should be initiated to determine the limitations of zirconium.

2. Columbium

Columbium is second only to zirconium as a metal structural material for use in the heat generation zone. Compared to most metals columbium is remarkably resistant to corrosion; however, it is inferior to zirconium in this respect.

3. Iron

Pure iron would appear to be superior to aluminum for applications above 200°F; however, its applications are severely limited because of susceptibility to attack by corrosion. In addition, irradiation accelerates the corrosion rate of iron. The products formed by the corroding process produces very objectional films on the surface of the metal.

4. Aluminum

Figure No. 2A indicates that aluminum is inferior to Be, Fe, Cb, and Zr. In addition the maximum operation temperature at which aluminum may be used is very low compared to the other metals.

5. Graphite

Figure No. 2A indicates that graphite is initially a very good material. Its applications are severly restricted by the detrimental effects of fast neutrons. Not only do the physical properties suffer deterioration due to fast neutron bombardment but the uneven growth resulting from uneven flux densities produces distortion or perhaps failures in the elements. These difficulties may be somewhat alleviated at high temperatures. (Data reported in AL-327 proves that the above is a very conservative evaluation of graphite.)

6. Beryllium Oxide

Figure No. 2A indicates that beryllium oxide is readily subject to failure due to thermal stresses. These values should be truly representative of performance. The material does have rather high strength properties as compared to graphite and thus lends itself more to structural applications. It is very inert except to water vapor at high temperatures.

7. Beryllium

Beryllium is an excellent moderator material. It is potentially superior to iron as a structural material. Severe limitations on the uses of beryllium are due to the low ductility and nonuniformity of the present metal.

3. PHYSICAL PROPERTIES OF ZIRCONIUM

The data reported in the literature are not in good agreement. The purity of the metal from the different methods varies considerably. The following table of general data is from S. L. Hoyt, "Metals and Alloys Data Book".

Table No. 10

General Data on Zirconium

Zirconium	alpha up to	1584°F
Zirconium	beta above	1584°F
Symbol		Zr
Atomic No.		40
Atomic Wt.		91.22
Density		6.4
M. P.		3100°F
B. P.	above	5200°F
Specific heat		0.066
Coef. of Exp.		3.5×10^{-6} $^{o}F^{-1}$
Elec. Res.		41 (mi/cm^3)
At. Vol.		14.3 (cm^3/g atom)

	alpha	beta
Crystal system	Hexagonal	Cubic
Atomic arrangement	HCP	BCC

The calculated density of the HCP zirconium is 6.49; the measured value is 6.50 when corrected for purity.

[redacted]

Tensile Strength of Zr (from Hoyt)

Material	Tensile Strength psi	Elongation %
Anneal at 932°F	56,000	12
Anneal at 1472	38,000	--
Cold-swaged	113,000	2
As cold drawn	142,000	1

The modulus of elasticity was reported by Hoyt as 10.7×10^6 psi.

The following tables of data as reported by Foote Mineral Company, give an indication of the variation in physical properties of their product:

Table No. 11

Variations in Physical Properties

Ultimate strength	34,000 to 45,000 psi
Yield @ 0.2% offset	11,000 to 20,000 psi
Yield @ 0.1% offset	10,000 to 18,500 psi
Proportional limit	5,000 to 10,000 psi
Reduction in area	25% to 45%
Elongation in 4 diameters	28% to 40%
Modulus of elasticity	9.5 to 12×10^6 psi
Coef. of Exp.	2.8×10^{-6} °F^{-1}
Specific gravity	6.54
Melting point	3370°F

Table No. 12[3]

Ultimate Hot Tensile Strength

Temperature °F	Helium Atmosphere	Nitrogen Atmosphere
932	24,000 psi	15,000 psi
1292	10,000 psi	7,000 psi
1472	6,600 psi	500 psi
2365	1,500*	

*Same type of metal, Ref. 11.

[redacted]

[redacted]

The melting point as reported varied from 3180 to 3870°F. The ductile zirconium as obtained by the testraiodide method normally contains small percentages of titanium and hafnium. These impurities could change the melting point.

	Atomic No.	Atomic Wt.	Density	M. P. °F
Hafnium	72	178.6	11.4	3090
Titanium	22	47.90	4.51	3200

The experimental data on the physical properties of the Bureau Mines product will probably be available within 90 days.

See the graphs for the known information on mechanical properties.

4. CHEMICAL PROPERTIES OF ZIRCONIUM

It is of interest to locate zirconium in the periodic systems of elements.

Table No. 13

Rare Metals in the Periodic System of Elements

Group No. 1	Group No. 2	Group No. 3		Group No. 4	
Lithium	Beryllium	Boron*		Titanium*	
Rubidium'	Strontium*	Scandium	Gallium'	Zirconium*	
Cesium'	Barium*	Yttrium	Indium'	Cerium	Germanium'
		Lanthanum	Thallium	Hafnium	
				Thorium	

Group No. 5	Group No. 6		Group No. 7
Vanadium	Uranium	Selenium	Rhenium'
Columbium		Tellurium	
Tantalum			

Notes: * Elements which are available by thousands of tons.

' Fairly rare metals -- those not marked are in between.

Extremely rare metals like radium and most of those of the cerium group metals have been omitted.

[redacted]

The first and second groups contain the alkali and alkaline earth metals which have in common a high halide affinity and are volatile. They also show a strong affinity for O_2, S, As, Sb, Pb and Bi. The second group plus Li have a high affinity for C, N_2 and H_2.

The third group, main series, have a high C, S and O_2 affinity. The rare earths belong more to the second group as shown by their hydrides and lead alloys. The lateral series have generally greatly reduced affinities.

The fourth group has the highest possible N_2 and C affinity -- more affinity for O_2, S, H_2 and halides -- low affinities in lateral groups -- rather high affinity for Fe group metals.

The fifth group has a strong affinity for C, N_2, O_2, S, H_2 and halides; that for Fe group metals is slightly reduced.

A. Reaction of Zirconium with Gases

Zirconium is a very reactive metal; except for the rare gases it shows great affinity for gases, for example, O_2, N_2, CO, CO_2, H_2 and water vapor. It forms definite chemical compounds with O_2, N_2 and H_2. It appears that considerable quantities of these gases can be absorbed without the formation of a new phase.

Zirconium will absorb or form solid solutions with oxygen up to 40 atom percent -- x-ray examination shows only a single hexagonal lattice. The limit of solubility of nitrogen was about 20 atom percent. If more nitrogen is absorbed, then the cubic nitride ZrN is found in addition to the saturated hexagonal solid solution. The absorption of gases decreases the tensile strength of the metal and produces embrittlement.

There is considerable difference of opinion as to the absorption characteristics for the different gases. Figures 5 to 8 inclusive contain most of the available data.

1. Hydrogen Absorption[3,4,6,7,8,9]

Figures 5 and 6 show the data on the absorption of hydrogen. Large quantities of hydrogen can be absorbed by zirconium in solid solutions; unlike oxygen and nitrogen, the process is a reversible one and the dissolved gas may again be liberated under certain conditions.

Fast[6] found a favorable temperature range between 575 and 750°F for the absorption of hydrogen. In this region the gas pressure of the solid solution is very low but the rate of absorption is already very high. The gas is again liberated between 900°F and 1562°F as shown in Figure 5. The metal which was used to obtain the data shown in Figure 6 was evidently contaminated with hydrogen since no absorption was indicated in the range 575 to 750°F. The spread between these curves after one complete cycle of heating and cooling indicates that some of the hydrogen was permanently absorbed. The hydride decomposes at 750°F; therefore, it is difficult to explain the wide spread in curves in Figure 6. These discrepancies may, perhaps, be attributed to the inherent differences in the properties of the powder and the pure ductile metal.

2. Oxygen Absorption[6,8,9]

Figure No. 7 shows the data obtained using zirconium powder sprayed on a molybdenum ribbon. The heat of solution of oxygen in zirconium is of the same order magnitude as the heat of formation of zirconium oxide (259 Kg. cal.). Oxygen is absorbed in the interstices of the metal lattice. Oxygen atoms have great mobility in the zirconium lattice at high temperatures.

Fast (6) reported that the pressure of oxygen in equilibrium with the saturated solution of oxygen in zirconium was too low for direct measurement -- somewhat less than 10^{-8} atmospheres even at 2700°F.

The zirconium oxide forms a very good protective coating at low temperatures. At high temperatures the oxide film dissolves in the metal and the metal surface remains active. The practical temperature limit above which the oxide film does not give reasonable protection has not been determined. The oxide film does dissolve rapidly at temperatures above 1860°F.[3]

When zirconium with an oxidized surface layer is heated in vacuo the metallic luster reappears. A number of physical properties are altered by this process. The melting point is raised; the hardness is increased; the electrical resistivity is increased; the temperature coefficient of the electrical resistivity is decreased; the atomic distance is somewhat increased; the ductility is decreased; and both dissolved oxygen and nitrogen produce some embrittlement.

3. Nitrogen Absorption[6,8,9]

Figure No. 8 shows the data obtained using zirconium powder sprayed on a molybdenum ribbon. As previously point out, this metal was evidently contaminated with hydrogen. Nitrogen acts somewhat similar to oxygen. The heat of formation of ZrN is 82 kg. cal.

Table No. 12 shows the effect of dissolved nitrogen on the hot tensile strength. Figure No. 8 might indicate that no decrease in tensile strength would be expected below 800°F.

4. Halogens

Iodine(9) combines with zirconium at a temperature of about 750 to 900°F to form the tetraiodide. Other investigators have reported the initial reaction as low as 480°F. The iodide can be sublimed in vacuo without decomposition. The pure ductile metal may be obtained by thermal decomposition of the iodide at temperatures above 2000°F. Zirconium with an oxidized surface is apparently not attacked by iodine.

Chlorine reacts with zirconium at a dull red heat to give the volatile tetrachloride, the tetrabromide may be formed in a somewhat similar manner.

B. Corrosion Resistance[1,5,8,10,15,18,23]

Considerable information is available on the corrosion resistance of zirconium as compared to tantalum and 18-8 stainless when in contact with a large number of the common corroding agents.

[redacted]

The chemical behavior of Zr shows that it is resistant to many chemical solutions. It resists nitric acid in all concentrations even at 212°F, and presumably all typically oxidizing solutions, concentrated hydrochoric up to 212°F, hot 20% sulphuric acid, chorine gas either with or without moisture, hot 10% and 50% sodium hydroxide, fused sodium hydroxide, 20% sodium chloride solution at 212°F, acetic and oxalic acids, hydrogen sulphide gas, cold aqua regia, and cold dilute silver nitrate. It does not tarnish in the atmosphere. Zirconium exposed to distilled water at 480°F for 1000 hours showed no corrosion.

Zirconium is slightly attacked by fused potassium hydroxide. It is also attacked by concentrated sulphuric acid at 212°F, ferric chloride, 75% phosphoric acid, nascent chlorine, bromine, or fluorine in water, hydrofluorsilicic acid and dissolves rapidly in hydrofluoric acid.

In general, for most metals, corrodibility is increased by cold working; however, cold-worked zirconium showed an increase in corrosion resistance.[9] Perhaps the oxide layer gives better protection after cold-working. The hardness of the oxide layer is about 7 on the Mohs scale.[10] Hot rolled materials become coated with an oxide layer which is yellow or brown on the outside and black at the contact with the metal. The outer oxide layer is soft and is readily removed with abrasives, but the black inner oxide layer is very hard and neither acids nor ordinary abrasives remove it easily.

In conclusion, the alkali resistance of zirconium was greater than that of tantalum. The two metals showed about the same resistance to hot, concentrated hydrochloric acid. Zirconium was corroded less than 18-8 stainless by hot 75% phosphoric acid. Concentrated nitric and aqua regia had a negligible effect on zirconium.

C. Theoretical Aspects of Corrosion

If only the thermodynamics of the problem were being considered, one would expect to find no metal which is corrosion resistant when in contact with the oxygen in the air or dissolved in water. All metals, even the precious metals, have oxides which at room temperatures have an oxygen dissociation pressure below the partial pressure of oxygen in air. Therefore, one might expect that metals should in time oxidize completely when in contact with air. If the metal is in the form of a monoatomic layer this oxidation actually does take place spontaneously at not too low a temperature. In the case of compact metals the reaction comes practically to a standstill after the formation of a very thin (often invisible) oxide film. Further reaction requires a diffusion of at least one of the reacting substances through the film already formed; in many cases, such a transfer of matter in the solid state does not take place at room temperature to any practical extent. Therefore, the resistance of a metal to corrosion does not depend on the affinity between the metal and the gas under consideration, but on the protection against further corrosion offered by the oxide film already present. Corrosion resistant metals are therefore usually metals with a very good protective oxide film.

Oxygen will migrate through the metal at temperatures above 1600°F and collect at the anode when a D.C. potential is applied to a bar of zirconium.

[redacted]

[redacted]

However, oxygen ions, molecules, or atoms probably do not diffuse interstitially through the oxide layers at moderate temperatures. Therefore, one would expect zirconium to be similar to aluminum and chromium in that for moderate temperatures the oxide films tend to reach a thickness of 50 A and then virtually stop growing unless damaged by cracking or in some other way.

The heats of formation of the oxides of the relatively corrosion resistant metals are as follows:

Oxide	Heat of Formation Kg. cal. per gram atom of oxygen
Al_2O_3	134.3
ZrO_2	129.5
TiO_2	112.5
Ta_2O_5	100
Cr_2O_3	89.6
Ag_2O	6.5

At high temperatures the oxide film protects a metal much less effectively against further corrosion, although it does have a retarding effect which is greater the thicker and the more impervious the layer.

The following thermodynamic data are of interest when related to experimental work on corrosion:

$$2\ H_2O + Zr = ZrO_2 + 4H^+ + 4\ e^-$$

$$E^o = 1.43$$

$$\Delta F_f = -\ 246{,}400 \text{ cal.}$$

$$\Delta H_f = -\ 258{,}100 \text{ cal.}$$

$$\Delta S_f = -\ 42.5 \text{ cal/deg.}$$

$$Zr + 2H^+ + H_2O = ZrO^{++} + 2\ H_2$$

$$\Delta H^o = -\ 129{,}000 \text{ cal.}$$

$$\Delta F^o = -\ 141{,}000 \text{ cal.}$$

$$(\Delta F^o = -\ 198{,}100 \text{ cal. for free zirconyl ion})$$

$$ZrO(OH)_2 \text{ (solid)} = ZrO^{++} + 2\ OH^-$$

$$K\ ca = 1 \times 10^{-26}$$

[redacted]

[redacted]

$$ZrO_2 + H_2O = ZrO(OH)_2 \text{ (solid)}$$
(This hydrate decomposed at ca. 200°C)

$$\Delta F^o = \text{ca} - 5600 \text{ cal.}$$

$$ZrO(OH)_2 \ \Delta F^o \text{ (formation)} = - 307,600 \text{ cal.}$$

The protective value of the oxide film must be evaluated by experimental work. The surface layer of oxide dissolves in the metal at high temperatures -- the rate of solution should be measured as a function of the temperature. In addition, the effect of erosion on the oxide layer should be investigated.

5. PRODUCTION OF ZIRCONIUM

Zirconium oxide is not easy to reduce. It is not reduced by hydrogen. Reduction of the oxide with carbon yields the carbide. Calcium and calcium sodium mixtures in evacuated reactors, have been used to produce a crude metal. Magnesium and sodium mixture also give an acceptable crude metal.

Foote Mineral Company produces ductile zirconium at the rate of about 100 pounds per month. The method used is based on the fact that certain metallic iodides are decomposed by contact with a glowing wire so that the metal is deposited on the wire. Iodine serves as the vehicle which combines with the crude metal at temperatures above 480°F forming the tetraiodide. The temperature of the process is so controlled that the tetraiodide is vaporized and deposits the pure metal on a tungsten-core wire operating at a temperature of 2370°F. The process necessarily involves high vacuum of the order of 10^{-4} mm of mercury. Different methods in the various operations for the production of ductile zirconium have been developed by the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Oregon. Malleable zirconium is produced by reduction of chloride vapors with magnesium in a furnace with a noble gas atmosphere. The process requires the following steps:

1. Production of zirconium carbide from zircon.

2. Chlorination of zirconium carbide.

3. Purification of raw zirconium chloride.

4. Reduction of pure zirconium chloride with magnesium.

5. Eliminating of residual salts by vacuum treatment.

6. Melting of zirconium ingots.

The Bureau of Mines have used charges containing more than 60 pounds of zirconium with recovery of about 90 percent. They have produced 10 pound ingots of malleable zirconium. They estimate that zirconium can be produced for ca. $10 per pound. (Foote Mineral Company quotes sheet at $180/lb., $225/lb. for 1/8" rods). The Bureau of Mines have constructed a pilot plant which will permit establishing the commercial possibilities of this method of obtaining pure, malleable zirconium.

[redacted]

[redacted]

1. Fabrication[10,11]

Heavy sections of zirconium are usually rolled hot, although a tenacious oxide layer is formed when the metal is heated to 1300°F. The black inner oxide layer is very hard and neither acids nor ordinary abrasives removes it easily, although a silicon carbide grinding wheel will slowly remove it.

Thin sections can be cold-rolled with intermediate annealing. Soft ingots can be reduced 50 percent before reheating. The annealing of zirconium presents some difficult problems. Bright annealing of finished strip is done in a helium atmosphere. Tests have indicated that zirconium heated for one hour at 1472°F in pure nitrogen remained malleable. A good anneal on partly fabricated metal has been obtained by placing it in a furnace (in air) at 1500°F and then removing the metal as it attained a red heat. The ductility of the metal was not appreciably affected. This annealing in air must be done quickly and not repeated more than two or three times or the ductility is lost.

It is very easy to roll zirconium out of contact with air by enclosing it in a metal sheath. Sections as thin as 0.01 inch can be readily obtained. After rolling, the sheets are taken out of the sheath and cold-rolled to give them a polished surface. This material (Brinell hardness of 180) can be bent sharply at an angle of 180° on a 0.01 inch radius without cracking. The zirconium will fuse to the metal sheath at temperatures above 1472°F but above 1730°F it may ignite and burn.

The basic properties which make zirconium metal advantageous for many applications cause trouble during drawing operations. The metal work-hardens very rapidly; consequently, considerable annealing is required throughout the drawing process. The metal has the property of seizure to die walls; however, a very thin film of oxide may serve as a lubricant in the drawing operation.

Fully annealed ductile zirconium will withstand a limited amount of drawing and spinning, perhaps 10 percent deformation, before it again becomes brittle through work hardening.

The metal is readily machineable and parts can be fabricated by riveting, crimping, and slotting. Spot welding techniques have been developed to give a satisfactory bond which does not embrittle. For spot welding, the current and time cycle are maintained at compatible minimum values.

6. OCCURRENCE AND AVAILABILITY

Some metals, such as Zr, which are frequent in nature are called rare only because present methods for making them are elaborate, thus the prices tend to be prohibitive.

The zirconium content of the earth's crust is estimated to be about 0.026 percent; thus zirconium is actually present in larger quantities than many familiar elements such as nickel, copper, zinc, or lead.

[redacted]

[redacted]

The most abundant mineral, the silicate $ZrSiO_4$, commonly called zircon, is isomorphous with the well-known titanium mineral, rutile, TiO_2. Zirconium is also found as the oxide which is commercially known as zirkite. Zirkite is found in Brazil in a fairly pure form.

Table No. 14

Average Elementary Composition of Igneous Rocks in the 10-mile Crust of the Earth

(Clark, F. W., Washington, H. S., U. S. Geol. Survey, Professional Paper 127, 1929)

1.	Oxygen	46.59	12.	Manganese	0.10
2.	Silicon	27.72	16.	Chromium	0.037
3.	Aluminum	8.13	17.	Carbon	0.032
4.	Iron	5.01	19.	Zirconium	0.026
5.	Calcium	3.83	20.	Nickel	0.020
6.	Sodium	2.85	24.	Copper	0.010
7.	Potassium	2.60	28.	Zinc	0.004
8.	Magnesium	2.09	29.	Cb & Ta	0.003
9.	Titanium	0.63	32.	Lead	0.002
10.	Phosphorus	0.13	35.	Beryllium	0.001

[redacted]

[redacted]

Table No. 15[20]

Estimated Approximate World Production of Rare Metals in Ores

(Based on the average output of the last three prewar years).

Elements	Metric Tons of Contained Elements per Year
Rb	10 (pounds)
Au	1,250
Be*	72
B	120,000
Ti	100,000
Zr	15,000
Hf	150
Th	350
Ta	160
Cb**	360
U	1,200

* Estimated world production was ca. 700 tons (2000 lbs.) in 1946.

** Fansteel Met. Corp. has made Cb sheet 30" x 30" -- it can be seam-welded-therefore, the fabrication of larger assemblies is practicable. The potentially available supply is 20,000 lbs/yr.

[redacted]

[redacted]

Table No. 16[20]

Prewar Prices of Rare Metals

(in dollars per pound)

Element	Elementary	Ores	Master Alloys
Au	510	----	-----
Be	75	0.35	15.00
B	38	0.01	8.90
Ti	5	0.02	1.35
Zr	7*	0.07	0.50
Hf	13,000	----	-----
Th	135	1.16	-----
Ta	55*	2.90	-----
Cb	125*	0.53	2.25
U	----	3.20	-----
V	5	0.52	2.80

Notes:

1. *Powders
2. Be in Cu/Be master alloy (4.5% Be)
3. Ti in low C ferroalloy
4. B in ferroalloy
5. U in oxide
6. Zr sheet $900/lb (1948 estimates are -- Foote $180/lb). Bureau of Mines may be able to produce ingots for Ca. $10/lb.

The price table, No. 16, may be used to estimate the relative efficiency of an extraction process, for example:

Element	Elementary	Ore	Master Alloy
Be	$75.00	0.35	$15.00
V	5.00	0.52	2.80

It is of interest to compare these prewar prices with more recent data.

[redacted]

[redacted]

Table No. 17

Relative Prices of Separated Metal to Metal in the Form of Ore

	Cost in Ore $/lb.	Percent of Total for Ore	Cost of Metal $/lb.	Percent of Total for Processing
Iron	0.005	50	0.010	50
Vanadium	0.49	17.5	2.80	82.5
Magnesium	0.02	9.75	0.205	90.25
Manganese	0.031	9.38	0.320	90.62
Chromium	0.052	5.84	0.300	94.16
Aluminum	0.007	4.66	0.150	95.34
Zirconium	0.06	0.86	7.00*	99.14
Titanium	0.025	0.47	5.25	99.53
Beryllium**	0.35	0.47	75.00	99.53

* Powder, not the ductile metal.

** Prewar prices of ore (it is now about 4 times this value) included for comparison.

7. CONCLUSIONS

Zirconium is apparently suitable as a structural material in high temperature thermal piles when cooled by one of the rare gases, such as helium. The practical maximum limiting temperature for this type of operation is not known.

Zirconium cannot be used at very high temperatures in an atmosphere of oxygen, nitrogen, water vapor, carbon dioxide, carbon monoxide, etc. The maximum temperature limit for a long operating life in such atmospheres is certainly below 1200°F. The limitations of the protection given by the oxide film are not known.

In comparison with the meager data that are available on the performance of beryllium and aluminum in contact with water at high temperatures (ca. 500°F) the tests using zirconium were very promising. The limitations imposed by the presence of free hydrogen and free oxygen in the water have not been investigated.

At the present time zirconium is being used in the chemical industry because of its extremely high resistance to corrosion. In the course of normal development, it will have a wide application because of its superior physical and chemical properties and the large potential supply which can

[redacted]

readily be made available. Since the use of zirconium may obviate some of the serious operational limitations inherent in the present designs of thermal piles the feasibility of some of its applications should be investigated.

For similar reasons the limitations on the applications of columbium should be determined. While it is not as promising as zirconium, it does appear to be superior to some of the other structural metals. Compared to most metals, columbium is remarkably resistant to corrosion -- the temperature limitations on its use in water are unknown.

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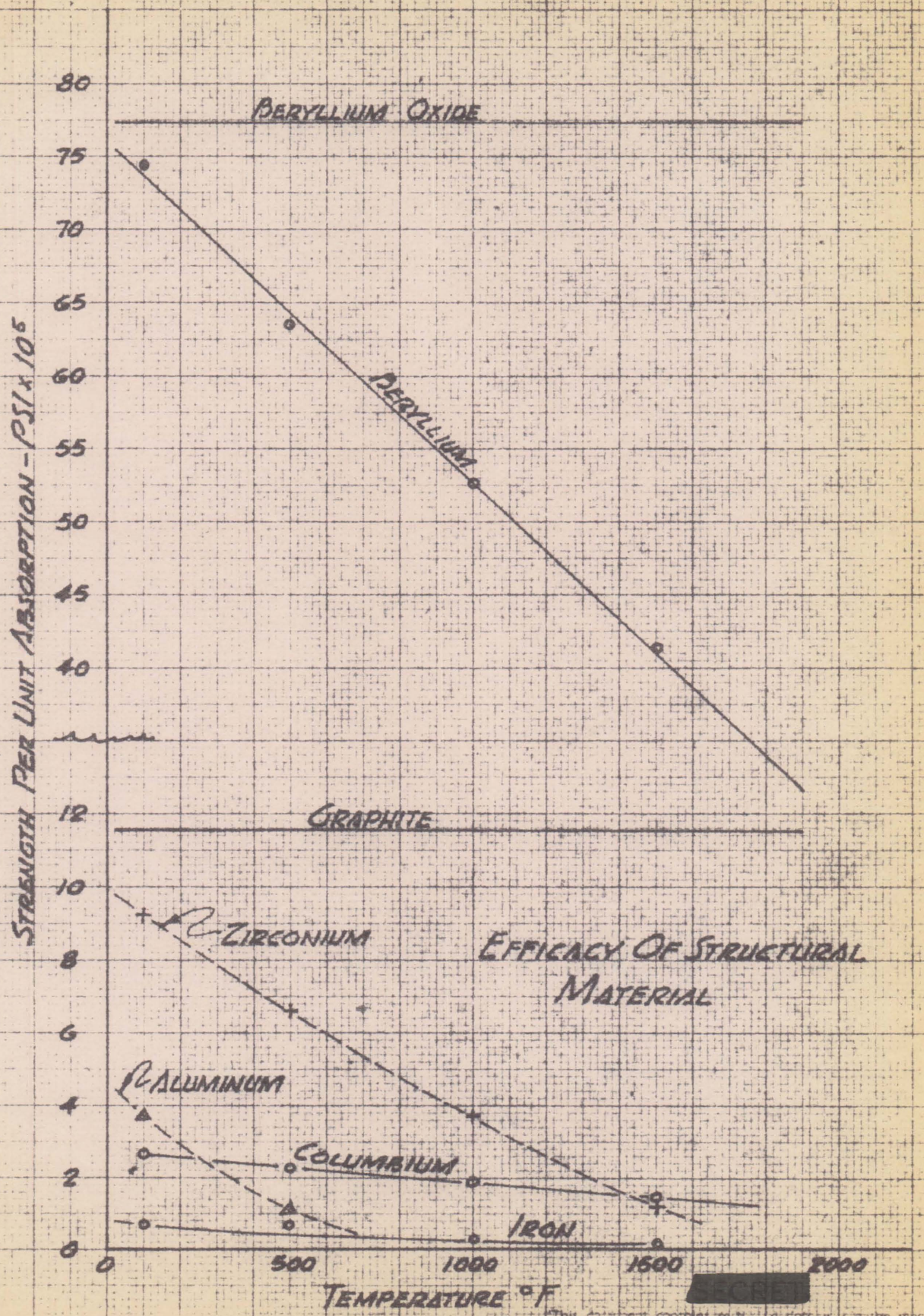

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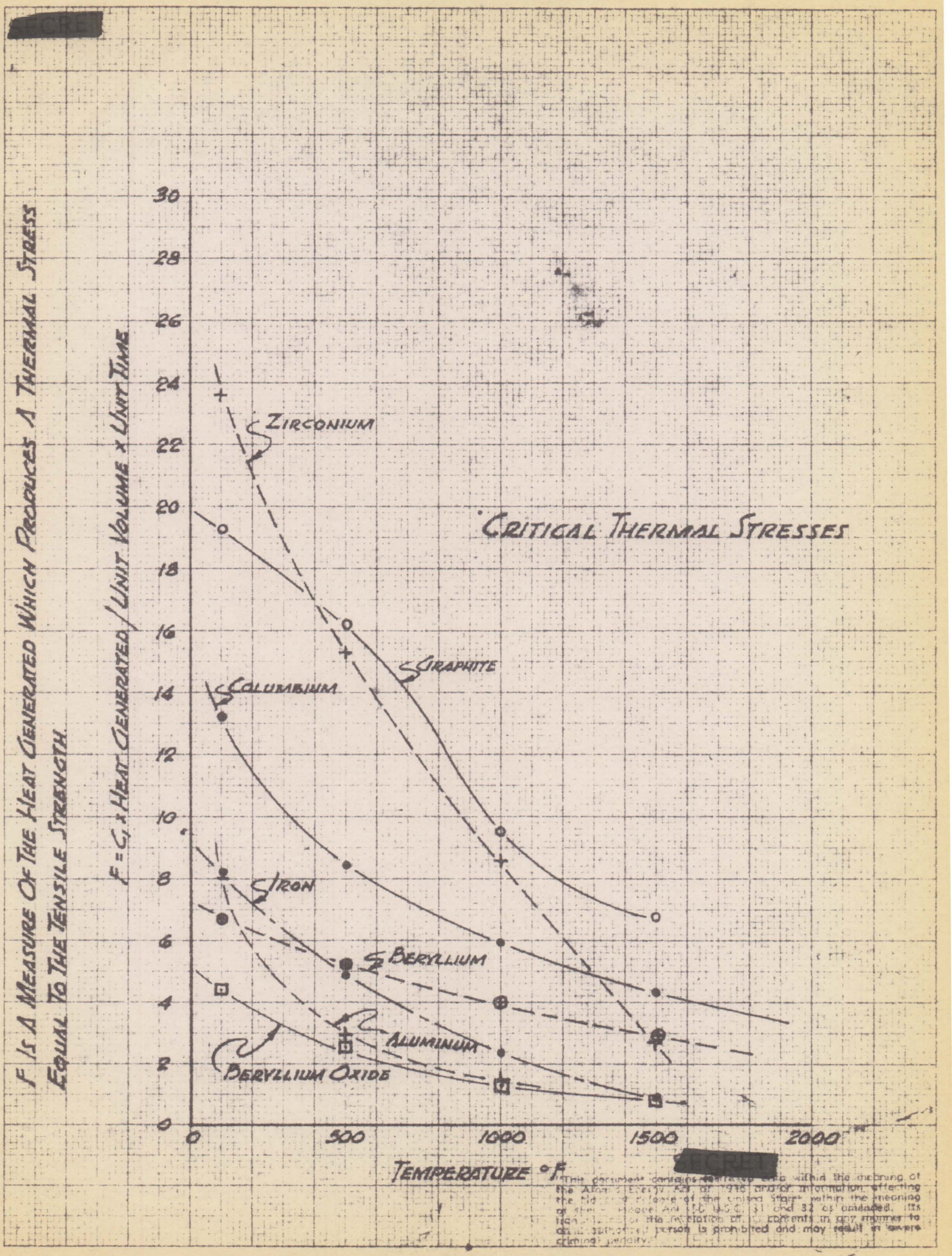

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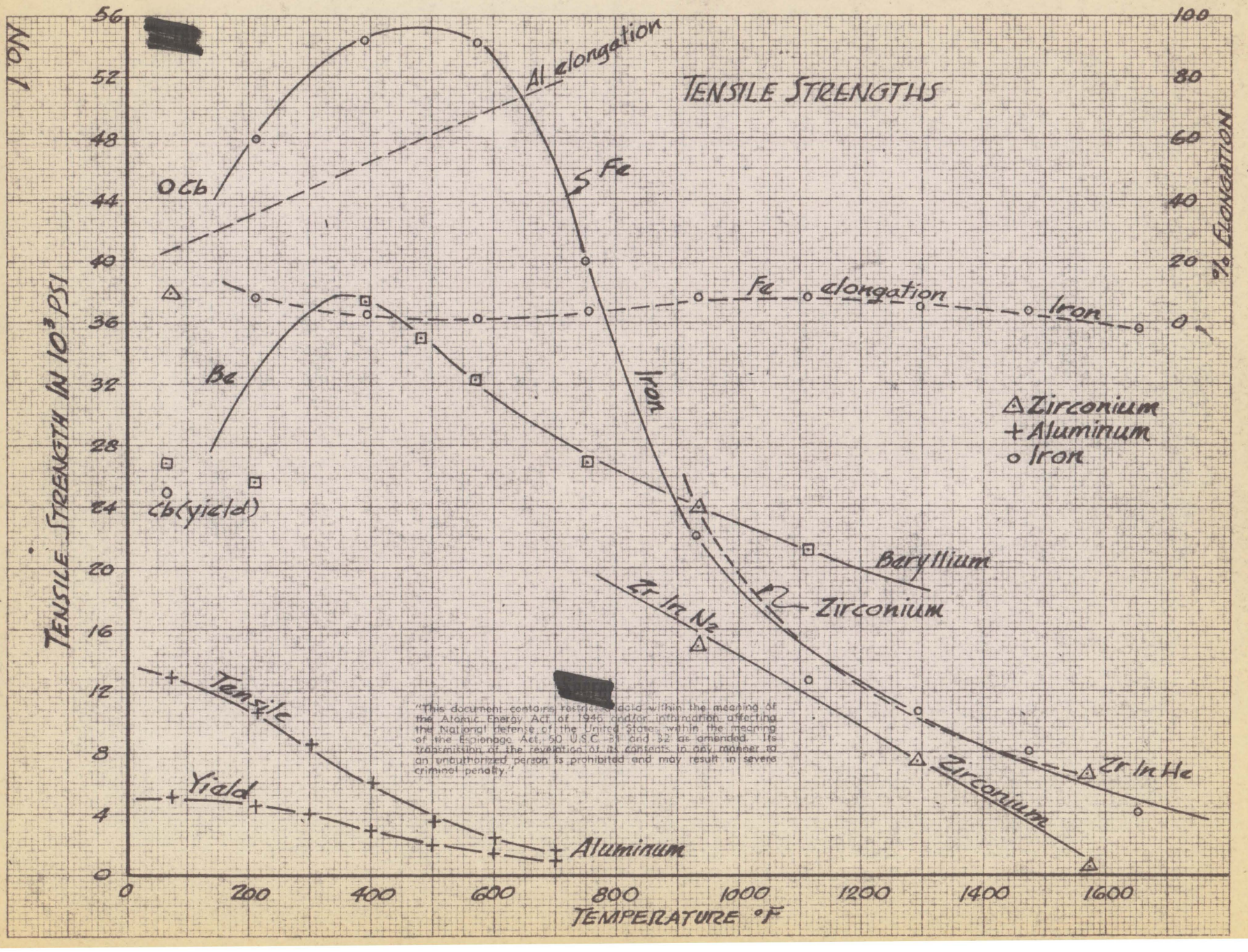

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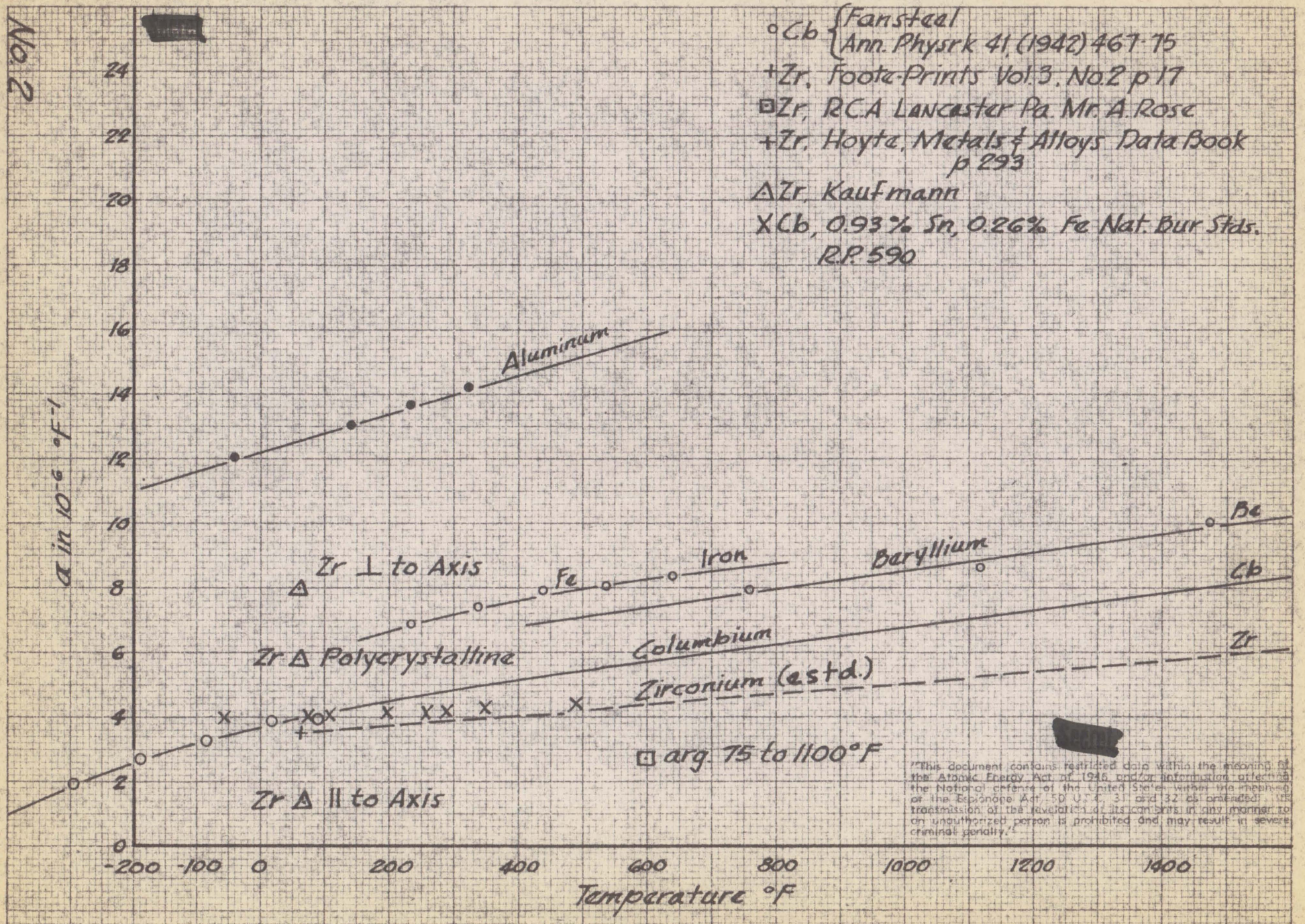

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Temperature Coefficient Of Linear Expansion

Material	Tm.p °R	Tm.p °F
+ Fe	3255	2795
• Al	1680	1220
+ Mg.	1661	1201
⊡ Zr	3830	3370 (Foote) may be 3870
△ Be	2922	2462
○ 18-8	3050	2590
⊕ Cb	4840	4380 (Fansteel)

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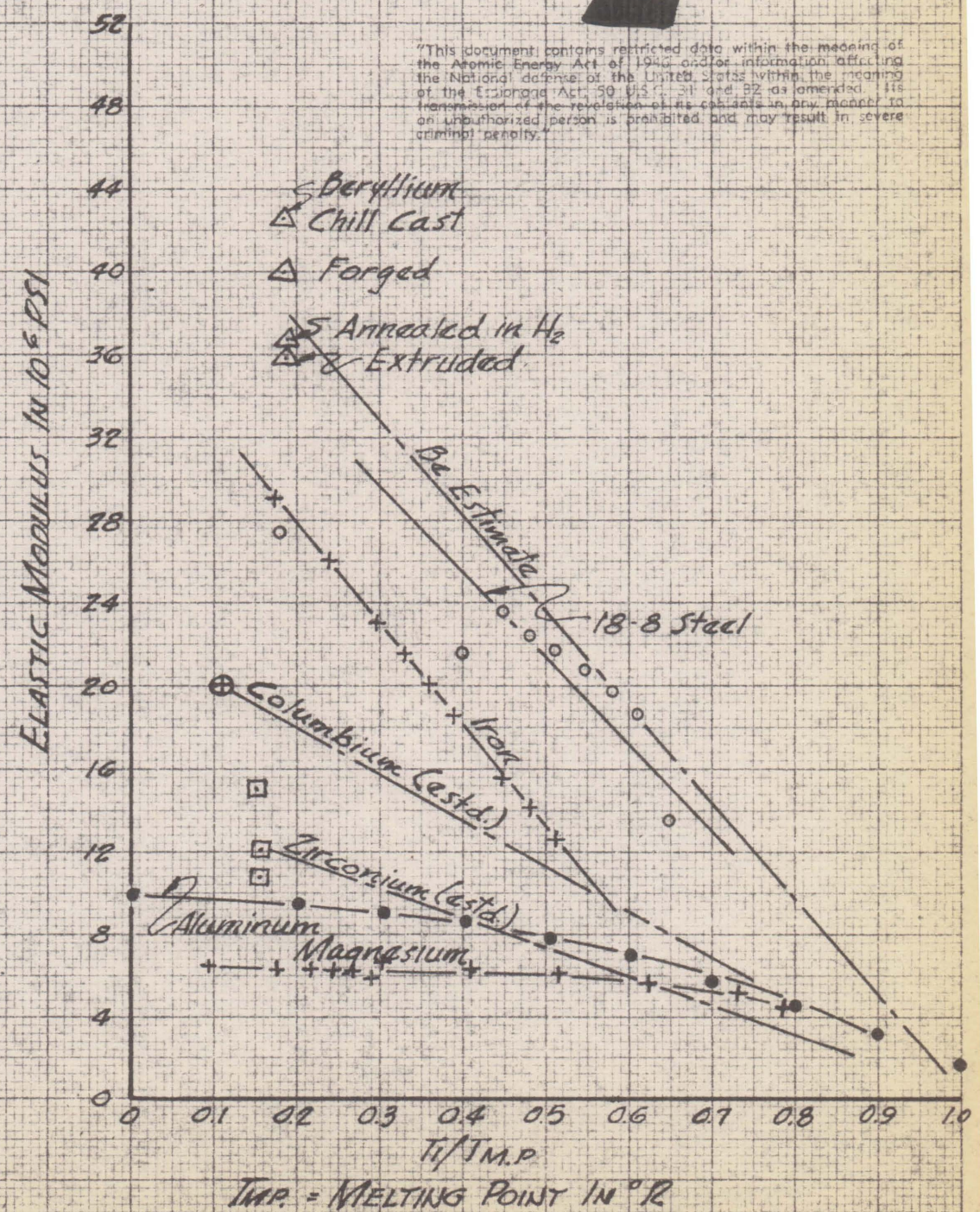

YOUNG'S MODULUS

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Tm.p = MELTING POINT IN °R

No. 3

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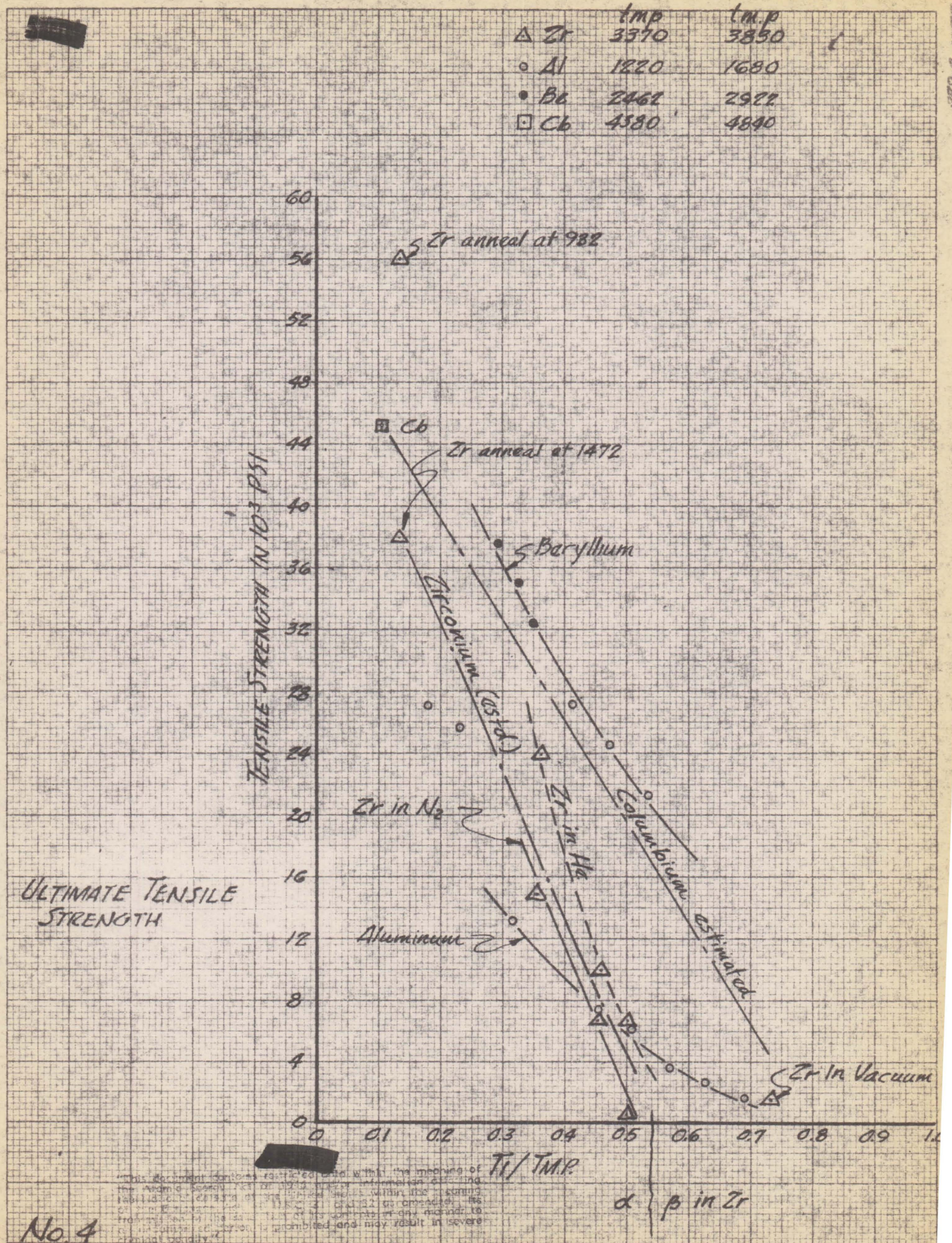

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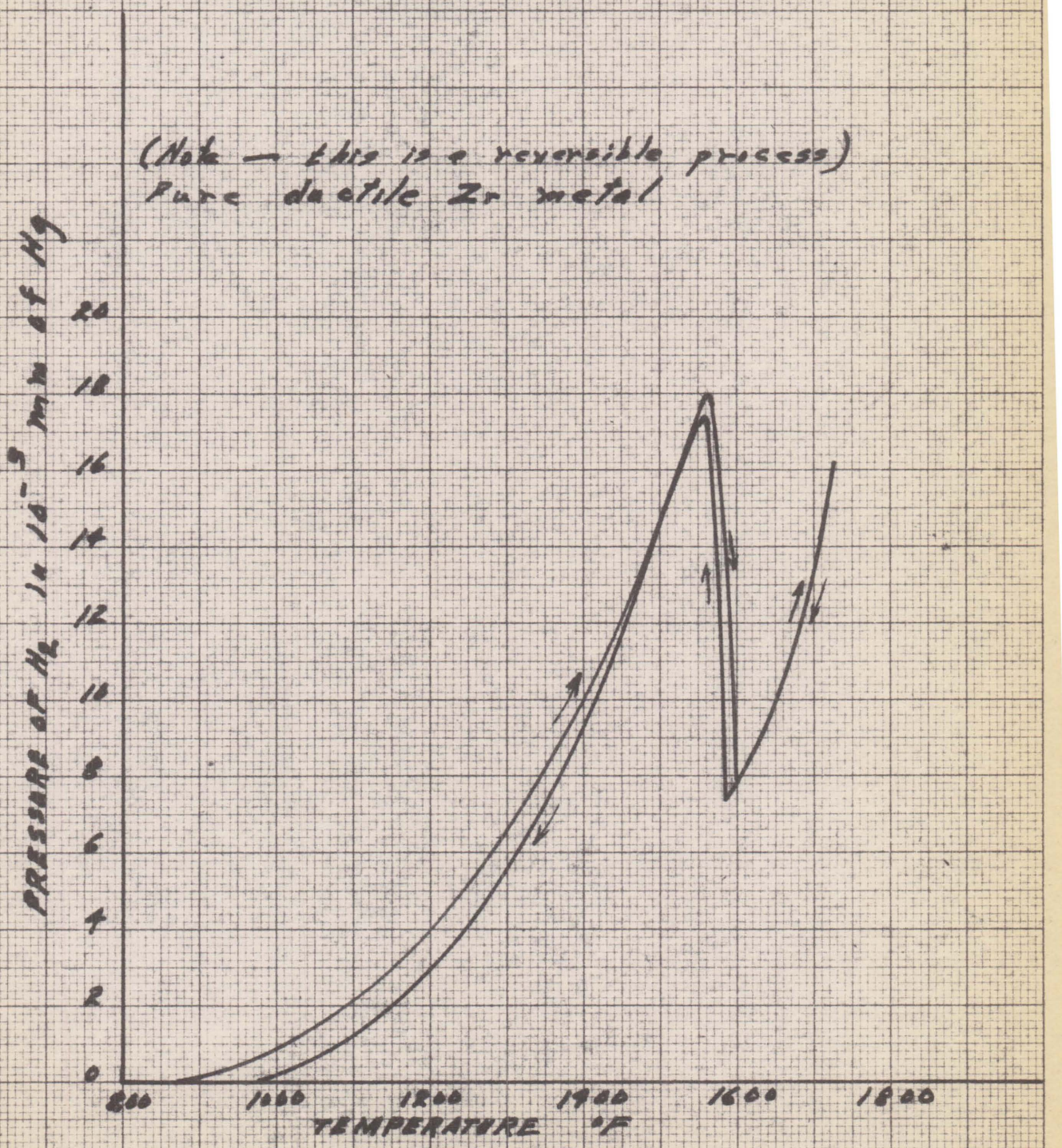
No. 4

PRD-A-1677

Drawing # 5657

unclassified



ABSORPTION OF H_2 by Zr (J. D. Fast)

No. 5

3-2-48

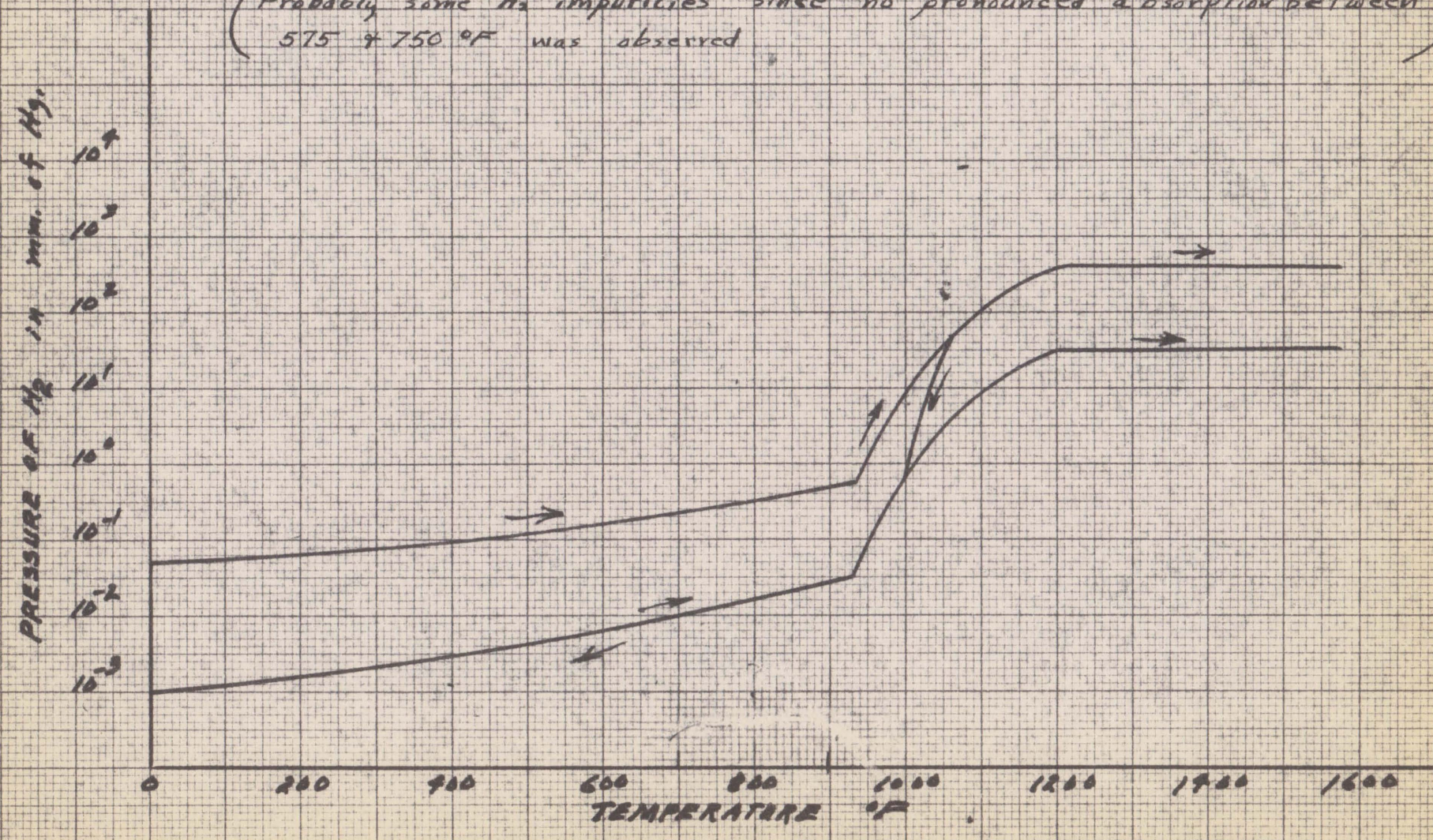
5

Drawing # 5658

unclassified

(Zr powder sprayed on a molybdenum ribbon)
t < 1475 °F therefore the transition point was not found

(Probably some H_2 impurities since no pronounced absorption between 575 & 750 °F was observed)



ABSORPTION of H_2 by Zr (Hukagawa & Nambo)

No 6

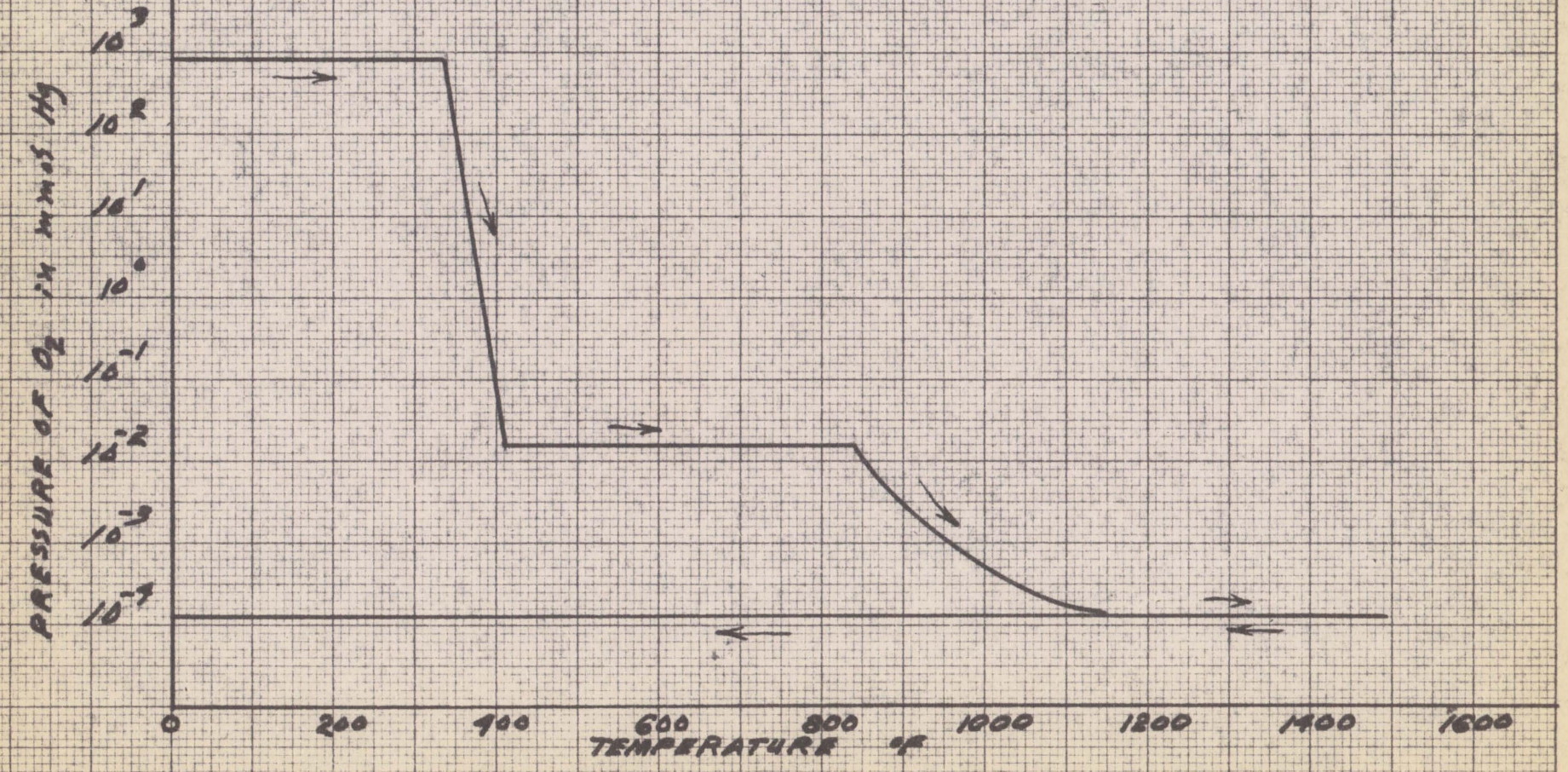
2088 3-2-48

Drawing # 5659

unclassified

The production experience gives verification

(Zr powder sprayed on a molybdenum ribbon)



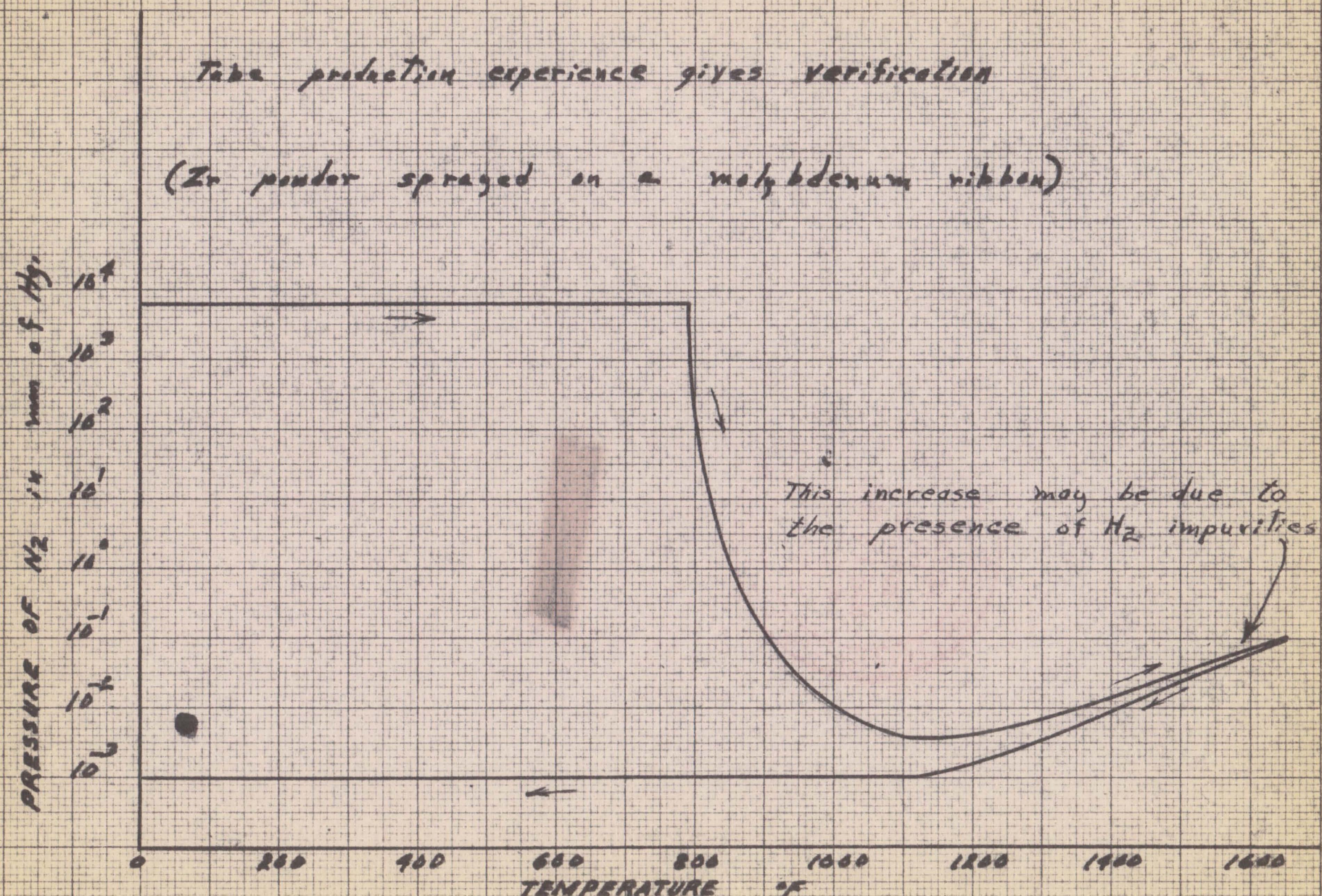
ABSORPTION OF O_2 by Zr (Hukagawa + Nambu)

No 7

WJD 3-2-48

Drawing # 5660

unclassified



ABSORPTION of N_2 by Zr (Hukagawa + Nambu)

No 8

~~No 8~~ 3-2-48