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INTERIM REPORT ON CALAMAR

by

C. B. Magee

C. R. Simmons

E. S. Funston

"PRELIMINARY REPORT"

This report is preliminary and informal in nature and was prepared for use at the Aircraft Nuclear Propulsion Department, General Electric Company in the course of work under AEC contract AT(11-1)-171, U. S. Air Force contract AF33(038)-21102, or U. S. Air Force contract AF33(600)-38062. Views, opinions, conclusions or proposals expressed in the report are those of the author(s) only. This report is subject to revision upon further evaluation or availability of additional data.

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ABSTRACT

The history of yttrium is presented. Recent data is given on the procurement and separation of yttrium oxide and preparation of the metal. Pertinent physical, mechanical, and chemical properties are summarized.

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PREFACE

In the latter part of 1954, General Electric-ANPD initiated a program directed toward the development of an yttrium metal suitable for reactor applications. A considerable amount of information has now been collected pertaining to metal procurement, technology, and fundamental properties.

This document is published with the intent of providing a single source of information for Project use. Since it is a preliminary report, any constructive criticisms or corrections will be appreciated.

CONTENTS

HISTORY AND OCCURRENCE OF YTTRIUM

In 1794 the Finnish chemist, Johann Gadolin(1,2) found a new earth in a mineral that had been discovered six years before by Arrhenius at Ytterby, Sweden. He obtained about 38 per cent of the new oxide from the mineral and proposed to call it ytterbia. He named the mineral ytterbite. In 1797, A. G. Ekeberg verified Gadolin's observations and proposed to call the oxide yttria and the mineral yttria-stone. The name of the mineral was later changed to gadolinite in honor of Gadolin. Both Gadolin and Ekeberg considered the oxide (yttria) to contain only one metal. In actual fact, this original yttria contained all the lanthanide elements as well as yttrium.

Probably the first fairly pure yttrium oxide was obtained by C. G. Mosander in 1842 who separated the old yttria into three new earths by fractional precipitations of the oxalates or hydroxides. The most basic fraction he termed yttria, the others, erbia and terbia. Mosander's erbia and terbia have been shown to be mixtures of many oxides, and his yttria undoubtedly contained considerable amounts of the oxides of gadolinium, terbium, dysprosium, holmium, erbium, and perhaps other lanthanides.

As the methods of separating the various lanthanides and of separating yttrium from the lanthanides improved in selectivity the individuality of yttrium was confirmed. As far back as 1860, N. J. Berlin gave 89.55 for the atomic weight of yttrium. Many other values have been given from that time to the present, all ranging around this figure. The presently accepted value is 88.92 (on the chemical acale). The spectrum of yttrium confirmed its position in the periodic table - atomic number 39.

Many chemists in the past century and in the present one have attempted to prepare elemental yttrium (see section on yttrium metal). Judging from the physical properties (e.g. melting point and density) reported in the past for metallic yttrium, it is evident that relatively pure yttrium had not been obtained until very recently.

OCCURRENCE

Yttrium falls in sub-group III-A in the periodic system. The other elements in this group are scandium, the lanthanides, and actinium. The lanthanides include the fifteen elements from lanthanum-57 to lutecium-71. The term "rare earth metals" is often used for the whole eighteen elements of the sub-group, and even stretched to include thorium which is not a member of the sub-group at all, in order to avoid confusion, it will not be used here.

As was implied above in tracing the history of yttrium, it is impossible to discuss the occurrence or chemistry of yttrium without reference to the lanthanides. From the point of view of atomic structure, the number of electrons in the fourth quantum group in the lanthanides is increasing from 18 to 32. The fifth and sixth quantum groups remain unchanged throughout the series containing 9 and 2 electrons respectively.

Compare this with yttrium where the fourth quantum group contains 9 and the fifth group 2 electrons. This similarity in the electron configuration of the outer-most orbits is observed in any sub-group in the periodic system, but in the case of yttrium and the lanthanides there is another factor which places yttrium even closer in its chemistry to that of the lanthanides. It is the lanthanide contraction.

As the atomic number increases through the lanthanide series the size of the trivalent ions of the group decreases. Goldschmidt's(3) values for the ionic radii are given below:

Element	Ionic Radius	Element	Ionic Radius
57 La	1.22 A°	65 Tb	1.09 A°
58 Ce	1.18	66 Dy	1.07
59 Pr	1.16	67 Ho	1.05
60 Nd	1.15	68 Er	1.04
61 Il		69 Tm	1.04
62 Sm	1.13	70 Yb	1.00
63 Eu	1.13	71 Lu	.99
64 Gd	1.11		

This contraction is accounted for as follows: The increased positive charge on the nucleus outweighs the screening effect of the added electrons in the fourth quantum group, thus the outer electrons are in a stronger positive field in lutecium than in lanthanum and hence move in smaller orbits. The effect of this contraction is reflected chemically in the basicity of the ions. The basicity decreases as the atomic number increases through the group, i.e. as the ions become smaller the hydroxyl ion is more tightly held to the positively charged lanthanide ion.

The lanthanide contraction is an extremely interesting study in itself, but it is mentioned here only because of its relationship to yttrium.

Goldschmit's(3) value for the ionic radius of the yttrium trivalent ion is $1.06\ A^{o}$. Thus, besides having the same electronic configuration in its outer orbits as do the lanthanides, yttrium has an ionic size just between dysprosium and holmium. Consider the geochemical principle that ions tend to exist in nature with other ions of approximately the same size, and it is no wonder that there is such a close association of yttrium with the lanthanides, especially the heavier ones.

Yttrium and many of the other sub-group III-A elements, relatively speaking, are not rare. Goldschmit's estimate(4) (modified by recent data) of the concentration of yttrium in the earth's crust is 28 grams per ton. This compares to 24 grams per ton of niobium and 23 grams per ton of cobalt. As another example, consider scandium. Goldschmidt estimates that 5 grams per ton of the earth's crust is scandium whereas uranium comprises 4 grams per ton and boron 3 grams per ton. The actual unavailability of the individual sub-group III-A elements gives striking evidence for the difficulty of separating them, one from another.

Goldschmidt(5) distinguishes three classes of minerals in which yttrium and the lanthanides are found: (1) minerals in which the trivalent ions of these elements are essential constituents, (2) minerals in which the trivalent ions enter as subordinate constituents and act as substitutes for one or more of the common rock-forming elements, and (3) minerals in which divalent lanthanide ions act as substitutes for certain common monovalent and divalent ions. This last class is of no importance as far as yttrium is concerned since yttrium does not form a divalent ion. The minerals in Classes 2 and 3 are examples of ionic substitution, i.e., the ions of yttrium and the lanthanides replace other ions of similar size in their crystal lattices. In Class 2 a great many minerals are known into which assemblages of yttrium and the lanthanide elements enter as substitutes for divalent calcium, strontium or lead, e.g. calcite, strontionite, apatite, fluorite, etc. Some such minerals (the apatite family) contain only a few tenths of a per cent of these elements. Some contain up to 1% or more. Certain minerals closely related to apatite, e.g. cappelenite, contain the phosphates and borates of yttrium and the lanthanides as the major constituents. Another mineral, yttrofluorite (related to fluorspar) contains up to 16 or 20% yttrium and lanthanide fluorides. Yttrium and the heaviest lanthanides are found in varieties of the mineral zircon (alvite or cyrtolite).

It may be that in the future the minerals of Class 2 will become important as sources of yttrium and/or the lanthanides, but certainly for the present only those in Class 1 are of significance. Goldschmidt(5) lists the following examples of Class 1 minerals: the fluoride tysonite, the fluorocarbonate parisite, the silicates thalenite and gadolinite, the phosphates xenotime and monazite, and the niobate samarskite.

These mirerals can usually be divided into three types: (a) those in which the cerium earth elements (lanthanum-57 to europium-63) are predominately concentrated as in monzaite, (b) those in which yttrium and the yttrium earth elements (gadolinium-64 to lutecium-71) are concentrated as in thalenite or xenotime, and (c) those in which the whole lanthanide series and yttrium is rather evenly represented as in certain gadolinites. All three types of Class 1 minerals are important as sources of yttrium, in fact the yttrium produced today mainly coming from Type B minerals and from the yttrium earth residues from monazite (Type A) after thorium and most of the cerium earths have been extracted.

In addition to those already mentioned, there are a number of fairly well-known yttrium and lanthanide bearing minerals of Class 1. Hopkins(2) lists the following besides some of those given above: the niobate-titanates euxenite, ploycrase, and fergusonite; the niobate-tantalate-titanate aeschenite; the silicates cerite and orthite; and the fluoride yttrocerite. More recently Kremers(6) mentions the fluorocarbonate bastnasite as an important Class 1 mineral of Type A. Table I lists the more important minerals of Class 1, giving the type (A,B,C) and the principal locations where the minerals are found.

Of the minerals listed in Table I only monzaite, xenotime, and euxenite are of importance for the production of yttrium at the present time. The others are considered quite rare or distributed in such a way that their recovery would not be economical. However, even today a good deal

TABLE I

Some better known yttrium and lanthanide bearing minerals of Class 1.

Mineral	Type	Location
Monazite	A	South Africa, Brazil, India, Idaho, Florida, Carolinas, Australia, Scandinavia
Bastnasite	A	New Mexico, California
Aeschenite	A	USSR, Norway
Cerite	A	Sweden, USSR
Orthite	A - C	Greenland, Scandinavia
Euxenite	B	Norway, Australia, North Carolina, Idaho
Xenotime	B	Brazil, Norway, South Carolina
Polycrase	B	Norway, Sweden, Carolinas
Fergusonite	B	Norway, Australia, Texas
Samarskite	B - C	USSR, North Carolina
Gadolinite	B - C	Norway, Sweden, Texas, Colorado
Yttrocerite	C	Scandinavia

of prospecting for yttrium bearing minerals is being carried on, particularly in the western part of the United States, and it may be that some of these minerals will become important.

The compositions of the various minerals are not given in Table I because they vary considerably with the origin of the ore. In general monazite will contain the equivalent of about 65% yttrium and lanthanide oxides, and the equivalent of 3 to 28% thorium oxide. Of the lanthanides present the cerium earths predominate (Type A mineral) accounting for about 95% of the total equivalent yttrium and lanthanide oxides. The equivalent amount of yttrium oxide in the mineral may be as much as 4%. In xenotime (Type B) yttrium and the yttrium earths predominate with yttrium comprising about 33% of the mineral. J. F. White(7) gives an analysis of Idaho euxenite showing yttrium oxide to be about 42.2% of the contained yttrium and lanthanide oxide.

This analysis is fairly typical of euxenite deposits. The yttrium content in the other minerals listed in Table I will not be given here. It will be noted, however, that some minerals such as gadolinite vary sufficiently in composition to fall in two types (for gadolinite, B and C).

J. F. White(7) has recently surveyed the domestic sources of yttrium. The results of his survey are given in Table II.

Some comments may be made regarding Table II. The monazite processed by the Lindsay Company now comes from the Union of South Africa. Thorium

TABLE II

Important Domestic Sources of Yttrium

Source	Location	Owner	Condition	Quantities Available	
Monazite	West Chicago, Illinois	Lindsay Chemical Co.	In sludge	Approx. 5 tons	25-30 tons per year
Monazite	Pompton Plains, New Jersey	Davison Chemical Co.	In sludge	Approx. 10 tons	
Monazite	Baltimore, Maryland	Davison Chemical Co.	In effluent liquor		Approx. 300 lbs. per day
Monazite	Summerfield, New Jersey	GSA	In mixed chlorides	Approx. 30 tons	
Euxenite	St. Louis, Missouri	GSA	In sludge		Approx. 300 lbs. per day
Xenotime	Aiken, South Carolina	Heavy Minerals, Inc.	Ore		Approx. 40 tons per year

and most of the cerium earths are removed leaving a so-called yttrium concentrate (75 to 81% contained Y_2O_3). This concentrate is now being used in the large scale ion exchange separations of yttrium.

Provisions have been made for saving the yttrium in the effluent liquor from the Davison Company's thorium plant in Baltimore. Also, negotiations are in progress for processing of the GSA owned sludge in St. Louis.

It has been learned recently from representatives of Heavy Minerals, Inc. that the ore deposits at Aiken, S.C. are sufficient to produce 100 tons of xenotime per year for at least 200 years. The present dredging facilities limit the maximum xenotime output to about 140 tons per year. With added equipment the yearly capacity could be increased greatly.

In addition to the sources listed in Table II, the yttrium bearing ores in Brazil may become available thorough the Davison Company. Recently an agreement was made between this company and Brazilian interests. Other companies have indicated that they have control of ore supplies. How good these supplies are is not known. Certainly it is known that many companies are searching rather intensely for yttrium bearing minerals. It is indeed interesting that what was at one time considered an extremely rare material and what was until very recently a laboratory curiosity is now being mined and soon will be produced in ton quantities.

RECOVERY OF YTTRIUM FROM ORES AND MINERALS

TREATMENT OF ORE

The treatment given ore containing yttrium bearing minerals follows pretty closely the routine methods of the mining and metal refining industries. The most extensive experience in this field has been gained in the treatment of monazite ores. Monazite was important in the early part of this century because of its thorium content (gas mantles), and later for the production of cerium, cerium earths, and misch metal. The only known deposit of massive monazite of commercial significance is in the Van Rhynsdorp district of the Union of South Africa. Most monazite is found in placer deposits of what is called "monazite sand". Mixed with monazite in these sands are such minerals as ilmenite, rutile, zircon, gold, garnet, etc. These sands are separated first by gravity devices in which the heavier sands are concentrated. Then magnetic separators are used to further concentrate the various minerals. Monazite is the least magnetic of the minerals in the sands and can be concentrated to 95% purity in this manner.

The deposits in Aiken, S.C. now being worked by Heavy Minerals, Inc. are also called "monazite sand". This is a misnomer since monazite is not one of the principle minerals in this ore. This ore is mined with a dredge and then separated by gravity and magnetic separators into four principle minerals: rutile, zircon, ilmenite, and xenotime.

The specific treatment given to any yttrium bearing ore would, of course, depend on the type and condition of the ore itself. However, since most yttrium bearing minerals are found mixed with other minerals in the form of sand, it is likely that the treatment of such deposits would follow pretty closely the methods described above for the concentration of monazite and xenotime.

OPENING OF MINERALS

The method used for extracting yttrium and the lanthanides from minerals depends upon the nature of the mineral itself, the presence or absence of certain related elements and the particular purpose of the extraction. The following discussion from Hopkins(2), is general and not exhaustive.

The mineral, ground to a fine powder, is first treated with acid or fused. The acid used is generally HCl or H_2SO_4, although HF is sometimes employed. The materials used in fusion may be $KHSO_4$, NaOH, or HKF_2. The use of HF or HKF_2 is generally limited to cases where niobium or tantalum are present. The fluorides of these elements are soluble and may be readily separated from the insoluble yttrium and lanthanide fluorides. The latter can be decomposed with H_2SO_4.

Such elements as copper lead, bismuth, molybdenum, etc. may be removed from solutions of yttrium and the lanthanides by treating the latter with hydrogen sulfide. Yttrium and all the lanthanides may be precipitated from solution as oxalates, separating them from the soluble alkali metal oxalates. For this precipitation the solution should be boiling hot. The precipitated oxalates are filtered and thoroughly washed.

There are many methods of removing thorium from yttrium and the lanthanides (two such methods are described below) but both thorium and zirconium may be removed by boiling the precipitated oxalates with ammonium oxalate. This treatment dissolves the zirconium and most of the thorium, and repeated treatment will dissolve all of the thorium.

The lanthanide contraction makes it possible to affect a partial separation of these elements in one precipitation. Usually Na_2SO_4 or K_2SO_4 are employed for this purpose. The double sulfates of sodium or potassium and the cerium earths are quite insoluble while those of yttrium and the yttrium earths are quite soluble. Sometimes a third group is distinguished. This group is comprised of europium, gadolinium, and terbium whose double sulfates are slightly soluble. However, in practice this group is rarely separated as such. It must be recognized that the solubility does not differ sharply between the two (or three) groups but changes gradually as the atomic number increases along the entire lanthanide series (the solubility of yttrium is about the same as that of dysprosium). Thus, there is an overlap of groups, and the elements near the group divisions will be pretty evenly represented in each group. It is possible to obtain the cerium earths free of yttrium and the yttrium earths by taking only the most insoluble fraction. In so doing, much of the cerium earth group must be left in solution. Conversely it is possible to obtain yttrium and the yttrium earths free of the cerium group, but here again much of the former must be sacrificed in the process.

As a specific example of the treatment of a yttrium bearing mineral consider the opening of monazite. H. E. Kremers(8) describes two methods, both in current usage, for extracting thorium, the cerium earths, and yttrium and the yttrium earths from monazite. In one method, monazite is mixed with an equal amount of 98% H_2SO_4 and some fuming sulfuric acid. The mixture is heated to 160°F and allowed to stand until reaction is complete. The residue is added to cold water, dissolving yttrium sulfate and the lanthanide sulfates but not thorium which remains insoluble. In the second method, more 98% H_2SO_4 is used and no fuming sulfuric acid. In this case, thorium will dissolve along with yttrium and the lanthanides but may be precipitated from solution by adding sodium pyrophosphate or a base. In either case the solution of yttrium and the lanthanide sulfates is treated with oxalic acid if all the ions are to be precipitated together, or with Na_2SO_4 if a separation into the cerium and yttrium groups is desired. In the latter case, about 95% of the lanthanides in solution will precipitate as the double sulfate. This precipitate will contain predominantly cerium and the other cerium earths. Yttrium and the remaining 5% of the lanthanides will remain in solution. The lanthanides here will be predominatly the yttrium earths with some "trailings" from the cerium group. Yttrium and these remaining lanthanides may be precipitated as oxalates, and, if desired, the oxalates may be fired to give oxides. M. M. Woyski(9) of the Lindsay Chemical Company has given the following composition as typical of the mixture of oxides prepared in this way. This mixture of oxides is called "yttrium concentrate".

Yttrium Oxide	81%
Terbium Oxide	not analyzed
Dysprosium Oxide	9.4%
Holmium Oxide	3.9%
Erbium Oxide	3.5%
Thulium Oxide	.7%
Ytterbium Oxide	1.4%
Praseodymium Oxide	.2%
Neodymium Oxide	.3%
Samarium Oxide	.7%
Gadolinium Oxide	5.2%

Treatment quite similar to that described above for monazite is given to xenotime and other yttrium containing minerals. In particular the double sulfate precipitation is quite standard for separating the cerium and yttrium earth groups, and producing a form of yttrium concentrate.

SEPARATION OF YTTRIUM FROM THE LANTHANIDES

In the discussion of the occurrence of yttrium considerable emphasis was given to the great chemical similarity exhibited by the lanthanides and yttrium. It was pointed out that, because of the lanthanide contraction, the size of the yttrium trivalent ion is intermediate to the sizes of the dysprosium and holmium ions. This great similarity precludes the use of any simple chemical or physical method for separating yttrium from the lanthanides. Any separation method must depend upon differences in properties. The greatest difference between yttrium and the lanthanides is in their weights. The atomic weight of yttrium is 88.92 while the weights of the lanthanides range from 138.92 (lanthanum) to 174.99 (lutecium). This immediately suggests the use of the mass spectrograph for extracting yttrium from the lanthanides, and indeed such an extraction has been made. A small sample of yttrium was electromagnetically separated from the contaminating lanthanides in one of the Calutron units at the Oak Ridge National Laboratory. This sample is now being used as a standard of purity for yttrium. This method while straightforward in theory and practice is, unfortunately, not suited for large scale production of yttrium.

The difference most usually taken advantage of for the separation of yttrium and the lanthanides is the difference in the ionic sizes. The difference in the ionic sizes of neighboring lanthanides is not great. Hence, the differences in chemical and physical properties, which are reflections of the difference in ion sizes, are correspondingly small.

Consider, for example, the differences in the aqueous solubilities of the double sulfates. It has already been seen that the solubility changes gradually from one ion to the next and any single precipitation will give, not a single element, but a complicated mixture of elements. In order to separate a single element by solubility methods it is therefore necessary to perform many fractional precipitations or crystallizations.

In fact, in any separation method based on the difference in ionic sizes, many steps are required for complete separation. Methods of this kind devised to date, other than fractional crystallization or fractional precipitation, are ion-exchange and liquid-liquid extraction. Although ion-exchange is a continuous process and liquid-liquid extraction is often run on a continuous basis, it is well to keep in mind that these methods are no less stepwise in nature.

What follows is a brief description of the three primary methods of separating yttrium from the lanthanides. This is not to say that one of these methods, as described, represents the final answer. Today this field is the subject of considerable research and development. Modifications of the present methods or even entirely new schemes may, and probably will, come out of these efforts.

FRACTIONAL CRYSTALLIZATION AND FRACTIONAL PRECIPATION

The method of fractional crystallization for the separation of the lanthanides (and yttrium from them) is quite clearly described by Hopkins(2). The following is quoted from his text:

"Its (fractional crystallization) general principle may

> be illustrated in this manner: If we have a saturated solution of a mixture of salts of differing solubility and evaporate 1/10 of the solvent 1.10 of the solute will crystallize: the crystals will be composed largely of the least soluble members of the mixture, while the mother liquor will contain nearly all the more soluble salts. If, now, the crystals are dissolved in enough solvent to form a saturated solution, then again partly evaporated, a new crop of crystals is formed more nearly pure than the first. By adding the second mother liquor to the first and repeating the partial evaporation, another crop of crystals is produced. By continuing in this fashion adding the mother liquor from each fraction to the next more soluble portion, the original mixture may finally be separated into a series of fractions each one differing from its neighbor."

A number of salts have been used in the fractional crystallization scheme of separation. A salt of intermediate degree of solubility is most convenient since if the salt is difficultly soluble large volumes of solvent are needed and if the salt is readily soluble high concentrations are necessary and difficulties are experienced in separating the crystals from the mother liquor. Some of the salts of the lanthanides and yttrium that have been used are the double magnesium, manganese, ammonium nitrates, the ethyl sulfates, the double alkali metal carbonates, the cobalti-cyanides, the oxychlorides, the oxalates, the bromates, and the chromates.

Quite similar to, and usually coupled with, fractional crystallization is the method of fractional precipitation. If for example, a small amount of ammonia is added to a solution of a mixture of the lanthanides and yttrium, the hydroxides of the least basic constituents will precipitate. The precipitate can be redissolved and the process repeated in the same manner as that described for fractional crystallization yielding a number of different fractions. Other basic materials may replace ammonia as the precipitant as, for example, soda, magnesia, or urea. There are variations of the method taking advantage of the differing basicities of the lanthanides (and yttrium), such as moderately heating the salts of oxyacids forming basic salts of differing solubilities. Another approach is to carefully precipitate insoluble salts such as the oxalates. It is sometimes possible, by varying the precipitating conditions, to change the solubility characteristics of one or more of the lanthanides or yttrium. Thus a particular system or combination of system can be devised for each of the lanthanides and yttrium that will give the most efficient separation.

It must be said of fractional crystallization and fractional precipitation that these are in general laborious and inefficient methods. Consider that in the purification of a given element thousands of fractionations are necessary, and that in every fractionation some material is lost. It is small wonder that before the development of more efficient methods of separation the chemistry of yttrium and the lanthanides developed slowly.

ION EXCHANGE

Before the discovery of synthetic organic ion exchangers by Adams and Holmes(10) in 1935, ion exchange processes were limited to a single major application - the softening of hard water. The excellent properties that these synthetic resins possess, such as their high capacity, their stability, and the rapidity and reversibility of their exchange reactions, have made possible the application of the ion exchange technique to many processes both in the laboratory and in the chemical industry. The problem, faced by the Plutonium Project, of separating fission products led to what was probably the first use of cation exchange for the separation of the lanthanides and yttrium. Many deserve credit for the development of this technique, such names as J. Schubert, G. E. Boyd, B. H. Ketelle, D. H. Harris, E. R. Tompkins, and many more are prominent in the literature on this subject. However, to F. H. Spedding and his associates at the Ames Laboratory (Iowa State College) must go the principle credit for developing the technique to a point where it is applicable for the large scale production of highly pure yttrium.

Generally speaking, the synthetic cation exchange resins (Dowex 50, Amberlite, etc.) are organic polymers (e.g. phenol formaldehyde) with acid groups (e.g. sulfonic acid) providing negative centers. Usually the resins are contained in columns. The size of the columns depends on the scale of the separation desired. For laboratory separations the columns may be six inches in diameter by 5 or 6 feet high. For large scale production the columns may be 30 inches in diameter by 15 feet high (more will be said of this later). Except on a very small laboratory scale many columns are connected in series. Before charging the columns with the mixture to be separated, the resins are put into the ammonium cycle, i.e. ammonium ions are absorbed on the negative sites on the resin. The affinity of cations for the exchanger increases with the positive charge on the ion, i.e. $+3 > +2 > +1$. Thus, if a solution of lanthanide chlorides were added to the top of an ion exchange column in the ammonium cycle, the trivalent lanthanide ions would replace the ammonium ions at the negative sites on the resin and ammonium chloride solution would drain from the bottom of the column.

With cations of the same valence the affinity for the exchanger increases with increasing basicity. To say this another way: the affinity is greatest for the cation with the smallest hydrated ionic radius and least for the cation with the greatest hydrated ionic radius. Now in the lanthanide series the cations decrease in ionic radius as one goes from La^{+++} to Lu^{+++}, which brings about a corresponding decrease in basicity. But as the basicity decreases the hydrated ionic radius increases. Thus, with the lanthanides, La^{+++}, the most basic of the group and the cation with the smallest hydrated ionic radius, is the most strongly absorbed by the resin, and Lu^{+++}, the least basic and the cation with the largest hydrated ionic radius, is the least strongly absorbed by the resin. It follows then that if, for example, one were to charge the upper 1/10 of a column with a mixture of the lanthanide cations, and pass water through the column from top to bottom at a steady rate the cations would migrate down the column at different rates. The order of migration would be lutecium first, then ytterbium and so on by order of decreasing atomic number down to lanthanum. Theoretically, if the column were long enough and if the elution (passing of water through the column) were carried on for a long enough time, a separation of all the ions in the mixture would be effected.

In practice, water is not used as the eluting agent for separating the lanthanides but rather an aqueous solution of a complexing agent is used. The complexing agent is chosen such that those ions most strongly complexed are the ones least strongly absorbed by the resin. Obviously such a practice greatly increases the separation efficiency of the process. At the present time the complexing agent most commonly used is ethylene diamine tetra-acetic acid (E.D.T.A.). The order of elution of the lanthanides using this complexing agent is the same as that mentioned above, i.e. lutecium first and lanthanum last. Yttrium with this system is eluted between dysprosium and terbium.

There are many factors such as eluting rate, length of resin bed, etc. that affect the over-all efficiency of the ion exchange process. Perhaps the best way to bring out the effect of these factors and to give the reader an understanding of how an ion-exchange separation is carried out would be to consider a specific example. What follows is a description of a typical ion exchange run carried out at the Lindsay Chemical Company(9). The purpose of such a run is to obtain high purity yttrium. The practices followed by the Lindsay Company are patterned after those of Dr. Spedding and his associates at Ames.

The columns used are six inches in diameter and the resin bed length in each is five feet. The resin used is Dowex 50. Fifteen kilograms of yttrium concentrate (75 to 80% Y_2O_3) are dissolved in hydrochloric acid and the solution is added to the columns. The solution fills five columns and this is called one bed length. Yttrium ions and lanthanide ions have now replaced the ammonium ions originally present on the resin. The eluting agent used is ethylene diamine tetra-acetic acid (E.D.T.A.). Ammonium hydroxide is added to an aqueous solution of this material to maintain a pH of 8. This solution is started through the first column and passes through all the columns in series. The sixth column in line (the one next to the first five that were charged with yttrium concentrate) contains cupric ions. As the eluting solution pushes the charge material into column six the cupric ions are displaced by yttrium and lanthanide ions. The boundary between the charge material and the colored cupric ions indicates how far and how fast the solution is moving. When first started, the eluting rate is one liter per minute.

As the charge material is eluted through the columns the various ions begin to separate into bands. The amount of overlap of these bands is greatly affected by the eluting rate. To cut down the overlap the eluting rate is cut down to 1/5 liter per minute after the charge material has passed through two bed lengths. One more bed length at this slow rate is usually all that is required to separate high purity yttrium.

The solution from the last column is collected in twelve gallon batches. The first lanthanide coming out will be lutecium, then lutecium will give way to ytterbium with an area in between wherein both are eluted, then ytterbium will give way to thulium again with an overlap area. This will continue up the series to dysprosium, the dysprosium-yttrium overlap, and then yttrium. Since yttrium is present in the charge material in the highest quantity its band will be long, perhaps filling three of the five columns in a bed length. After the yttrium is eluted, if it is desired, the remaining lanthanides can be eluted in order of decreasing atomic number. The whole run (up to terbium) requires sixty days. The yttrium is precipitated from solution as the oxalate which is fired to the oxide. A run such as this would yield about 10 kilograms of yttrium oxide.

As was mentioned on the preceeding pages, the ion exchange column dimensions for large scale production of high purity yttrium oxide had been tentatively set as 30 inches in diameter and 15 feet high. Recently, twelve columns having such dimensions were installed and placed in operation at the Ames Laboratory. These columns were of stainless steel construction and each contained approximately 45 cubic feet of amberlite IR 120 resin. An example of the efficiency of large column operation can best be given by describing a typical yttrium oxide separation in the Ames facility. Four of the columns were charged with a chloride solution of 1040 pounds of yttrium concentrate obtained from treatment of 1750 pounds of xenotime ore. This concentrate in terms of oxide contains approximately 57 per cent yttrium with the remainder consisting mainly of the heavy lanthanides. The eluting solution was E.D.T.A.

buffered with ammonium hydroxide to a pH of 8.4 and the elution rate was set at 5 liters per minute. This rate was not changed during the entire process. When the lutecium band had reached the 8th column in line, the heavy lanthanides (lutecium thru dysprosium plus some of the dysprosium-yttrium overlap fraction) were removed to a secondary series of 6 inch diameter exchange columns. Approximately 533 pounds of spectroscopically pure yttrium oxide (99.95% Y_2O_3) were collected from the twelfth 30 inch column representing a yield of about 90 per cent. The yttrium elution band under these conditions was broad and sharply definitive at the leading and trailing edges. Further elution rate studies at Ames have shown that an increase to 10 liters per minute decreases the yield of pure oxide, the rate of 5 liters per minute apparently being close to an optimum.

Large scale in exchange facilities have now been established at Michigan Chemical Co., St. Louis, Michigan; Lindsay Chemical Co., West Chicago, Illinois; and Dow Chemical Co., Midland, Michigan. Production from these sources has not yet reached a peak rate although some 6,000 pounds of reactor grade oxide (i.e. yttrium oxide having a thermal neutron absorption cross-section of less than 1.4 barns) was realized during the period January, 1957 to May, 1957.

LIQUID-LIQUID EXTRACTION

The distribution of solutes between two immiscible solvents, commonly refereed to as liquid-liquid extraction, is an important operation which has applications commercially in both organic and inorganic chemistry. Extractions are generally of two types, batchwise and continuous; the continuous method having the most importance in commercial applications. A continuous liquid-liquid extraction is a chemical equilibrium process which involves bringing two immiscible solvents, one of which contains the elements to be separated, into intimate contact. Generally, this is carried out in separation towers or countercurrent assemblies which have been especially designed to provide a greater surface area of contact between the two liquid phases. Separations then occur between two elements or groups of elements according to the magnitude of individual distribution co-efficients of each specie in the given solvent phases. In practice, inorganic separations are carried out by opposing an aqueous solution of the inorganic mixture with a specific liquid organic phase or an organic phase containing a specific complexing agent.

Although a comparative newcomer to the chemical process field, continuous liquid-liquid extraction methods have shown their utility in the past in separations involving zirconium and hafnium, columbium and tantalum, uranium, thorium, and other actinides. Since liquid-liquid operations often permit large scale production with low cost, many investigators have considered this method as having definite potentialities for an economical preparation of high purity yttrium and the individual lanthanides. The importance of this method for fractionation of the lanthanides has been stressed in the reviews of Bock(11), Quill(12), and Wylie(13). However, the search for systems by which total separations of yttrium and the lanthanides could be made feasible is still in its infancy.

Any investigation of the separations of yttrium through liquid-liquid extractions naturally encompasses a study of the distribution co-efficients for all the lanthanides in various chemical extraction systems. The first use of solvent extraction for lanthanide salt separations was reported in 1937 by Fischer Dietz, and Jubermann(14). They claimed a 50 per cent difference in distribution co-efficients of neighboring lanthanides when extracting aqueous chloride solutions with ethers, alcohols, and ketones. None of these data has been substantiated by other investigators. Templeton's(15) results on aqueous solutions of rare earth chlorides opposed by alcohols indicated a regular increase in extractability with atomic number for all the lanthanides from lanthanum to samarium inclusive.

In 1952, Peppard, Foris, Gray, and Mason(16) reported that the extraction of the lanthanides by tributyl phosphate (TBP) from either a hydrochloric acid solution or from an 8.0 to 15.6 molar nitric acid solution increased with increasing atomic number (This order was inverted from an extraction system using a 0.3 molar nitric acid aqueous phase). Yttrium was extracted between dysprosium and holmium; the position predicted from consideration of atomic radii. From this work, they concluded that increasing the nitric acid concentration diverges the distribution ratios for a given pair of lanthanides and consequently the theoretical maximum separation occurs in concentrated nitric acid. However, these experiments were carried out on tracer quantities and on salt mixtures consisting mostly of the light lanthanides. The conclusions may not be valid, in applications to higher concentrations or higher yttrium oxide concentrates.

In 1954, Foos and Wilhelm(17) obtained single stage and continuous extraction data on yttrium concentrates in an aqueous nitric acid solution opposed by tributyl phosphate. These concentrates consisted of yttrium tailings from the ion exchange process and products from the treatment of fergusonite and gadolinite ores. In each case, the mixtures in terms of oxide were composed of from 50 to 60 per cent yttrium and 5 to 15 per cent heavy lanthanides with the light lanthanide fraction constituting the remaining material. A number of 20 stage counter current extractions were carried out. For a concentrated nitric acid system the organic product phase generally contained yttrium and the heavy lanthanides, while the aqueous product phase contained the light rare earth fractions plus a small amount of yttrium and dysprosium. In one multiple stage extraction, the organic product phase delivered 90 per cent of the total yttrium which analyzed 91 per cent pure on an oxide basis. Single stage extraction data on the same system indicated that preferential extraction from an aqueous system greater than 3.0 molar in nitric acid increased with increasing atomic number while in other nitric acid systems yttrium extracts with the lower atomic number rare earths.

Recently Peppard(18), of the Argonne National Laboratory, has investigated a variety of chemical systems which were considered applicable to the industrial scale isolation of high purity yttrium and the individual lanthanides. In order to acquaint the reader with the methods used by Peppard, a summary of his work on the isolation of pure yttrium follows.

Peppard utilized the operations of a batch counter-current extraction assembly of seven stages in which the lower and upper phases were barren and the feed enters in the middle phase. The important quantity referred to in extraction processes is the separation factor which is defined for a binary solution of A and B as the ratio of the separation constants,

$$\beta = K_A/K_B$$

$$\text{where } K_A = \frac{\text{conc. A, organic}}{\text{conc. A, aqueous}}$$

Peppard devised several chemical systems in which the K values increase or decrease with increasing atomic number (Z) of the lanthanides. In some systems investigated, the separation constants follow a geometric progression, $K_{Z+p} = (r)^{p} K_{Z}$, where r is a characteristic constant of a particular chemical system obtained by measurement. In other systems, this progression was inverted; in still others, the above expression holds reasonably well for the high Z members as a group or for the low Z members as a group. In some chemical systems which Peppard investigated, yttrium assumed an atomic number greater than 71 and in others less than 57. The simplest isolation should result from use of such systems where yttrium assumes the position of a terminal psuedo-lanthanide. However, the r values for these particular systems were so small that they were of little interest from a separations viewpoint. In the most promising systems, yttrium assumes an atomic number in the range 61 to 70. Here, the possibility exists that the heavy and light lanthanides could be separated as groups with one of the resulting groups having yttrium either as a terminal element or adjacent to a terminal lanthanide.

The system found to be most promising by Peppard involved the use of aqueous chloride solutions of the lanthanide mixtures opposed by DEHP-HCL (bis-2-ethyl-hexyl orthophosphoric acid equilibrated with HCL) in a carrier solvent of toluene. The lanthanides in this system are ordered according to Figure 1 and yttrium is placed between holmium and erbium, the position in which it fractionates. The separation of yttrium from the lanthanides using this system occurs similar to that shown schematically in Figure 1, and results indicated that yttrium may in 2 passes using a seven stage extraction assembly be satisfactorily separated from all the lanthanides except holmium and erbium.

A secondary system is necessary in order to accomplish the necessary decontamination from holmium and erbium. At present, Peppard has demonstrated that an aqueous solution of lanthanides thiocyanates (1$\underline{M}$ in NH_4CNS) opposed by a 50 per cent solution of bis-(2-ethyl-hexyl) phenyl phosphonate using either hexone or toluene as a carrier solvent will accomplish this separation. In both systems, yttrium reports into either the aqueous lower or organic upper phase preferentially depending on its position as a terminal* psuedo-lanthanide. All of Peppard's experiments were conducted on a lanthanide chloride concentrate which had the approximate composition of the concentrate from monazite (see Page 21).

In summing up the results of past liquid-liquid extraction studies on the preparation of high-purity yttrium, considerable progress has been made toward a fundamental understanding of the distribution of yttrium and the lanthanides in different solvent systems. In the light of Peppard's work a definite breakthrough has been made toward achieving high-purity yttrium oxide by extractive means, and furthermore, the

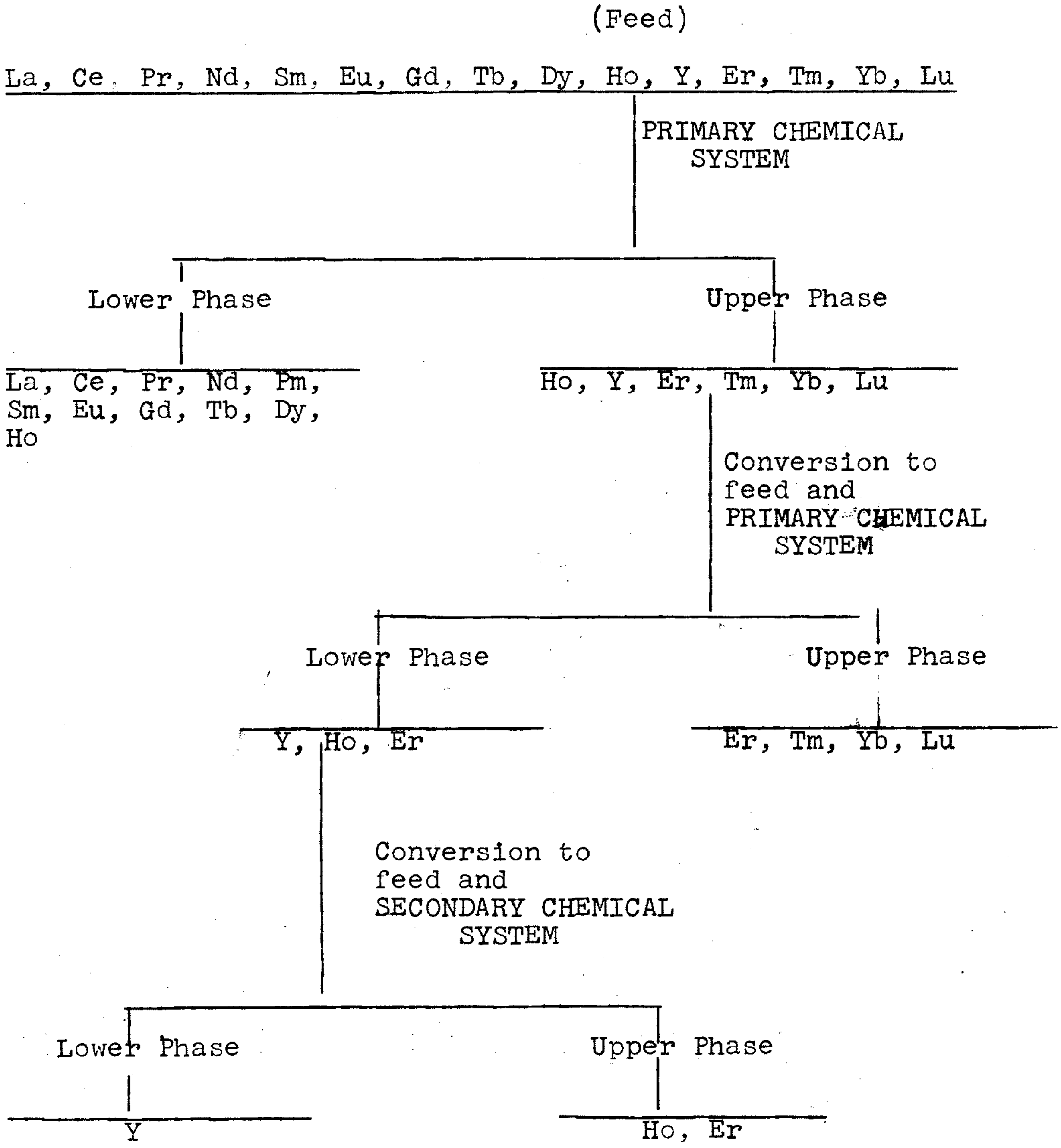

FIGURE 1. Schematic Diagram for Partition of Yttrium from the Lanthanides by Counter-Current Extraction

methods which his work suggests can conceivably be adapted for large scale production.

PREPARATION OF YTTRIUM METAL

Until the development of an ion-exchange method for the separation of yttrium from the lanthanides, pure compounds of yttrium could be obtained only by painstaking recrystallization procedures requiring many steps. Consequently, the number of attempts by early investigators to reduce yttrium compounds has been limited and the reduction history sketchy. Many of these reductions were carried out on mixtures of the yttrium subgroup compounds and the results obtained cannot be considered completely representative of yttrium reduction technology. Furthermore, the metal products were largely in either a powder or alloy form which were difficult to melt or sinter into solid yttrium. As a result, a great deal of confusion existed up to 1951 as to the true melting point and density of yttrium which were reported to range from 2282°F to 2732°F and 3.8 g/cc to 4.57 g/cc respectively. However, the information that was obtained from early reduction investigations has served as a basis for the improved methods now in use.

Methods which have been utilized in reducing yttrium compounds can be classified into two groups: (a) electrolytic reduction to form the metal, alloy or an amalgam; and (b) metallothermic reduction to form the metal or an alloy. Both have required investigations into methods of preparing suitable yttrium compounds, thermodynamic consideration of the potential reduction systems to be used, and methods of obtaining the yttrium metal product in a pure, massive form. Probably the most significant results and greatest degree of success has been achieved through use of the metallothermic technique. Consequently, a great deal of emphasis has been placed on this method in the past two years due to an increased interest in yttrium metal as a material useful in nuclear reactors. The work which has been carried out in the past on both electrolytic and metallothermic reductions will be described and discussed separately below.

ELECTROLYTIC REDUCTIONS

Hicks(19) in 1818 reported the preparation of an impure yttrium powder by electrolysis of the fused chlorides of the yttrium sub-group. An attempt to compact this powder by sintering or fusion met with little success. Hicks noted that the powder was extremely reactive in air and when in contact with water.

An extensive series of electrolytic reductions were carried out on recrystallized anhydrous yttrium chloride and oxide by Thompson, Holten, and Kremers(20) in 1926. These reductions involved electrolysis of (a) a saturated alcoholic solution of yttrium chloride using a nickel cathode, (b) a saturated alcoholic solution of yttrium chloride using a mercury pool-cathode, (c) a fused mixture of anhydrous yttrium chloride and sodium chloride using a graphite cathode-anode pair, and (d) a fused mixture of yttrium oxide and cryolite. The electrolysis performed in alcoholic solution using a nickel cathode produced a slimy deposit believed to be yttrium hydroxide, while the primary product from electrolysis with the mercury pool-cathode was believed to be an amalgam of yttrium. Attempts to distill off mercury from this amalgam resulted in the formation of a gray powder which could not be fused. Electrolysis of the fused mixture of yttrium oxide and cryolite gave back aluminum.

The most encouraging results were obtained by Thompson from electrolysis of the fused salt mixture at 1500°F. There were indications that if a high temperature could be maintained in the fused salt system during electrolysis, the metal powder produced could be compacted at the graphite cathode as it was formed. However, from the temperature conditions obtained in these experiments, definite compacting or sintering of the metallic deposits did not occur. The most compact product which was collected developed a skin of oxide when attempts were made to melt it after preliminary washes in water or alcohol to remove the adhering sodium chloride. There were also some indications that the yttrium product had reacted with the graphite cathode.

Hopkins and West(21) prepared amalgams of yttrium by two methods. They electrolyzed a saturated alcoholic solution of anhydrous yttrium chloride with a mercury pool-cathode and reacted a similar solution with sodium amalgam in a displacement type of reaction. In both cases, an amalgam was reportedly obtained which upon decomposition gave a black powder, not entirely free of mercury, which was difficult to melt into massive metal.

In 1945, Trombe(22) prepared a ternary alloy of yttrium by electrolysis of a fused salt bath consisting of yttrium chloride, sodium chloride, magnesium and cadmium at 1472°F. The ternary alloy of 24% yttrium-20% cadmium-56% magnesium was formed at a molten magnesium-cadmium cathode. This alloy was heated to 2192°F in argon and the cadmium and magnesium removed. The resulting sponge-like mass of yttrium was then melted into a block of massive yttrium metal. Trombe reported a melting point of 2714°F and a density of 4.5 g/cc on metal produced in this manner.

In 1954, Moeller and Zimmerman(23,24) made the observation that, because of the highly electropositive character of yttrium, the electrodeposition of this element from non-aqueous media would most probably be realized from a highly basic solvent. Such solvents, because of their strong donor characteristics, provide media in which solvated electrons can readily exist and in which lower oxidation states are strongly stabilized. To test their theory, Moeller and Zimmerman prepared anhydrous yttrium acetate and electrolyzed a saturated solution of this compound in ethylenediamine at room temperature. The electrodes were bright platinum separated by medium porosity glass discs and the current densities ranged from 1.6 to 0.20 milliampere/cm^2. After each electrolysis, the cathode was immersed in dry ether and the deposits removed mechanically in a nitrogen-filled dry box. In a few instances, water was added ranging from one to six drops per 60 mils of solution. It was observed that the addition of water up to four drops facilitated the formation of a black, lustrous deposit, but larger quantities of water gave hydrous yttrium oxide. The deposits formed in anhydrous ethylenediamine were smooth, metallic, and iron-gray in color. The products from both methods were reported to have oxidized in air or water, evolved hydrogen in acids, and gave x-ray diffraction patterns characteristic of yttrium metal. However, it was noted that the deposits contained entrapped or absorbed organic material, and there were indications that the metal could have reacted with hydrogen which may have been evolved during the electrolysis.

It is evident that one main difficulty must be overcome if high purity massive yttrium metal is to be successfully prepared by electrolytic means. This difficulty arises from the extreme reactivity of yttrium in a finely divided form. There are four factors which apparently must be considered if this reactivity is to be minimized: (a) the electrolysis must be carried out in media which is anhydrous, can be maintained anhydrous, and is stable at the high temperature which must be utilized to compact the metal product, (b) means must be provided whereby the metal product or alloy can be isolated from the media either during or after the electrolysis, (c) electrode systems must be utilized which either do not react at all with yttrium or react to form unstable alloys, and (d) suitable methods must be found for forming massive metal from either alloy or compacted deposits which do not lead to contamination of the metal. Although it is conceivable that high purity yttrium metal can be produced economically by electrolytic means, extensive research and development work directed toward finding a suitable method has not been conducted recently.

METALLOTHERMIC REDUCTION

As early as 1816, Berzelius(25) described the reduction of yttrium chloride by means of sodium and potassium. The product of his reduction was reported to be a metal powder. Wohler(26) and Papp(27) later claimed to have also prepared a yttrium powder by this method. In each case, attempts were made to eliminate the chloride by-product from the metal powder by washing with water or alcohol. This generally resulted in reaction of the metal powder and subsequent inability to fuse it into massive metal. The yttrium chloride used in these experiments undoubtedly was a mixture of the yttrium sub-group lanthanide chlorides.

Thompson, Holten, and Kremers(20) attempted to reduce recrystallized anhydrous yttrium chloride with sodium and calcium metal. The primary products obtained consisted of an intimate mixture of metal powder and the chloride slag by-products. The metal powder in such mixtures proved to be extremely reactive in air and attempts to isolate it by washing out the slag with water or alcohol were unsuccessful. An attempt was made to isolate the metal by heating the mixture to the melting point of yttrium; the separation theoretically occurring due to differences in the densities of liquid slag and metal. However, when one of the mixtures was heated above 2732°F, the resultant product was found to be a hard, clinker-like mass with no distinct separation of phases.

The first successful preparation of massive yttrium metal by direct metallothermic means was due to a series of investigations carried out by Spedding and co-workers in the Ames Laboratory beginning in 1951. These investigations will be described in detail in the following pages since the present method being used to produce large quantities of yttrium metal stems from this work.

Bomb Reduction of Yttrium Chlbrlde

Spedding, et a l ^ ^ in 1952 initiated a program of study from which they hoped to obtain a general metallothermic method for preparing all of the lanthanide metals plus yttrium. In studies on yttrium, they prepared anhydrous yttrium chloride and attempted to reduce this compound with calcium in a bomb reaction. The charge consisted of yttrium chloride, 10 per cent excess calcium and an iodine booster placed in a calcium oxide crucible and contained ir a capped steel bomb. The bomb and contents were heated in a gas-fired furnace maintained at 1202° to 1382°P. Prom previous experience with the lanthanide chlorides, it has been found that excess calcium reacted with iodine at 752°P providing sufficient heat to complete the reduction and separate two liquid layers consisting of a top layer of calcium chloride-calcium iodide and a bottom layer of lanthanide metal. However, in the case of yttrium, the product was an intimate mixture of slag and metal. Apparently there was not.enough heat generated exothermically to reach the melting point of yttrium during the reduction. The slag-metal mixture was heated in an inert atmosphere to temperatures above 2732°P but excessive boiling of calcium chloride at these temperatures again resulted in mixing of metal and slag.

Direct Melt Reduction of Anhydrous Yttrium Pluoride

Daane and Spedding^^^) in 1953 undertook a study of the reducticn of' anhydrous yttrium fluoride by calcium metal. Thermodynamically, the calcium-yttrium chloride and calcium-yttrium fluoride reduction systfeems are both applicable with the chloride system holding a slight edge. The fluoride was selected as starting material because it was found to be easier to prepare and less hygroscopic; making it easier to handle in air than the chloride. Furthermore, the melting point and density of calcium fluoride indicated that this material would probably provide a more suitable slag layer for consolidating the metal. Daane and Spedding prepared anhydrous yttrium fluoride by a method which has since been commonly referred to as the "wet process". In this process, hydrated yttrium fluoride (YF_3-$1/2H_2O$) was precipitated from a hot, concentrated solution of hydrated yttrium trichloride (YCl_3-$6H_2O$) with 40 per cent aqueous hydrofluoric acid. The hydrated product was dried partially in air at 392°F and then under anhydrous hydrofluoric acid at 572° to 752°F.

To carry out the reduction, the fluoride was mixed anhydrously with purifie calcium metal in a tantalum crucible. The crucible and contents were placed in a graphite susceptor under argon or helium and heated by induction. The reaction was observed to proceed quietly as the temperature was increased to slightly above 2732°F. Upon cooling, two well-defined layers of calcium fluoride and yttrium metal were found to have formed in the top and bottom of the crucible respectively. In recovering the yttrium melt, the slag layer was broken loose easily, but it was necessary to destroy the tantalum crucible due to the wetting action of the yttrium.

Yields of greater than 99 per cent of theoretical were consistently obtained with tantalum contaminations reportedly running from 0.05 to 1.00 weight per cent and calcium contents ranged from 200 ppm to 1000 ppm. Metallographic examination of the yttrium microstructure revealed that there were inclusions throughout which were variable in form and could have consisted of a number of different phases. These were believed to be primarily non-metallic in nature consisting of possibly the oxides and/or fluorides of calcium and yttrium (more will be said of this later). Ingots of metal produced in this manner gave comparatively low hardness numbers ranging from 30 to 40 Rockwell A. Following a vacuum heat treatment at 1652°F, the hardness of these ingots characteristically dropped to 20 to 15 Rockwell A.

Daane(30) has continued his studies on the direct melt reduction method and is presently casting yttrium metal continuously from the calcium-yttrium fluoride reaction mix by means of a tantalum crucible which takes advantage of the density differences between the molten metal and calcium fluoride. This crucible has been fabricated with a bottom duct into which molten metal flows, solidifies and forms a plug. The reaction charge of calcium and yttrium fluoride is introduced from a continuous charging device mounted over the crucible. Following accumulation of metal and slag in molten layers, the plug is melted free and yttrium cast into cooled copper molds.

It has been reported by Daane and others that it is difficult to cast yttrium metal in this manner without voids being formed due to either shrinkage or "gas pocketing". To avoid this difficulty, several of the primary castings are now welded together and consumably arc-melted into larger ingots. The amount of inclusions has been lowered considerably in recent ingots prepared by the continuous technique, although the tantalum and calcium contaminations are about the same as those in the original direct melt reduction product. A summary of typical chemical analyses on metal prepared by this method is included in Table VI.

In the reduction method described, there are several factors which detract from its usefulness for economical production of high purity yttrium metal. These factors can be stated as follows:

a. The reactivity of molten yttrium with crucible materials and with impurities which may be present in the surrounding atmosphere necessitate the selection and use of expensive, refractory metal crucibles and careful control of the inert gas blanket. Metallic crucibles must be destroyed to recover the yttrium melt unless suitable production methods can be found for separating and casting the metal independent of the slag.

b. By virtue of the high melting point of yttrium, special high temperature furnaces and equipment are required.

c. The reduction involves direct contact and mixing of calcium with yttrium fluoride which could conceivably cause contamination of both the fluoride and the resultant metal product by impurities inherent in calcium handling, i.e. water, calcium oxide, nitrogen, carbon, etc.

Tests conducted on the reactivity of molten yttrium with various refractory metal and sintered oxide crucibles have shown that the oxides are, in general, unsuitable while tungsten gives the least contamination followed by tantalum and molybdenum in that order. Daane's work on the continuous casting method offers a possible solution to the problem of destruction of crucible materials, although it still has the disadvantage of using high temperature equipment and direct contact between massive calcium and yttrium fluoride during reduction. The purity of the "anhydrous" yttrium fluoride prepared by both the "dry" (described in succeeding pages) and "wet" process, at this time, had not been questioned. From recent investigations, it is now believed to be a major factor in the formation of inclusions present in yttrium metal produced by both the direct melt reduction method and the intermediate alloy process described below.

Intermediate Alloy (Sponge Process) Reduction

Spedding, Carlson and Schmidt(31) in 1956 undertook an investigation directed toward exploring the possibilities of developing a new metallothermic technique for preparation of yttrium at lower temperatures. Their studies indicated that yttrium could be prepared at comparatively low temperatures by formation of intermediate alloys of zinc or magnesium. Yttrium fluoride was again chosen as the starting material and calcium as the reducing agent. The most suitable fluoride for reduction was reportedly prepared through a "dry process" (see footnote bottom this page) although a few reductions were made using the "wet process" fluoride described previously. A description of the two methods for preparing zinc or magnesium alloys of yttrium are discussed in the following paragraphs.

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*In the "dry process", a one-half inch thick layer of Y_2O_3 powder is placed in monel reaction trays and heated under a stream of anhydrous hydrofluoric acid gas at 1067°F. Fluoride prepared by the "wet process" is quite fluffy, having a packing density of 0.9 g/cc whereas the fluoride prepared by the "dry process" has a packing density of 1.9 g/cc.

Since a zinc intermediate alloy was used successfully in the bomb preparation of thorium and zirconium metals, its possible use in preparation of yttrium was first investigated. It was found that zinc fluoride added to yttrium fluoride, calcium and iodine served not only as a booster but supplied zinc to form an intermediate alloy with yttrium. Sufficient heat was produced by the reaction of zinc fluoride and iodine with calcium to melt both the zinc-yttrium alloy and the slag mixture of calcium iodide-calcium fluoride thus forming two molten layers. Enough zinc fluoride and excess calcium was added to form a 80 per cent yttrium-20 per cent zinc alloy. Reactions were carried out in steel bombs lined with calcium fluoride and heated by a gas-fired furnace maintained at 1292°F. When the outside of the bomb reached approximately 1200°F, the charge ignited and the reaction and layer separation took place spontaneously. When cool, the contents of the bomb were removed and the liner and slag broken away from the massive zinc-yttrium alloy. The alloy was crushed, placed in a sintered calcium fluoride crucible and heated stepwise in vacuo at temperatures of 1544°F, 1786°F, and 2602°F respectively to remove zinc. The resultant product was a sponge of yttrium with a zinc content averaging 0.40 per cent by weight.

To consolidate the sponge, various melts were made in sintered zirconium oxide, magnesium oxide, calcium oxide, beryllium oxide, and graphite crucibles. In each case excessive contamination of the metal occurred from interaction of molten yttrium with the crucible materials. However, the sponge could be readily arc-melted under helium or argon using a water-cooled, tungsten electrode; the castings being formed in water-cooled copper molds. In this way, several ingots of metal averaging two inches in diameter and four inches long were prepared.

The yttrium metal yields from the zinc alloy process were variable, ranging from a low of about 85 per cent to a high of about 90 per cent of theoretical. Table III gives typical results obtained from chemical analyses of the arc-melted yttrium from zinc sponge. The metal characteristically was heavily contaminated by inclusions similar in appearance to those described on previous pages. From the high average carbon and nitrogen contents observed, these inclusions were believed to be primarily carbides, nitrides, fluorides and oxides although no analyses of oxygen were made on this type of metal. The hardness numbers on the as-cast metal ranged from 30 to 35 Rockwell A.

TABLE III

Typical Chemical Analyses of Arc-Melted Yttrium Sponge From the Zinc Alloy

Element	Content, per cent by weight
C	0.06
N	0.06
Fe	0.04
Zn	0.015
Ca	0.02
Cr	0.01
Mg	0.01
Si	0.02

Because of the difficulties in removing zinc, the undesirable amount of microscopic impurities in the final metal, and the low reduction yields observed in the zinc alloy process, an alternate method was explored by Spedding, Carlson and Schmidt. They substituted magnesium for zinc and conducted the reduction in open crucibles under a slightly pressurized inert atmosphere. The charge found to be most suitable consisted of yttrium fluoride, granular calcium, magnesium turnings and a calcium chloride flux. In the reaction, the melting point of yttrium was lowered markedly by alloying with magnesium and enough calcium chloride was added to form a 60 per cent $CaCl_2$-40 per cent CaF_2 slag mixture of low density which melted between 1372°F and 1472°F. This enabled reductions to be carried out at retort temperatures of 1742 to 1922°F. The reaction vessel was either a zirconium metal crucible or a sintered magnesia crucible inserted into a stainless steel retort (see Figure 2) which was equipped with a gas-tight head and a pressure relief valve. Alloys were prepared in this manner containing 15 per cent Mg, 17 per cent Mg, and 20 per cent Mg. These were actually ternary alloys since calcium was found to be present ranging from 7 to 8 per cent by weight, the amount depending on whether 10 or 20 weight per cent excess calcium was used as a reducing agent. Best results were obtained through the use of a 20 per cent excess of calcium and enough magnesium to form either the 20 or 17 weight per cent magnesium-yttrium alloy.

The alloys were most easily separated and removed from the magnesia crucibles by fracture of the crucible wall, whereas alloys formed in zirconium metal crucibles required separation by pulverization with an

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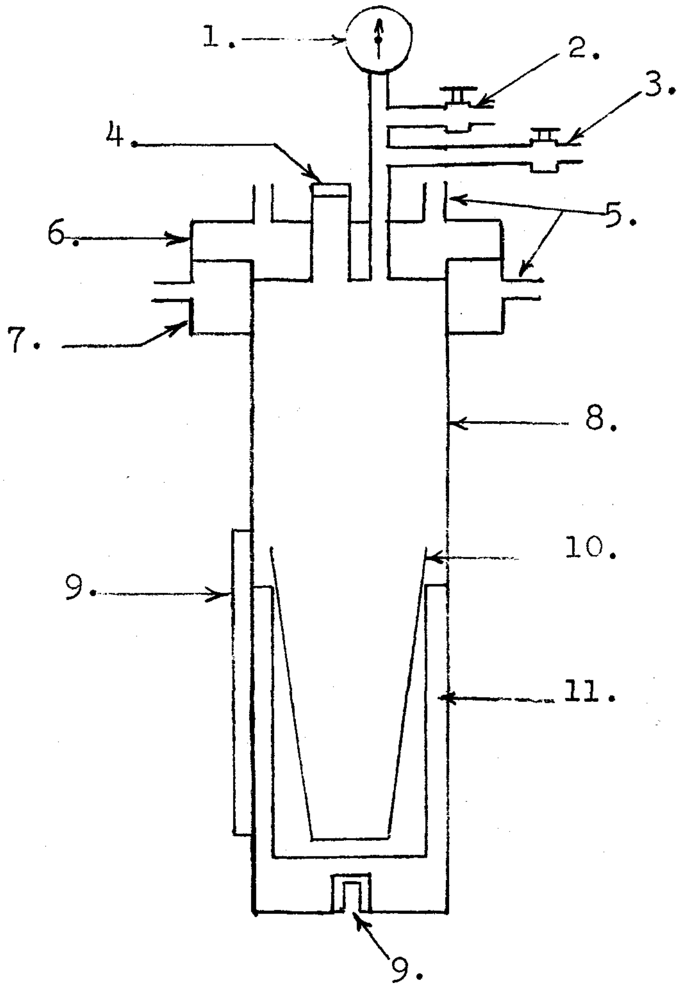
FIGURE 2

SCHEMATIC DIAGRAM OF AMES REDUCTION RETORT FOR PRODUCTION OF YTTRIUM-MGANESIUM ALLOY



1. Compound Vac-Pressure Gauge
2. Pressure Relief Valve
3. Vacuum Valve
4. Sight Port
5. Water Inlet (Outlet)
6. Water-Cooled Vacuum Head
7. Water Jacket
8. Stainless Steel Retort Wall
9. Thermocouple Wells
10. Zirconium Crucible
11. Graphite Retainer

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air hammer. Since this decreased the life of the metal crucible, an alternate method was investigated. It was found that the reaction mix could be maintained at a temperature where the alloy layer was a solid and the slag layer molten. A stainless steel retort with two side cooling chambers was designed which enable separation of alloy and slag by tilting and pouring at two different temperatures. Observations made on alloys obtained in this way indicated that some of the slag layer still adhered at the alloy interface even at molten slag temperatures. The subsequent melt and pouring operation to remove this alloy could conceivably cause contamination by mixing. Likewise, the zirconium pick-up by yttrium was increased by the double melt operation reaching higher than 1.5 weight per cent at times. Recently, Carlson(32) has gone back to the method of cooling in place with the modification that a tilt is given to the retort (which is normally upright) before solidification of the alloy layer. This has been found to help in the subsequent recovery of the alloy from zirconium crucibles, since Carlson reports that only a slight tap on the bottom of the zirconium serves to separate the massive alloys.

The alloys were crushed to approximately 1/2 inch pieces and heated in vacuo in either magnesia or zirconium metal crucibles to remove magnesium and residual calcium. The heating rate was carefully controlled and allowed to increase gradually from 1472 to 2192°F. No sintering or melting of particles occurred during this operation and the resultant sponge was easily removed from the crucibles. Table IV gives average results obtained in mid 1956 from the chemical analyses of 16 different lots of sponge prepared through the formation of an intermediate alloy of magnesium and yttrium. Yields of metal from 97-99 per cent of theoretical were consistently obtained by this procedure.

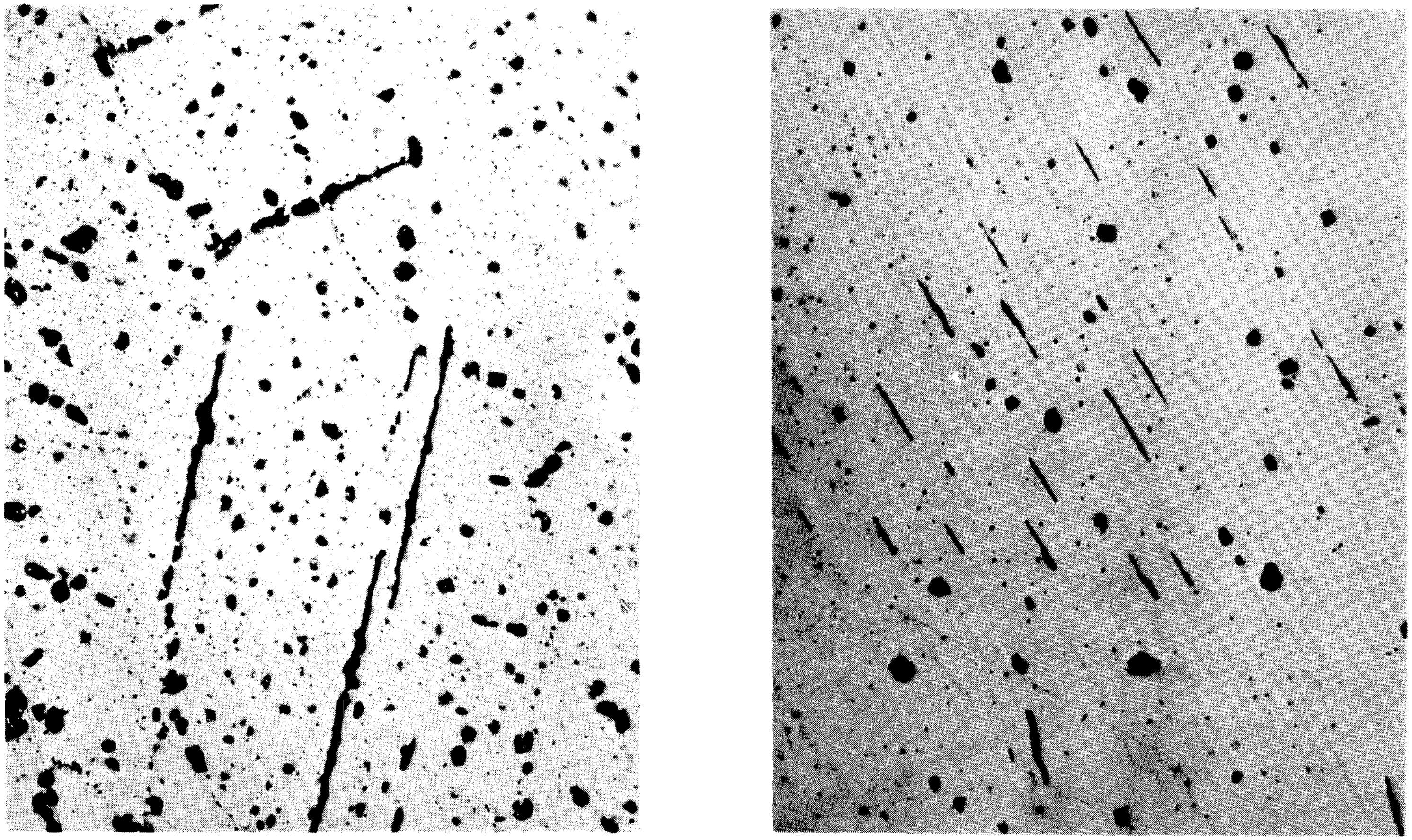
TABLE IV

Analysis of "Demaged" Yttrium Sponge Prepared in a Zirconium Crucible

Element	Content, per cent by weight
C	0.038 ± 0.007
N	0.032 ± 0.025
O	0.3 to 0.4
Fe	0.014 ± 0.005
Mg	0.02
Ca	0.02
Zr	1.0 ± 0.35

The yttrium sponge was arc-melted by a water-cooled tungsten electrode under a helium atmosphere producing ingots 2 inches in diameter and up to 8 inches in length. Table V gives an average of chemical analyses of samples taken from two arc-melted ingots of yttrium prepared in this manner.

Microscopic examinations of the yttrium produced through the magnesium alloy revealed that inclusions were still present in the microstructure of the arc-melted metal. Figure 3 depicts the microstructure typical of early sponge process yttrium produced in both zirconium and magnesia crucibles. Visual evidence of inclusion contamination as well as



250 X

Arc-Melted Yttrium as Polished, bright light. Sponge prepared in MgO crucible.

250 X

Arc-Melted Yttrium as Polished, bright light. Sponge prepared in Zr crucible

Figure 3 Photomicrographs of the microstructure of early sponge process yttrium produced in magnesia and zirconium crucibles. Characteristic inclusions are shown as dark gray or black platelets or rods

TABLE V

Analysis of Two Arc-Melted Ingots of Yttrium from Sponge Prepared in a Zirconium Crucible

Element	Content, per cent by weight
C	0.032 ± 0.009
N	0.039 ± 0.018
O	0.3 to 0.4
Fe	0.04 ± 0.003
Ca	0.02
Mg	0.02
Zr	0.72 ± 0.18

chemical analysis for carbon, nitrogen and oxygen have indicated that yttrium prepared in magnesia oxide crucibles contains a greater amount of inclusions. Several of the inclusions were removed by a mechanical probe and tentatively identified by x-ray diffraction as consisting primarily of yttrium oxide and some unidentified minor phases. Yttrium metal prepared in zirconium crucibles has had a characteristic hardness of 30 Rockwell A which has later been observed to decrease to 15-20 Rockwell A upon vacuum annealing at 1652°F.

The zirconium content is rather high, but Carlson(32) has demonstrated that sponge obtained from the product of an "in place" solidification of alloy and slag layers contains as low as 0.5 per cent by weight zirconium. Apparently, the proper control of retort temperatures during reduction and placing a limit on the time in which molten alloy is in contact with the zirconium crucible are factors in decreasing this contamination.

Further Studies on the Sponge Process Reduction for Yttrium Metal

The low temperature magnesium alloy method which will be referred to as the "sponge process", has been subjected to intensive research and development work during late 1956 and early 1957. This was primarily due to the need of a method for large scale production of yttrium metal. Spedding and co-workers have devoted considerable effort in attempting to solve problems posed by the method before a scale-up could be realized. These problems were three-fold:

(a) The relationship of the purity and stability of yttrium fluoride and the other reactants to the inclusions present in the final metal product.

(b) The relationship of unit operations, such as mixing, reduction, "demaging", and arc-melting to the quantity of inclusions.

(c) Fabrication of large retorts and equipment capable of producing yttrium metal of high purity in lots of 100 pounds or more.

Problems posed by consideration of the inclusions present have not been resolved. In the first place, all of the inclusions have not been identified. A method was devised at GE-ANPD(33) whereby yttrium metal was reacted in a solution of bromine in anhydrous methyl alcohol giving an insoluble residue which was believed to contain most of the non-metallic and probably some of the metallic inclusions. X-ray diffraction patterns of these residues have shown a predominence of two compounds, Y_2O_3 and YOF, with several minor phases which have tentatively been assumed to be mixtures of calcium compounds, magnesium compounds, yttrium fluoride, or carbide and nitride of yttrium. The amount of oxygen present in the metal has been estimated on samples whose bromine insoluble residues have shown a major phase of Y_2O_3. On the average, these estimated values have been different (generally higher) when compared with oxygen values obtained by vacuum fusion techniques or by a special spectrographic method devised by Fassel(34). However, there seems to be a general relationship between the bromine insoluble residue and the amount of inclusions present in the yttrium microstructure.

A study was made on the completeness of hydrofluorination of yttrium oxide by the "dry process" described previously. Factors which were studied included the effects of different firing temperatures in the conversion of yttrium oxalate to yttrium oxide, and the effects of variable times and temperatures of exposure in the hydrofluorination process itself. Carlson(32) has reported that oxalate ignition apparently has no effect if carried out at temperatures at which pronounced sintering does not occur in the oxide. On the other hand, the temperature, time, and depth of oxide layer exposed during hydrofluorination are definite factors. Conversions which were carried out at 1067°F for 8 hours on 1/2 inch layers of Y_2O_3 characteristically were 97-99 per cent complete. Upon increasing the temperature (to 1112°F thru 1292°F) and time of exposure during hydrofluorination, the percentage of conversion was generall increased to 99.3 to 99.5 per cent. For example, one batch of oxide hydrofluorinated in a 1/2 inch layer at 1112°F for 13 hours showed a

99.3 per cent conversion to fluoride. However, the results were observed to be variable on different lots of oxide and the calculation of per cent conversion are questionable since analytical methods for precise determination of Y_2O_3 and/or YOF in YF_3 have not been devised. Comparisons were also made on the amount of inclusions present in the microstructure of yttrium prepared from both "wet process" and "dry process" fluoride. Here again, the results were variable, although comparative differences in the amount of inclusions present were generally very small.

Recently analysis of oxygen in yttrium fluoride by spectrographic methods (see Fassel(34) above) has shown a definite correlation between the amount of oxygen in the fluoride and the resultant metal. The analytical method involves the arcing of YF_3 in a carbon cup under a partial pressure of argon and comparing the intensity of the resultant line with the pure excited argon line. The method is empirical since no pure standard exists for either yttrium or yttrium fluoride. Compilation of data by Carlson at Ames has shown that a fluoride having an "intensity ratio" of 0.3 to 0.4 generally gives a metal with oxygen contaminations ranging from 1000 to 1500 ppm on subsequent reductions.

The relationship of unit operations to the amount of inclusions present in the metal has been studied by analysis of products formed during successive stages of the reduction. Control of the purity of reactants has mainly involved preparation of distilled calcium, vacuum-dried calcium chloride, and high purity magnesium for use in the reduction mixture. The mixing of reactants has been carried out in a mixing drum which is provided with an inert atmosphere. Transfers are accomplished by means of polyethylene funnels and bags.

The bromine insoluble residue in the sponge has been observed to change during the "demaging" step, this change, in most cases, being an increase. It is probable that this is largely due to a concentration of non-metallic and/or metallic impurities which were originally present in the alloy. Carlson(32) has investigated the possibility of lowering the calcium and magnesium content in the sponge by exposing the alloy for longer periods of time at slightly higher temperatures during the "demaging" step. Initial results on these tests have indicated that calcium and magnesium contaminations can be lowered somewhat during this step of the sponge process.

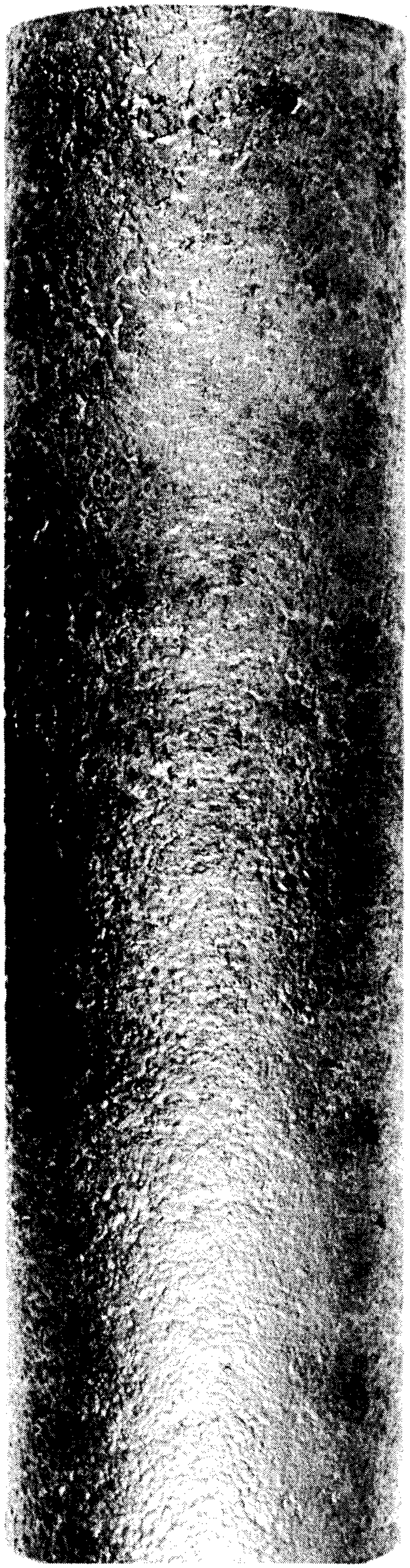
Changes in total amount of inclusions in yttrium during the arc-melting operation has been variable, sometimes showing an increase and sometimes a decrease. In order to bring about further lowering of the calcium magnesium content in the end metal, the Ames Laboratory is now arc-melting large yttrium ingots under a vacuum in the final fabrication step with some degree of success (see Table VI).

The fabrication of equipment suitable for preparing sponge yttrium in large lots has been accomplished for the most part. Spedding and co-workers now have a retort and gas-fired furnace with zirconium crucible accessories capable of reducing up to 100 pounds of yttrium fluoride at one time. In addition, two consumable arc-melting units are being used to process pressed yttrium sponge electrodes into ingot form.

Several large batches of yttrium sponge have been prepared at the Ames Laboratory and arc-melted ingots fabricated ranging up to 20 inches in length and 4 to 6 inches in diameter. The averaged chemical analyses of sixteen 4 inch ingots and ten 6 inch ingots received at GE-ANPD from Ames during the period January 1, 1957 to July 15, 1957 are given in Table VI. Included are analyses on 5 ingots of metal also produced at Ames but by the direct melt reduction process. Similar analytical data is given for comparison on all metal received at GE-ANPD during 1956. Figure 4 is a photograph of one of the 4 inch diameter ingots with its typical microstructure.

By comparison, the recent metal has been of somewhat higher degree of purity than earlier yttrium ingots. Calcium and magnesium contents are lower especially in the vacuum arc-melted ingots although oxygen contents remain high. Some arc-melted ingots of yttrium metal have shown segregation of impurities in the top and bottom sections, although this segregation has not been uniform with respect to any one particular contaminator. On the other hand, several large ingots have been prepared with little or no segregation. It is evident that more work is needed particularily with regard to elimination of or minimizing the oxygen, carbon, nitrogen, and metallic impurities in sponge process yttrium metal.

The relative merits of the sponge process and the direct melt reduction process are about the same if one considers the fact that neither has produced an end yttrium metal product which was completely free of inclusions. Perhaps this is not surprising since both processes use the same starting material and reducing agent and both have involved direct intimate contact between calcium and yttrium fluoride during reduction. However, the sponge process has achieved some measure of respect in that



30 lb. Yttrium ingot double consumable arc-melted from sponge

250 X

As-Polished, Bright Light, Representative microstructure of Yttrium Ingot Pictured at Left

Figure 4. Recent Yttrium Metal Produced through the Sponge Process

TABLE VI

Averaged Chemical Analyses of Ames Yttrium Ingots

(Analyzing Sites: Ames Laboratory and GE-ANPD)

Content, ppm or weight per cent (w/o)

	Sponge Process, 1956[2]		Sponge Process,[3] 4 in. P.D., 1957		Sponge Process,[4] 6 in.).D., 1957		Direct Melt[5] Process, 1957	
Element	Ames	GE	Ames	GE	Ames	GE	Ames	GE
C	322	217	150	122	216	145	117	116
N[6]	345	330	360	140	330	300	427	356
N[7]	---	1,270	---	82	---	160	---	260
O[8]	---	4,000	---	3,445	---	4,550	---	2,775
O[9]	1,845	---	2,160	---	2,847	---	1,694	---
Br_2, insol (w/o)	1.57	3.50	0.74	1.23	0.64	2.02	1.40	1.43
Ca[10]	582	578	460	304	15	5	438	500
Mg	530	875	433	287	30	23	---	---
Fe	226	363	173	270	191	540	213	200
H_2	---	---	---	105	---	109	---	118
Zr (w/o)	1.01	1.0	0.74	1.0-0.5	0.98	0.66	---	---
Ta (w/o)	---	---	---	---	---	---	0.84	0.50

See Page 65 for description of superscripts 1 thru 10

1. Data shown represents an average of all results on ingots in a group irrespective of whether analyses were made at the top or bottom positions.
2. Averaged from 27 arc-melted ingots totaling 200 pounds.
3. Averaged from 20 arc-melted ingots totaling 550 pounds.
4. Averaged from 10 vacuum arc-melted ingots totaling 433 pounds.
5. Averaged from 70 ingots totaling 127 pounds, arc-melted from primary castings prepared in tantalum.
6. Nitrogen by micro-Kjeldahl.
7. Nitrogen by vacuum fusion.
8. Oxygen by vacuum fusion.
9. Oxygen by spectroscopic method (see reference 34)
10. Calcium, magnesium, iron, silica, tantalum, and zirconium determined spectroscopically.

it has lent itself admirably to large scale production methods and has, in fact, already provided a significant amount of yttrium in massive form with a much cleaner microstructure. It is suspected that considerably more work is still needed on both the sponge and direct melt reduction process before a strictly high purity yttrium metal is realized.

METALLOTHERMIC REDUCTIONS WITH LITHIUM

Several reductions of yttrium fluoride have been carried out at GE-ANPD since early in 1955. Lithium was found to be suitable for direct melt reduction of the fluoride since lithium fluoride provided a good slag layer for consolidating yttrium melts. The reductions were generally conducted in tantalum and molybdenum crucibles under an atmosphere of argon or helium. However, the yields were low unless a considerable excess of lithium was used. It was also noted that metal formed by lithium reduction of the fluoride has still contained microscopic inclusions similar to those described previously.

A considerable amount of work is presently going on at GE-ANPD in perfecting a method which involves introducing lithium vapor to molten yttrium fluoride in an evacuated steel bomb at elevated temperatures. There have been indications that it may be possible to form a sintered yttrium metal matrix at some temperature below the melting point of yttrium and the molten lithium fluoride slag at least partially separated from the matrix by gravity.

Studies at General Electric on the problem of preparing anhydrous yttrium fluoride suitable for reduction have resulted in the preparation of a fluoride product which has a measured melting point ranging between 2110 and 2120°F. It was prepared by introducing anhydrous hydrofluoric acid gas to hydrated yttrium fluoride at temperatures from 2200 to 2250°F and subjecting the molten fluoride to electrolysis with a carbon electrode to remove oxygen. The cooling curves of this material characteristically showed another arrest at 1860 to 1890°F which could indicate either a solid state transformation of YF_3 or the presence of impurities. A series of melting point determinations are being conducted on fluoride prepared in this manner to ascertain the effect of extended electrolysis and exposure to anhydrous hydrofluoric acid gas at molten fluoride temperatures. In this way, it is hoped that the stability, and ultimately the purity of the final product can be deduced. Yttrium fluoride prepared by this method could conceivably be obtained in a high state of purity and, because it is molten, could be cast into various forms for subsequent reductions with a minimum of atmospheric contamination.

PROPERTIES OF YTTRIUM METAL

Introduction

Interest in the properties of yttrium has largely been generated by its potential application as a basic moderator material in nuclear reactors. Prior to 1955 yttrium metal was in limited supply and property data scarce. With the development of reduction methods in 1956 whereby yttrium could be obtained in fairly large amounts, General Electric-ANPD initiated a program to obtain information on a fairly comprehensive scale. As a consequence, most of the data on yttrium presented in the following pages were determined within the past year.

It should be emphasized that property measurements were carried out almost exclusively on yttrium metal produced either by the sponge process or direct melt reduction method. As stated in the previous section on reductions, the metal which has been prepared by these methods can not be considered as strictly "high purity" since it contains varying amounts of non-metallic and metallic impurities. The properties which were determined, while representative of yttrium metal, may in some cases be subject to re-evaluation when high purity metal becomes available.

In preparing this section on the properties of yttrium, the primary purpose has been to present to the reader a summary of its physical, chemical, mechanical, and nuclear properties which have been determined. For the sake of completeness, a general discussion has been included of the analytical and metallographic methods employed at General Electric-ANPD for quality control of the metal, its reactivity with other metals and alloys and its known biological effects.

Physical and Chemical Properties

Yttrium is one of the transition elements and it occupies a position in Group III-A of the periodic table. It is a light, silvery metal possessing one of the lowest densities of the metals in the subgroup, surpassed in this respect only by scandium. In order of ascending densities, yttrium ranks approximately 11th among the common metals. Arc-melted yttrium is comparatively soft (60-70 Brinell), similar to iron, and about twice as hard as magnesium. Upon arc-melting both the lanthanide metals and yttrium characteristically crystallize with microstructures possessing large, coarse grains. Yttrium has a high melting point similar to iron and is the third highest in the lanthanide series, both lutecium and thulium exhibiting higher melting points. Its vapor pressure is low by comparison with the lanthanide metals, being similar to lanthanum and cerium.

The physical constants measured for yttrium metal and its chemical behaviour in various environments are given in Tables VII and VIII, respectively. The singular hexagonal close-packed structure of yttrium has been confirmed to the melting point by both high temperature x-ray diffraction and high speed thermal analysis studies. A scrutiny of crystallographic data serves to illustrate the similarity of yttrium with the lanthanide metals and especially with those from gadolinium through erbium. For example, the mole atomic volumes, metallic radii, and axial ratios (i.e., c_o/a_o)

determined for a series of comparable lanthanides and yttrium are as follows:(35)

Element	Structure	C_o/a_o	Mole at. vol. (cm3)	Metallic Radii Å
La	hcp	1.613	22.544	1.8852
Pr	hcp	1.612	20.818	1.8363
Nc	hcp	1.613	20.590	1.8290
Gd	hcp	1.590	19.941	1.8180
Tb	hcp	1.581	19.258	1.8005
Dy	hcp	1.573	18.989	1.7952
Ho	hcp	1.570	18.745	1.7887
Er	hcp	1.570	18.458	1.7794
Tm	hcp	1.570	18.131	1.7688
Lu	hcp	1.585	17.768	1.7516
Y	hcp	1.571	19.886	1.8237

While yttrium has measured values for thermal expansion and thermal conductivity which are of the same order as zirconium metal, it differs from zirconium in one important respect. This difference is in the positive temperature coefficient of thermal conductivity which it has been observed to possess; a characteristic which yttrium shares with aluminum, brass, and various amorphous non-metallic solids. The electrical resistivity of yttrium is approximately 40 times that of copper at room temperature, the resistivity increasing almost linearly with increasing temperature.

Like the lanthanides, yttrium is a moderate reducing agent although it is much more stable, in general, in dry air. The purity of yttrium metal is believed to have considerable effect on its chemical reactivity particularly in corrosive or reactive environments. Pointing up this fact are the results in Table IX in which the static air oxidation resistance was observed to be much better on a vacuum arc-melted yttrium metal with lower impurity content. Likewise, the progress curves in hydriding yttrium shown in Figure 11 imply higher hydrogen contents with increasing purity of samples of metal produced from 1954 thru 1956.

Yttrium reacts with carbon tetrachloride decomposing it.(35) The latter is therefore not suitable for extinguishing yttrium metal fires. The metal reportedly reacts with boiling sulphur(35) to form the sesquisulfide and forms silicides, carbides, phosphides, arsenides, and antimonides by direct union.(35) An outstanding feature of the chemistry of yttrium is its reaction to take up hydrogen and form a solid, metallic hydride whose composition is temperature and hydrogen pressure dependent. It forms one of the most stable of the known metallic hydrides and, as such, has considerable potential in nuclear applications.

TABLE VII

Physical Constants of Yttrium Metal

Property	Value (s)	Reference
Crystal Structure	Hexagonal close-packed	(36)
	$A_o = 3.6474 \pm 0.0007$ Å	
	$C_o = 5.7306 \pm 0.0008$ Å	
Density, Crystal	4.472 gms. per cm^3	(36)
	279.2 lbs. per ft^3	
Density, arc-melted from sponge, average*	4.47 ± 0.01 gms. per cm^3	
Melting Point, tentative	2822 - 2826°F	See Fig. 5
Boiling Point, estimated	5840°F	(36)
Vapor Pressure	0.01 mm. Hg (2732°F)	See Fig. 6
	0.0001 mm. Hg (2480°F)	
Heat of Fusion, estimated	4.1 K cal per mole	(36)
Heat of Vaporization		
Estimated	94 K cal per mole	(36)
Calculated	80 K cal per mole	(37)
Heat Capacity, estimated	6.01 cal/mole - °F (0°C)	(36)

*Average of measured density values observed on a series of yttrium ingots as received. Densities determined by displacement in toluene at 70°F.

TABLE VII

Physical Constants of Yttrium Metal (Continued)

Property	Value (s)	Reference
Ionization Potentials	6.377 volts (YI)	(39)
	12.333 volts (YII)	
Free Energy Function, Gaseous = $(F^{\circ} - H^{\circ})/T$	37.371 cal/deg-mole (298°K)	(38)
	40.284 cal/deg-mole (500°K)	
	44.221 cal/deg-mole (1000°K)	
	48.015 cal/deg-mole (2000°K)	
Thermal Conductivity	6.9 ± 0.2 BTU/hr-ft-F° (800°F)	See Fig. 7
	5.95 ± 0.3 BTU/hr-ft-F° (212°F)	
	7.25 ± 0.3 BTU/hr-ft-F° (800°F)	
	11.06 ± 0.5 BTU/hr-ft-F° (1832°F)	
Average Coefficient, Linear Thermal Expansion	7.02×10^{-6} per °F (70-2000°F)	See Fig. 8
Electrical Resistivity	$69 \pm 3 \times 10^{-6}$ ohm-cms (70°F)	See Fig. 9
Wave Lengths of Characteristic X-rays		
K Series Alpha 1	0.82879 Å	(44)
Alpha 2	0.83300 Å	
Beta 1	0.74068 Å	

TABLE VII

Physical Constants of Yttrium Metal
(Continued)

Property			Value (s)	Reference
Wave Lengths of Characteristic X-rays				
	L Series	Alpha 1	6.4497 Å	
		Alpha 2	6.4555 Å	
		Beta 1	6.2117 Å	
Heat of Combustion, ΔE or Heat of Formation, Y_2O_3, ΔH_f			-455.45 ± 0.54 K cal/mole (25°C)	(45)

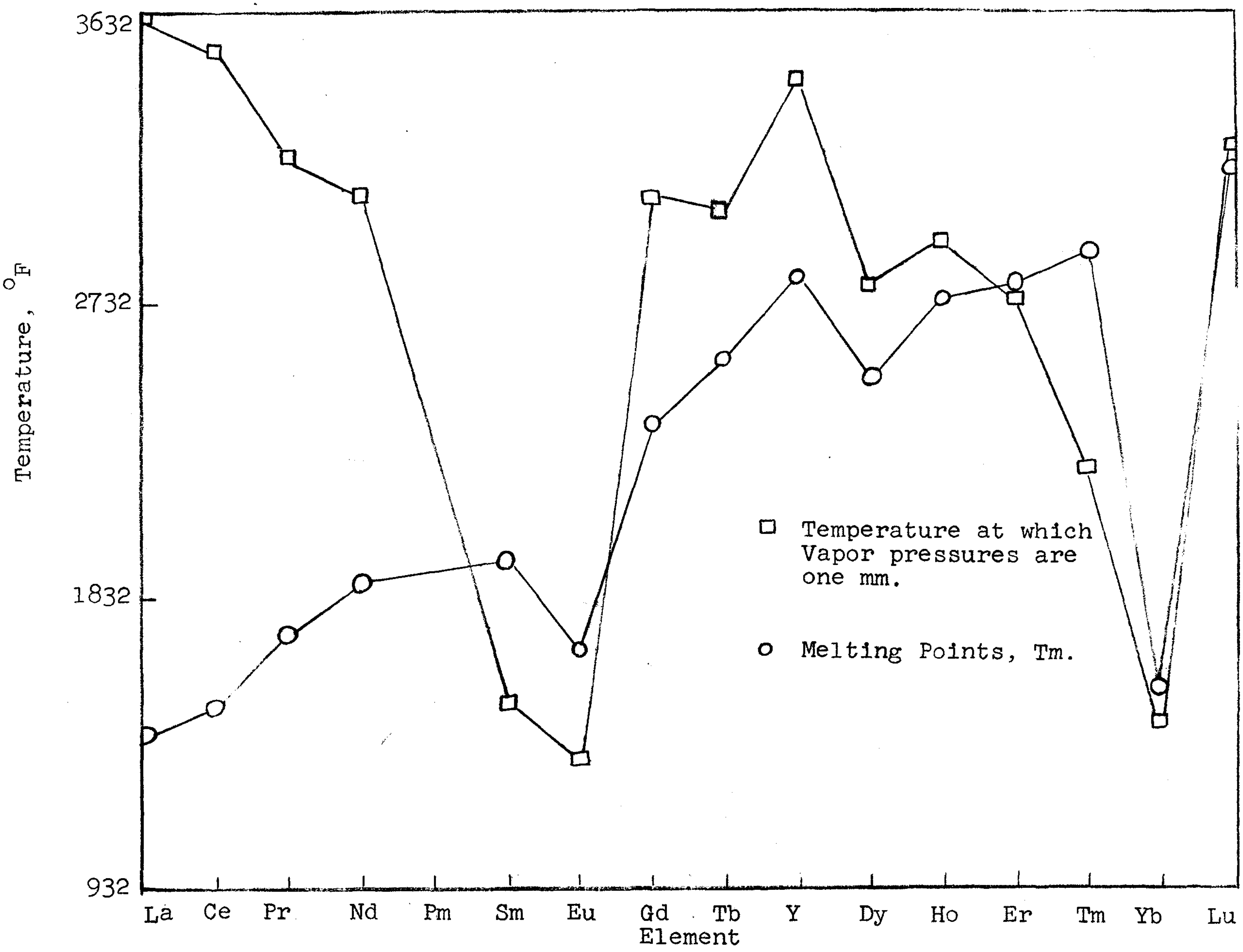


Figure 5. Melting Points and Vapor Pressures of the Lanthanides and Yttrium Metal (37)

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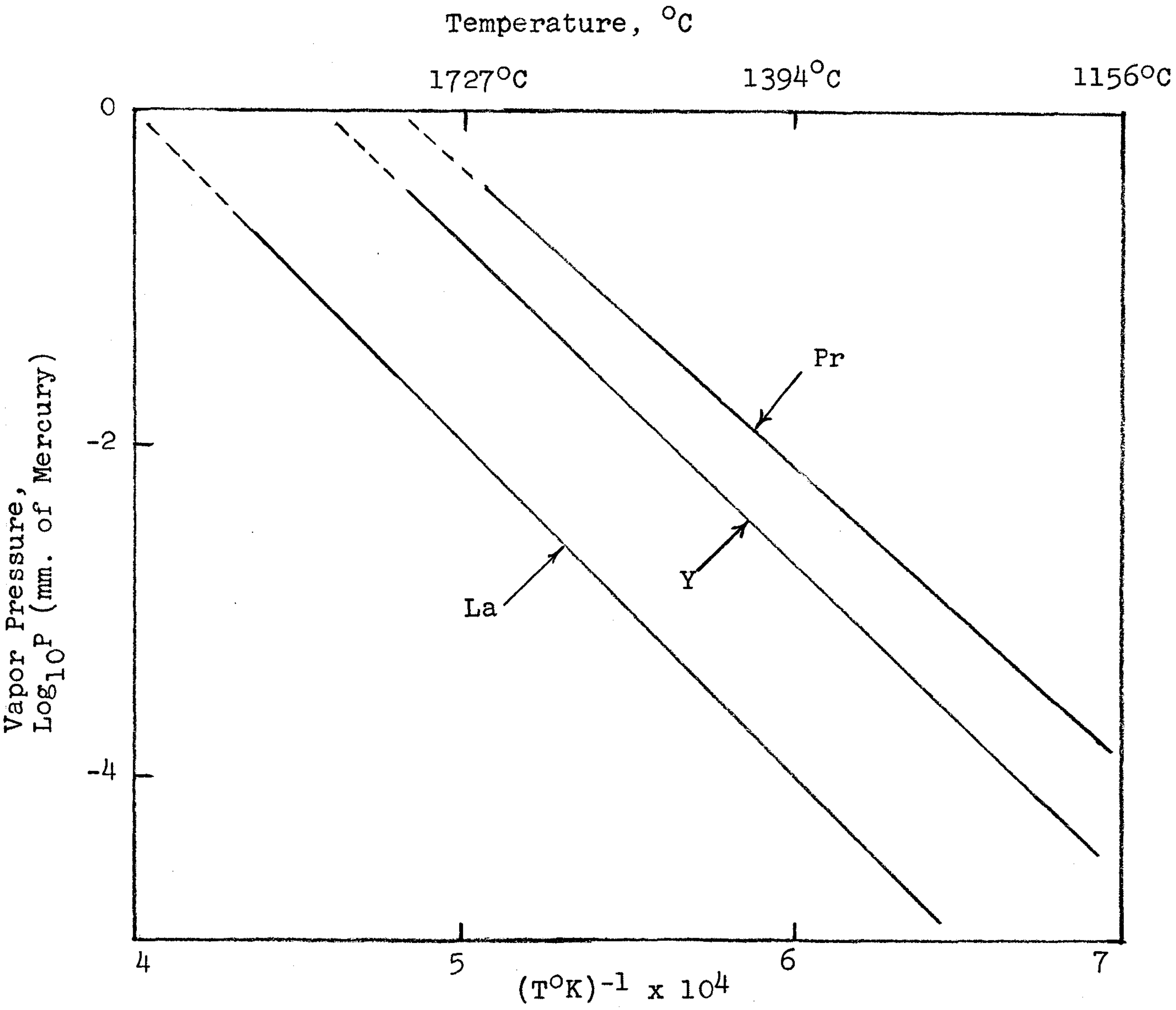

Figure 6, Vapor Pressures of Lanthanum, Praseodymium and Yttrium Metals(37)

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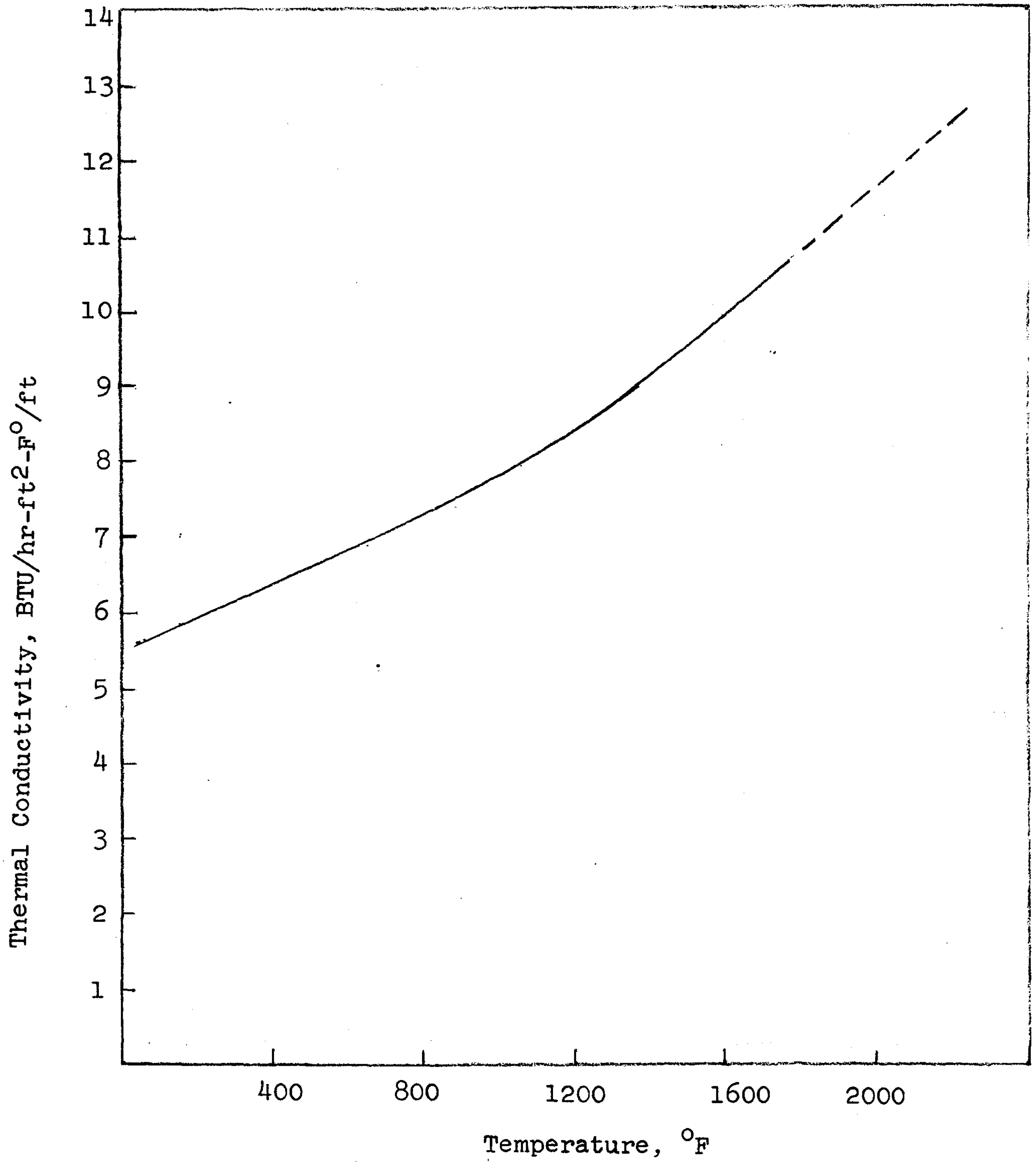


Figure 7. Thermal Conductivity of Yttrium Metal as Function of Temperature (40,41)

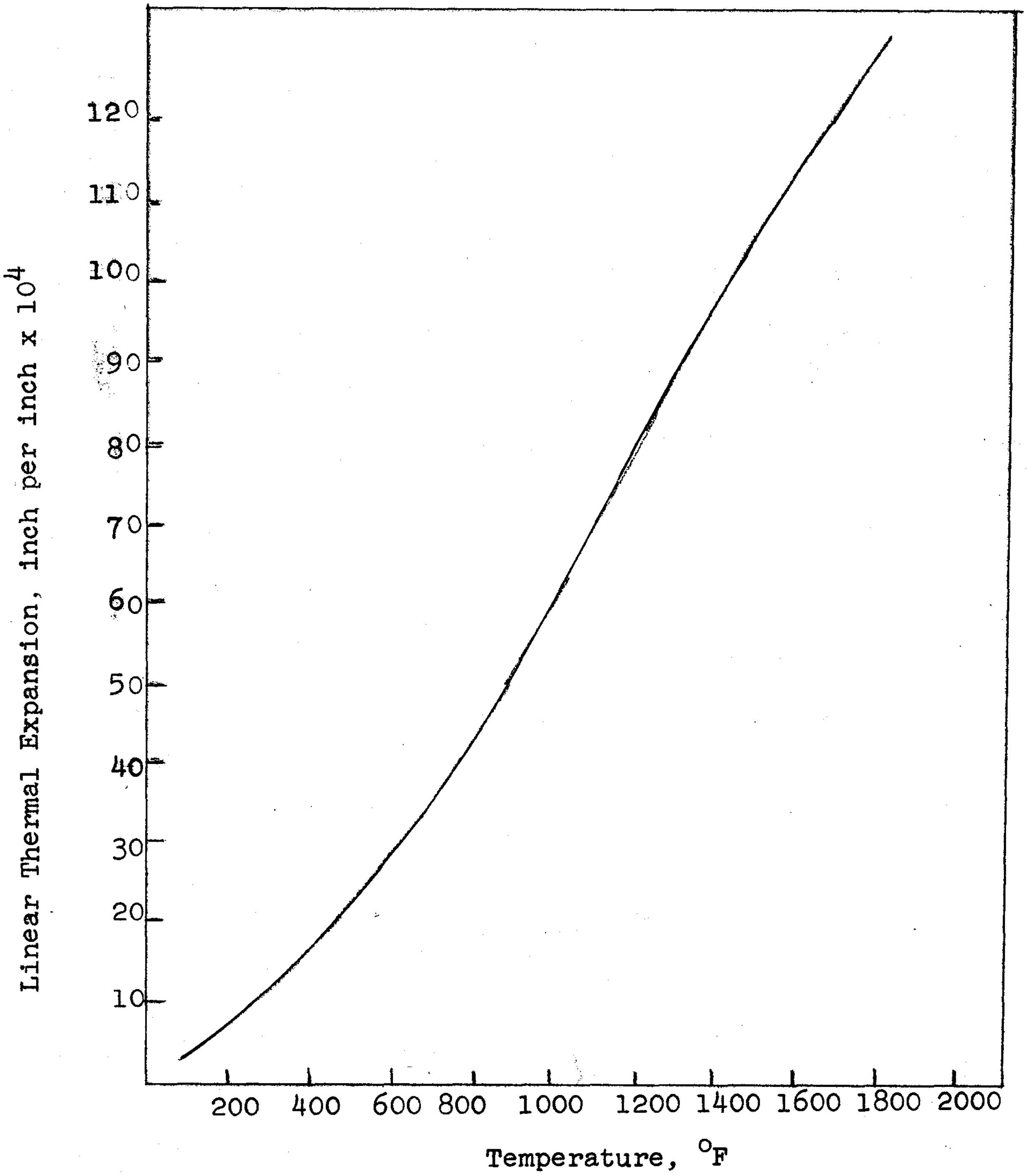


Figure 8. Linear Thermal Expansion of Yttrium Metal as a Function of Temperature (42)

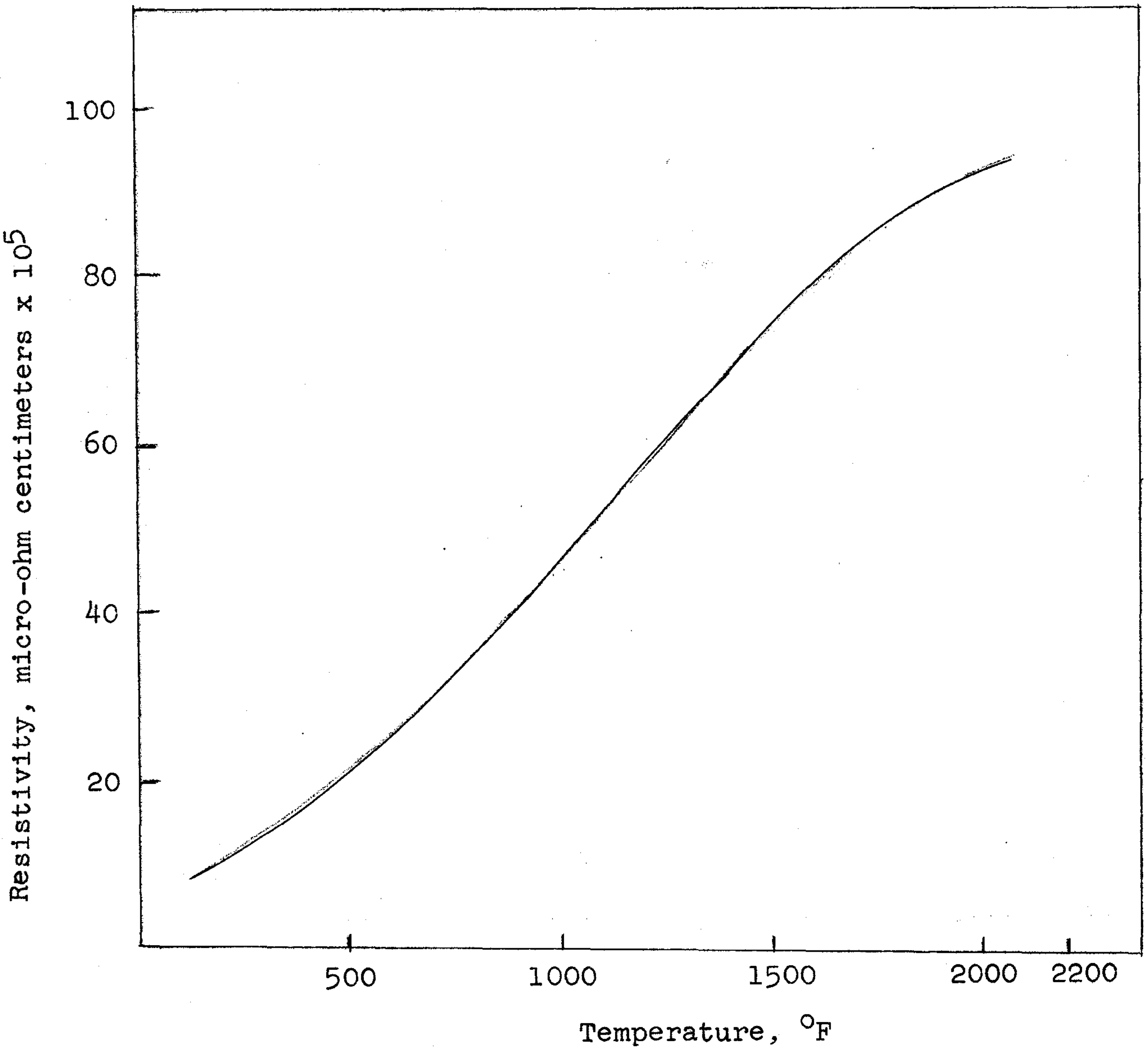


Figure 9, Electrical Resistivity of Yttrium Metal as Function of Temperature[(43)]

TABLE VIII

Chemical Properties of Yttrium Metal

Environment	Behaviour
Hydrochloric, sulfuric or nitric acids	Cold, dilute or concentrated: massive metal reacts readily with evolution of hydrogen and formation of salt with anion of acid.
Hydrofluoric acid, aqeous	Slight reaction between massive yttrium and 47-10 weight per cent aqueous hydrofluoric in the cold. Reaction occurs at very slow rate.
Water	Rapid reaction and oxidation of finely divided yttrium in boiling water. Considerable etching and oxidation of surface of massive yttrium after 5 hours exposure to boiling water.
Cupic Sulfate, aqeous	Solid yttrium reacts in the cold with a 5 to 10 per cent cupric sulfate solutions in water. Some evolution of hydrogen. Copper is plated on a platinum electrode if it is externally connected with an yttrium rod in the same solution.

TABLE VIII

Chemical Properties of Yttrium Metal (Continued)

Environment	Behaviour
Molten zinc chloride	Rapid deposition of zinc on surface of massive yttrium when dipped into molten salt.
Magnesium oxide, calcium oxide, beryllium oxide, aluminum axide	Partial reduction of the oxides by yttrium at temperatures above 2000°F. Order of decreasing reactivity is apparently $Al_2O_3 > BeO > MgO > CaO$.
Graphite	Forms carbides with yttrium at molten metal temperatures (2800°F). Some indications of reactions at lower temperatures.
Static Air Oxidation (Figure 10, Tables IX and X)	Lower impurity contents increases the static air oxidation resistivy of yttrium (See Tables). In general, the surface of massive yttrium blackens to 800°F. At higher temperatures pronounced oxide layers form and destructive oxidation apparently proceeds largely through intragranular penetration.

TABLE VIII

Chemical Properties of Yttrium Metal (Continued)

Environment	Behaviour
Nitrogen, gaseous	No apparent reaction with nigrogen gas at temperatures below 1400°F. At higher temperatures nitrogen is occluded, minor phases of yttrium nitride having been identified in the metal at 1800 - 2200°F.
Hydrogen (Figure 11)	Yttrium can be hydrided at temperatures as low as 1000°F and as high as 2700°F in 15 psi hydrogen to produce solid, hydrided bodies possessing metallic characteristics. Hydrogen composition depends on equilibrium conditions of temperature and hydrogen pressure during formation.

TABLE IX

One Hundred Hour Static Air Oxidation of Yttrium Metal(46)

	Weight Gain of Sample per Unit Surface Area, mgms. per $inch^2$	
Temperature, °F	Yttrium XC-100*	Oremet Yttrium, XC-109*
Room Temperature	0	0
300	1.6	
600	0.8	
700	7.0	
800	40.2	
900	126.5	
1000	352.5	200 (140 hours)
1200	500 (powdered)	

*Yttrium XC-100 was prepared by the sponge process and arc-melted twice under an inert atmosphere. Oremet yttrium XC-109 was prepared similarily with the exception that the metal ingot was double arc-melted under vacuum at the Oregon Metallurgical Corporation, Albany, Oregon. The chemical analyses of the two are:

	Oxygen	Calcium	Magnesium
XC-100	2900-3200	100-500	100-500
XC-109	2800	10-50	10-50

TABLE X

Static Air Oxidation of Yttrium at 1400°F(46)

Time, hrs.	Yttrium Specimen*	Wt. Gain of Sample per Unit Surface Area, mgms per in^2	Average Oxide Layer, mils
1	XC-100	100	8.4
	XC-109	28.3	---
2	XC-100	315.2	26
	XC-109	---	---
3	XC-100	329.5	28.5
	XC-109	54.8	---
4	XC-100	458.2	50
	XC-109	---	---
5	XC-100	562.9 (powdered)	---
	XC-109	125	10-15

*Yttrium specimens as designated are described in footnote to Table IX.

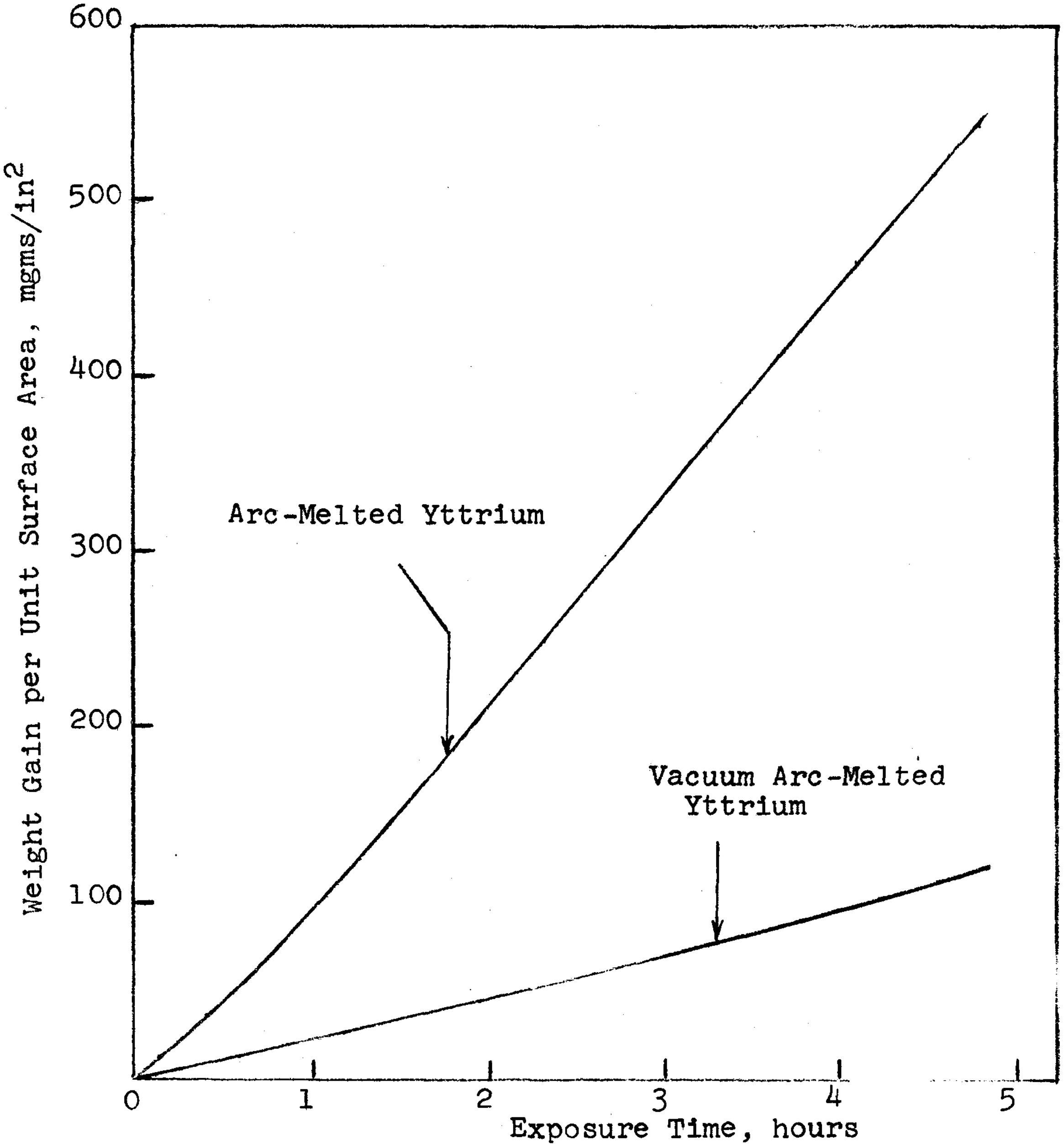


Figure 10 Rate of Static Air Oxidation of Vacuum Arc-Melted Yttrium Compared to Arc-Melted Yttrium at 1400°F

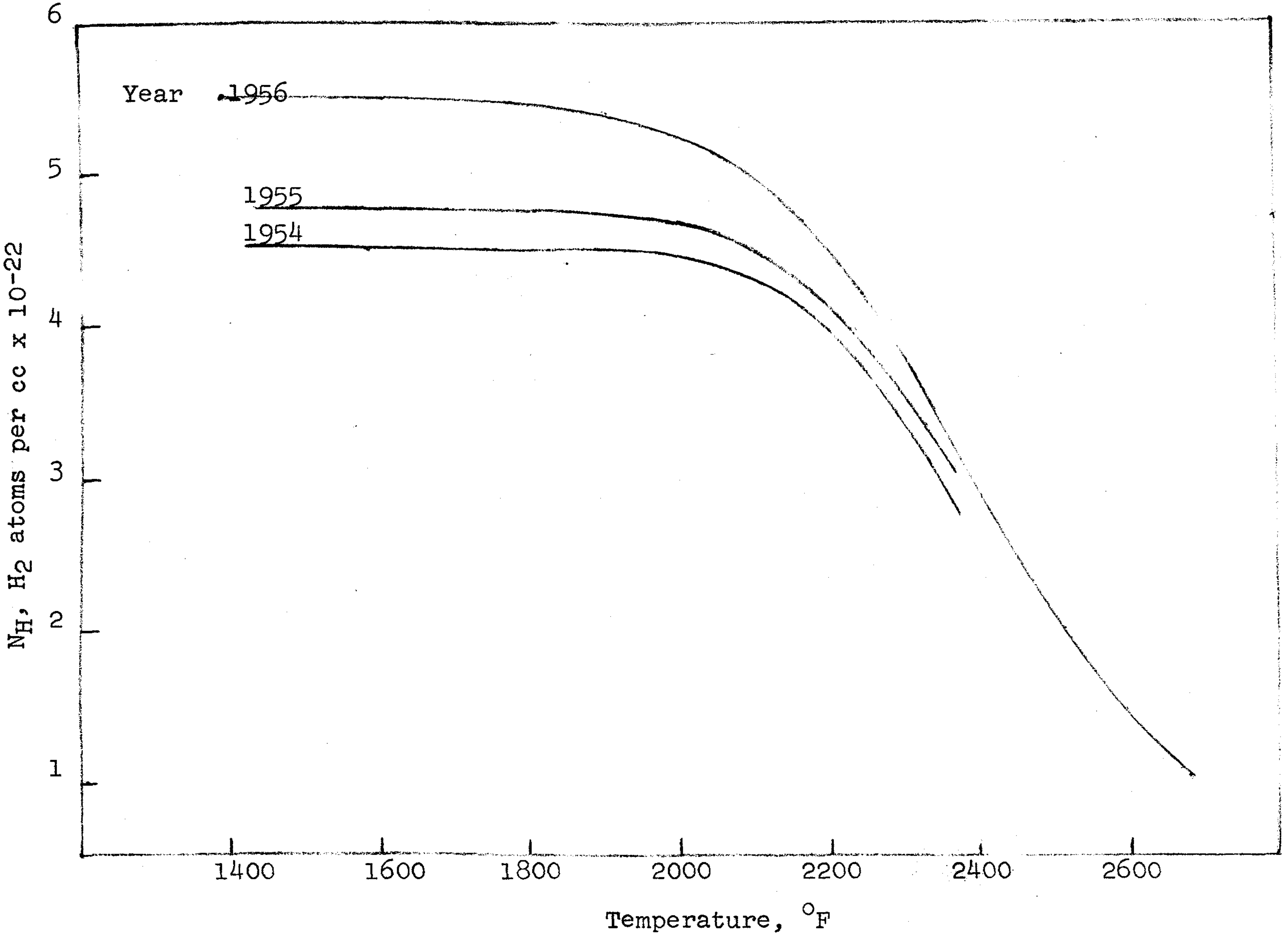


Figure 11. Chronological Improvement in Purity of Yttrium as Shown by Hydrogen Absorption as a Function of Temperature

Reactivity of Yttrium Metal with Other Metals and Alloys

The oxidation resistance of yttrium metal (or metallic hydrided yttrium) is such that some sort of a cladding material is needed if these materials are to be useful as high temperature components. Ordinarily, cladding must form a good, butnot excessive, diffusion or reaction bond with the substrate metal, and in most cases should exhibit adequate strength and good heat transfer characteristics. In order to determine what metals or alloys are most likely to form a useful clad, it is first necessary to study the basic reactivity or diffusion characteristics. For this reason, a series of such tests were conducted at General Electric-ANPD(47) on solid yttrium with several other metals or alloys which were potentially either hydrogen barrier or oxidation resistant clad materials. The manner in which these tests were conducted and the results which have thus far been obtained are described in the following paragraphs.

For the purpose of the tests, rods of yttrium approximately 1/8 inch in diameter were press fitted into blind-end capsules of various metals and alloys and end-plugs of the outer material press fitted and welded on top of the yttrium. The specimens were then heated for 100 hours (or less) at a number of temperatures either in air or under an inert atmosphere. They were then cooled to room temperature, cross-sectioned, and polished for microscopic examination of the interfaces. For low melting metals or alloys, reactivity tests were conducted either by immersion of yttrium in molten test material or by melting the material in yttrium crucibles. The results are given in Table XI. From these results it is apparent that there is only slight interaction or diffusion between yttrium and tantalum, molybdenum, titanium, and columbium up to 2200°F. The stainless steels, nickel, palladium, Nichrome V, lead, and aluminum show degrees of diffusion, interaction, and actual alloying at temperatures ranging from 1200°F to 1800°F. It is further evident that nickel, nickel-base or iron-base alloys are extremely reactive with solid yttrium. For example, Figure 12 is a photograph of the cross-section of a Nichrome yttrium couple which shows extensive diffusion of an element or elements from the Nichrome to form a low-melting phase in the center of the yttrium specimen. Also considering the original diameter and series of diffusion or reaction zones which are present, the yttrium specimen had lost its original integrity.

Molybdenum, tantalum, columbium and titanium may be considered as metallurgically stable for cladding applications. In order to form a bond with yttrium, these materials can probably be used if cladding is carried out at elevated temperatures and/or pressure exerted either by working or applying hydrostatic methods. The interface of a molybdenum and yttrium couple at 2200°F is also shown in Figure 12 indicating no extensive diffusion or reaction.

An interesting side-light of this work was realized when it was found that there was no interaction between uranium and yttrium at molten uranium temperature. Also, the copper-yttrium couple surprisingly showed little or no interaction at temperatures to 1300°F when exposed for a short length of time.

TABLE XI

Solid State Interaction of Yttrium Metal With Other Metals and Alloys

KEY: A - None Detected; B - Slight; C - Marked Diffusion Areas;

D - Extensive Interaction

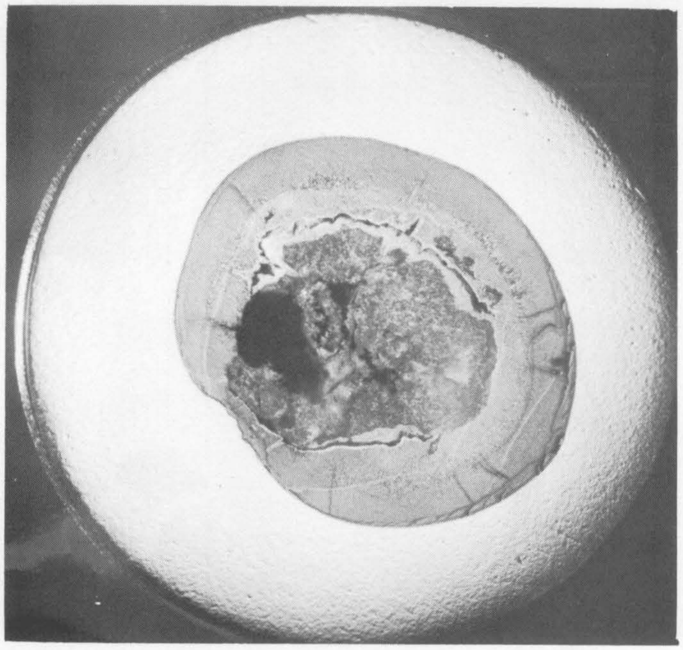
Test Material	Temperature °F	Time Hrs.	Extent of Interaction at Interface
Molybdenum	1500	100	A
	2000	100	A
	2200	100	A
Columbium	1500	100	A
	2200	100	A
Titanium	1500	100	A
	2200	100	A
Tantalum	1500	100	A
	2200	100	A
Zirconium	1500	100	A
	2200	100	B
Type 446 Stainless Steel	1500	100	B
	1800	100	C

TABLE XI

Solid State Interaction of Yttrium Metal With Other Metals and Alloys
(Continued)

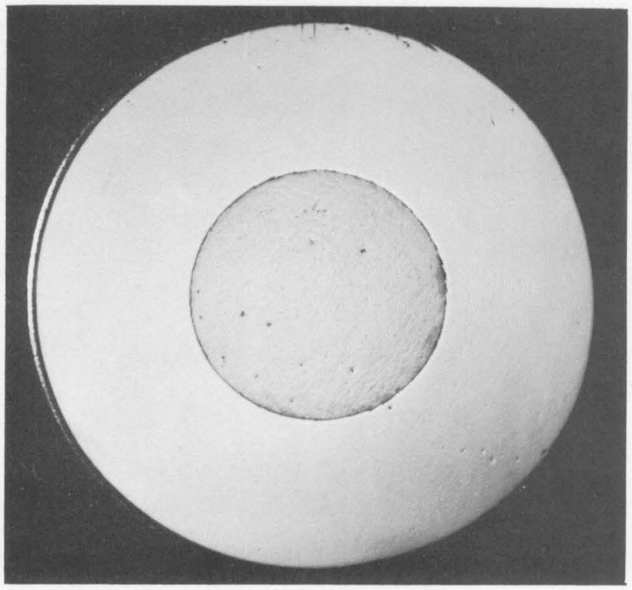
Test Material	Temperature °F	Time Hrs.	Extent of Interaction at Interface
Nickel	1500	100	C
	1800	100	D
Palladium	1800	100	C
Nichrome V*	1800	75	D
Uranium	Molten U	---	A
Copper, Annealed	1300	2	A
Chromium	2200	100	B
Aluminum	1800	2	D
Lead	1800	2	D

*80% Nickel-20% Chromium, trade name for alloy prepared by the Driver-Harris Company, Harrison, New Jersey



4X

As polished, bright light, Nichrome V (outer) - yttrium (inner) interaction couple, 1800°F for 100 hours



4X

As polished, bright light,

[redacted]

Mechanical Properties of Yttrium Metal

Studies on the mechanical properties of yttrium metal at General Electric-ANPD were undertaken in late 1956. Prior to that time sufficient quantities of yttrium had not been available for fabricating the large variety of test specimens required, especially for tests of a destructive nature. Consequently, the amount of information of this nature on yttrium is limited and has dealt almost entirely with the tensile properties and hardness. Some data has been collected pertaining to the dynamic modulus of elasticity, creep and impact strength characteristics of sponge process yttrium.

In most cases, the general inability of the direct melt or sponge process yttrium to lend itself to cold rolling of flats and rounds and the limited supply of large metal ingots has made it necessary to use test specimens which had been machined from hot extruded or rolled yttrium rods. These rods, in the extruded or rolled state, contained small grains which were elongated and aligned characteristically along the longitudinal length of the bars. As these grains grew in size and became more randomly oriented at temperatures as low as 1200°F, the hot tensile and elastic properties were customarily determined on specimens which had been given a preliminar stress-relieve anneal at 1800°F.

The results of tensile, hardness, elasticity, creep, and impact tests at room temperature and at elevated temperatures are given in Table XII and Figures 13, 14, and 15. To discuss the mechanical characteristics of yttrium at this time from available data would probably be most inopportune. However, a general opinion can be expressed that yttrium metal has mechanical properties quite similar to zirconium and, considering the field of metals in general, has comparatively low strength characteristics. The effects of inclusions and metal purity are not completely understood and probably will not be until a pure metal reference standard is obtained.

TABLE XII

Some Mechanical Properties of Yttrium Metal

Property	Value (s)	Reference
Tensile Strength, TS	39,400 psi (70°F) 3,300 psi (1800°F)	See Fig. 13
Yield Strength, 0.2%, YS	31,200 psi (70°F) 2,500 psi (1800°F)	See Fig. 13
Elongation, per cent, EL	5% (70°F) 22% (1800°F)	See Fig. 13
Impact Strength, Charpy	3-4 ft pound (70°F, arc-melted)	
Creep, per cent	4.8% (1100°F, 400 psi, 1000 hours) 6.3% (1100°F, 1000 psi, ruptured at 388 hours)	(49)
Dynamic Modulus of Elasticity, E	9 x 10^6 psi (70°F) 5 x 10^6 psi (1700°F)	See Fig. 14
Hardness, Room. Temp.	20-25 Rockwell A (arc-melted) 35-45 Rockwell A (extruded @ 1400°F) 10-15 Rockwell A (extruded, annealed @ 1800°F)	See Fig. 15

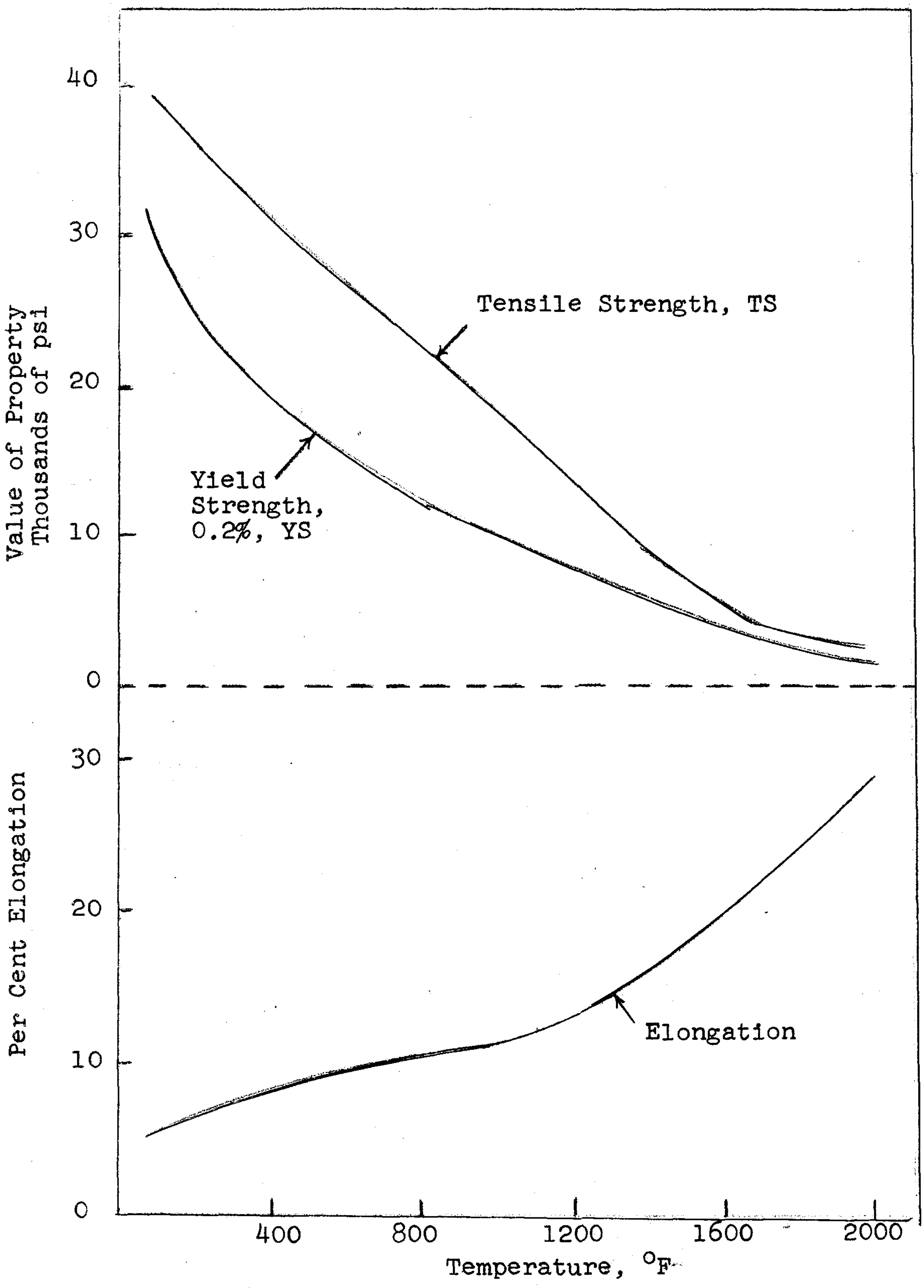


Figure 13 Short Time Tensile Properties of Yttrium Metal at Elevated Temperatures (48)

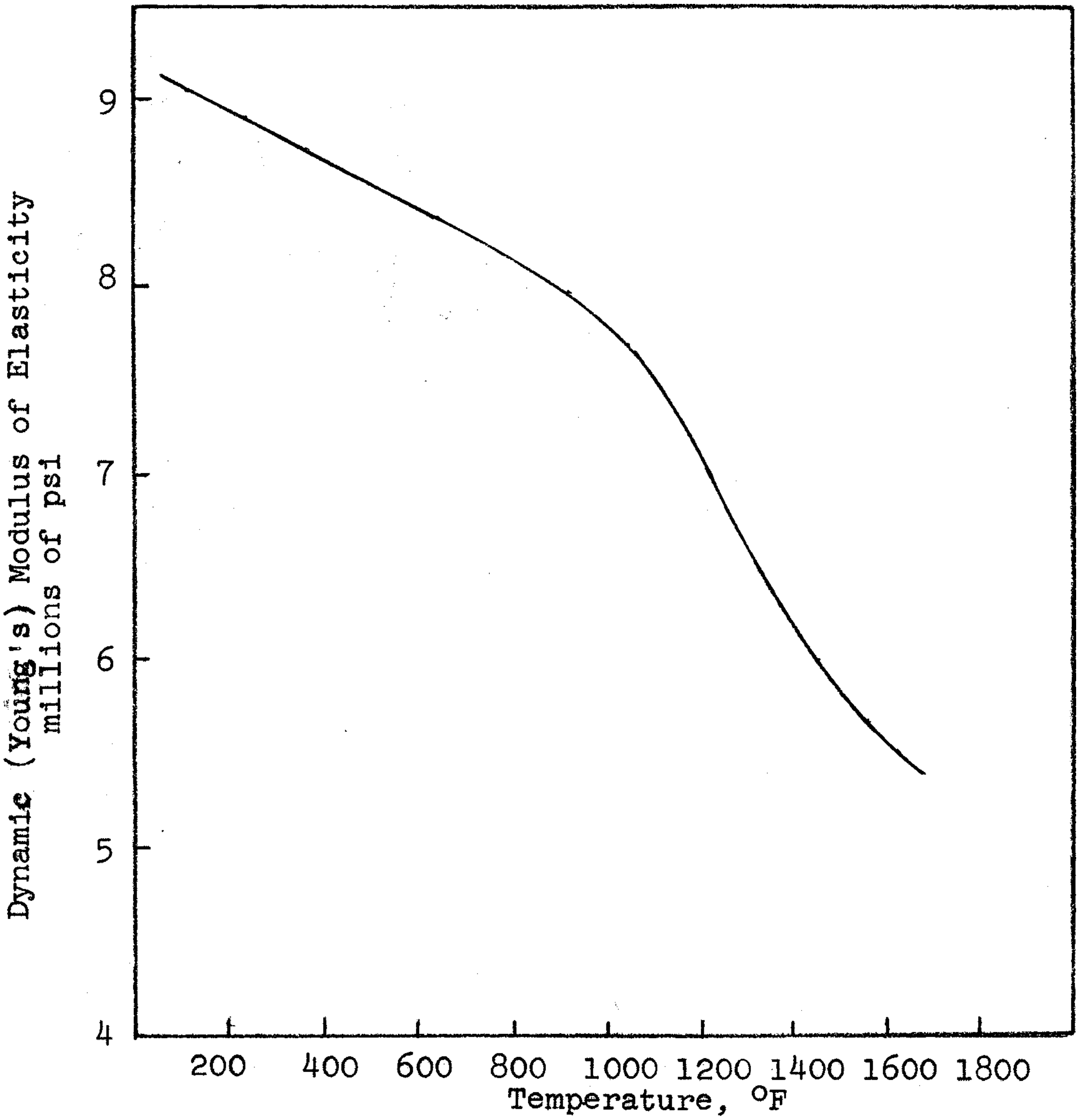


Figure 14 Dynamic Modulus of Elasticity of Yttrium as Function of Temperature(50)

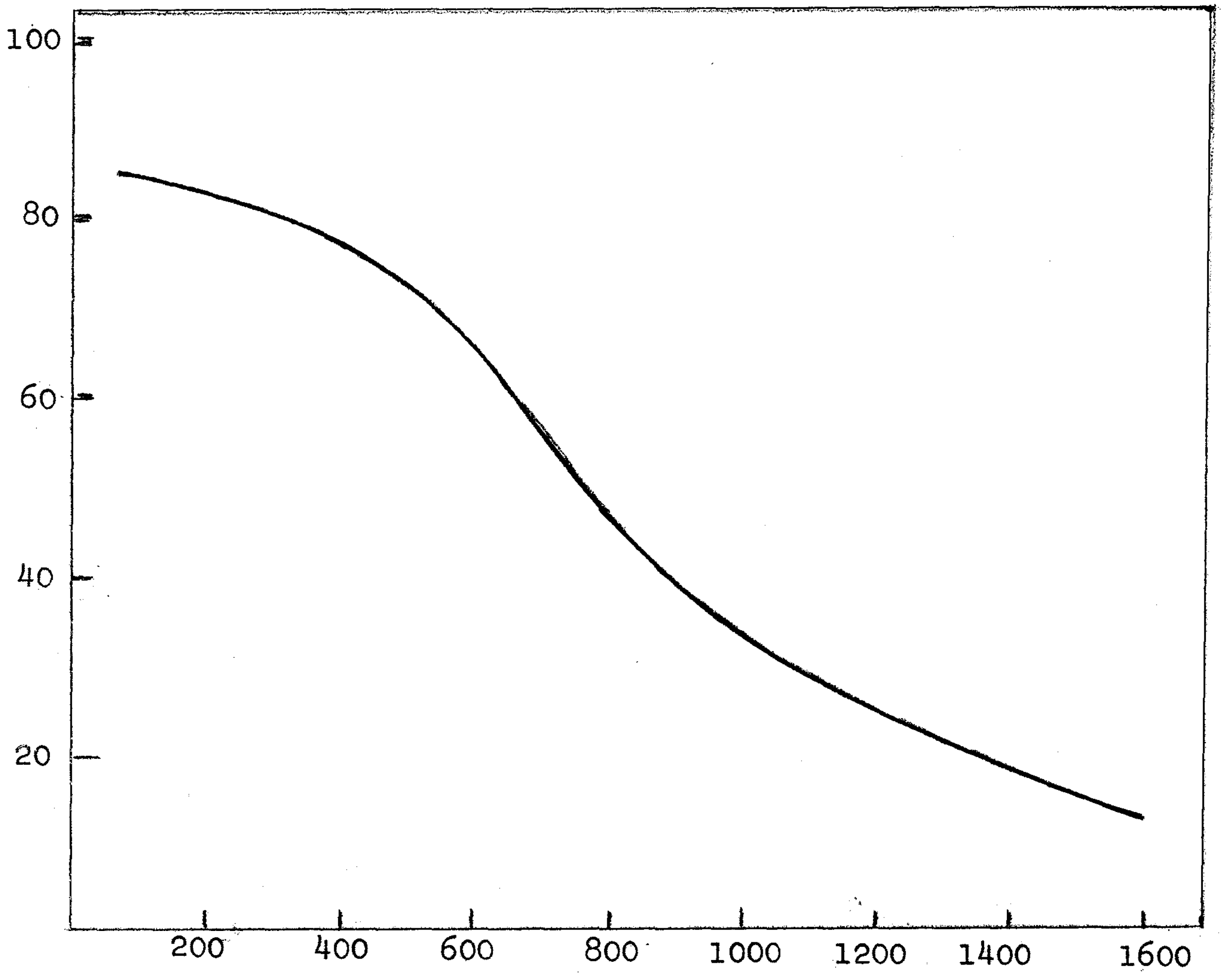


Figure 15 Hardness of Yttrium Metal as a Function of Temperature(51)

Nuclear Characteristics of Yttrium

Natural yttrium is reportedly composed of 100 per cent Y-89(52) and its major artificial radio-isotopes with mode of decay are given in Table XIII.

Up until early 1956, very little information was available on the neutron cross-sections of yttrium. The lack of data was largely due to the general unavailability of high purity yttrium compounds. Seren, Friedlander, and Turkel(53) found a pile activation cross-section of 1.25 ± 0.20 barns. Independent oscillator measurements of Pomerance(54) and Benoist, Kowarski, and Netter(55) gave values of 1.38 ± 0.14 barns and 1.25 ± 0.20 barns respectively.

Since yttrium-89 is a fifty-neutron nuclide and as such should be expected to have a low thermal neutron cross-section, the early values greater than one barn have been viewed with some doubt. In 1956, Lyon(56) at the Oak Ridge National Laboratory determined the activation cross-section of high purity yttrium oxide using cobalt as a flux monitor. The oxide which he used had been prepared carefully by ion exchange and was quoted as being spectroscopically pure, but the spectrographic limits then obtainable were rather high on some of the high cross-section lanthanides which could have been present. The thermal values obtained by Lyon were averaged at 1.26 ± .08 barns after a thermalizing correction factor was applied to the pile activation cross-sections. Hryder(57) at the Knolls Atomic Power Laboratory similarily has reported values of 1.26 ± 0.06 barns on yttrium oxide using the activation technique but with a phosphorus monitor.

TABLE XIII

Major Artificial Radio-Isotopes of Yttrium

Isotope	Half-Life	Mode of Decay and Radiation*		Energies, mev
Y 86	15 h		β^+ γ	1.80, 1.2
Y 87	14 h 80 h	IT K	β^+ γ	0.7 0.48 (0.39 short-lived daughter)
Y 88	105 d	K	β^+ γ	0.83 1.85, 0.91
Y 89	16 s	IT		0.91
Y 90	64 h		β^-	2.27 e⁻, 1.7
Y 91	50 m 58 d	IT	β^- γ	0.55, e⁻ 1.54 1.19
Y 92	3.5 h		β^- γ	3.60, 2.7, 1.3 0.94, 0.21, 2.4
Y 93	10 h		β^- γ	3.1 0.7
Y 94	17 m		β^- γ	5.4 1.4

* β^+ = positive beta particle
β^- = negative beta particle
K = electron capture
γ = gamma ray
e⁻ = internal conversion electron
IT = isomeric transition

General Electric-ANPD initiated a program late in 1955 whose ultimate goal was the determination of the true thermal neutron absorption cross-section of yttrium with an aim of establishing a standard of purity for yttrium in reactor applications. To do this a sample of high purity yttrium oxide obtained initially from an ion exchange separation was further purified by magnetic separation of the chloride in the Calutron at Oak Ridge National Laboratory. Approximately 38 grams of oxide was obtained in this way. Emission spectrographic analyses of this oxide were carried out at Oak Ridge, GE-ANPD, and the National Spectrographic Laboratory with the result that no major impurities were detected. At this time, spectrographic limits had been lowered considerably on some of the troublesome high cross-section lanthanides, i.e. Dy-1 ppm, Sm-50 ppm, Gd-10 ppm, etc. Samples of this oxide were measured as a function of a gold standard in the pile oscillator assembly located in the X-10 pile at Oak Ridge. The average thermal value found was 1.25 ± 0.05 barns. Lyons(56) determined thermal values of 1.25 and 1.21 barns on the same material by pile activation using a cobalt and maganese monitor. Neutron total cross-sections are also being determined on Calutron oxide at the Materials Testing Reactor (MTR) in Idaho.

Samples of high purity yttrium metal have also been used to ascertain the neutron total cross-section of yttrium as a function of a spectrum of neutron energies at Oak Ridge. Recently, Gibbons(58) obtained preliminary neutron total cross-section data on high purity yttrium metal over a range of neutron energies from 1 kev to 22 kev. The results are shown in Figure 16 giving a rough idea of the total cross-section picture. The metal

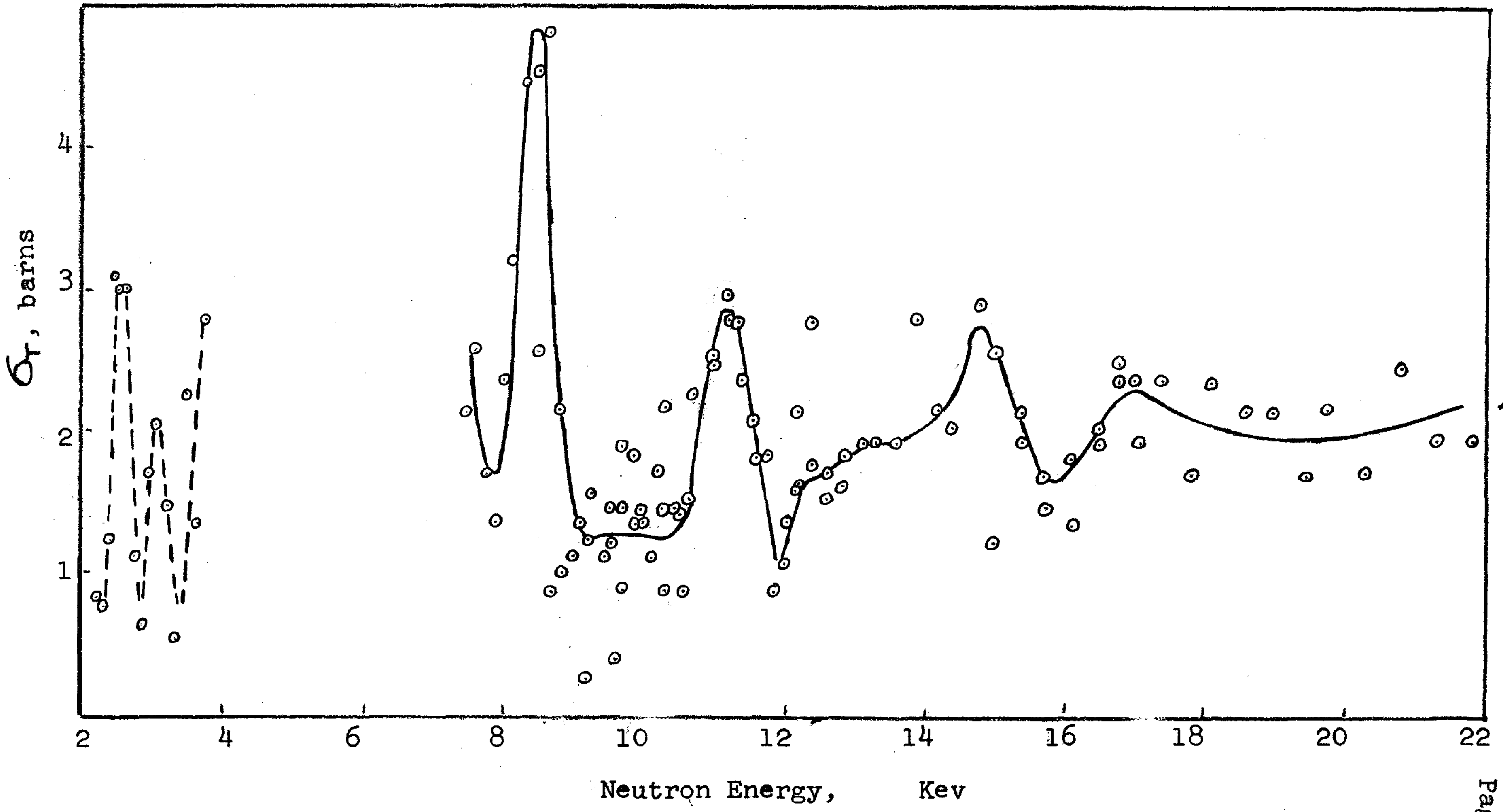


Figure 16 Preliminary Neutron Total Cross-Sections of Yttrium Metal

originally had a thermal neutron absorption cross-section of 1.33 ± 0.02 barns. Gibbons stated that the point scatter was due principally to counting statistics and his methods are still under development.

An interesting correlation between the lanthanide impurities and absorption cross-section of yttrium was made by Magee(59). He calculated the effect of lanthanide contamination on the apparent cross-section of yttrium oxide. His results are shown graphically in Figure 17. By way of explaining the use of these plots, consider an yttrium oxide containing 10 ppm gadolinium oxide (Gd = 38,000 barns). Using appropriate multiplicative factors, this much gadolinium increases the measured cross-section of yttrium oxide by approximately 0.29 barns.

The effectiveness of ion-exchange separation in removing troublesome high cross-section lanthanides can best be seen by a scrutiny of the cross-section data in Table XIV. Measured pile oscillator values for metal production ingots prepared during the period January, 1957 thru June, 1957 are given. Although the precision of measurement is only about 15 per cent, the absorption cross-section values are encouragingly low on the majority of the ingots.

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Line Equations: $\sigma_y^\circ - \sigma_y = (k)\ (\text{ppm}, RE_2O_3)$

Element	k	Element	k	Element	k
Er	9.81×10^{-5}	Sm	3.55×10^{-3}	Yb	2.07×10^{-5}
Tm	6.90×10^{-5}	Eu	2.95×10^{-4}	Pr	0.769×10^{-5}
Dy	6.65×10^{-4}	Gd	2.87×10^{-2}	La	0.618×10^{-5}
Ho	3.85×10^{-5}	Tb	2.72×10^{-5}		

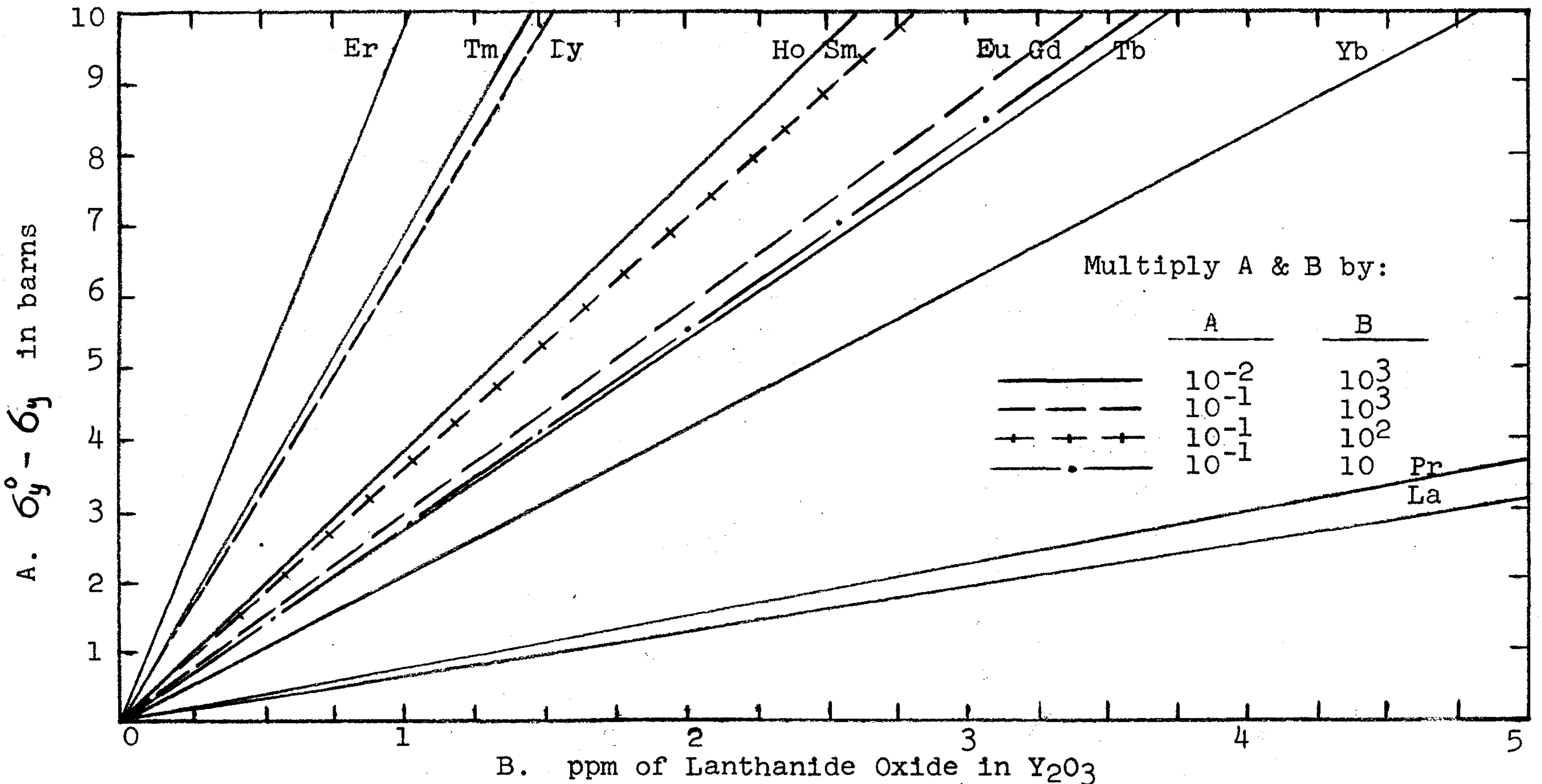

Figure 17 Effect of Lanthanide Oxides on Cross-Section of Yttrium Oxide

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TABLE XIV

Measured Thermal Neutron Absorption Cross-Sections on Ames Yttrium Produced During the First Half of 1957*

Sponge Process Metal

Ingot No.	Cross-Section, barns	Ingot No.	Cross-Section, barns
XC-107 Top	1.69	XC-123 Top	1.23
XC-108 Top	1.70	XC-123 Bottom	1.30
XC-109 Bottom	1.38	XC-124 Top	1.23
XC-109 Top	1.51	XC-124 Bottom	1.23
XC-110 Bottom	1.29	XC-125 Top	1.30
XC-110 Top	1.33	XC-125 Bottom	1.24
XC-111 Bottom	1.41	XC-126 Bottom	1.20
XC-111 Top	1.33	XC-126 Top	1.32
XC-113 Top	1.30	XC-127 Top	1.23
XC-113 Bottom	1.27	XC-127 Bottom	1.36
XC-114 Top	1.44	XC-128 Top	1.21
XC-114 Bottom	1.39	XC-128 Bottom	1.23
XC-117 Top	1.39	XC-129 Top	(1.12)
XC-117 Bottom	1.38	XC-129 Bottom	1.29
XC-118 Top	1.35	XC-132 Top	1.32**
XC-119 Top	1.38	XC-132 Bottom	1.31
XC-119 Bottom	1.33	XC-135 Top	1.30**
XC-121 Top	1.30	XC-135 Bottom	1.32
XC-121 Bottom	1.29	XC-139 Top	1.21**
XC-122 Top	1.33	XC-139 Bottom	1.23
XC-122 Bottom	(1.01)		

Direct Melt Reduction Metal

Ingot No.	Cross-Section, barns
DX-5 Top	1.29 (± 15%)
DX-5 Bottom	(1.11)(± 15%)
DX-6 Top	1.39 (± 15%)
DX-6 Bottom	1.38 (± 15%)
DX-7A Top	1.23
DX-7A Bottom	1.27
DX-7B Top	1.21
DX-7B Bottom	1.24

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*Cross-Sections measured by pile oscillator as function of a gold standard at Oak Ridge National Laboratory.

**6 inch diameter ingots produced by vacuum arc-melt.

Analytical Methods for Yttrium Metal and Yttrium Oxide

Analytical methods have been devised which are suitable for determining a variety of impurities in both yttrium oxide and metal. Procedures presently being used at GE-ANPD to perform analyses for several contaminators are described below.

Carbon in Yttrium Metal(60)

Carbon can be most readily determined by direct combustion. The technique involves fluxing a one gram sample of the metal with granular tin in an oxygen atmosphere at 2400°F. The carbon is converted to carbon dioxide which is absorbed in ascarite and the gain in weight noted. The accuracy of the method is ± 0.0005 per cent carbon.

Nitrogen in Yttrium Metal(61)

Nitrogen can be determined by both vacuum fusion and a micro-Kjeldahl technique. The vacuum fusion technique will be described separately as an analytical method for both nitrogen and oxygen.

The micro-Kjeldahl method involves the solution of a one gram sample of metal in 1:1 hydrochloric acid. This solution is made basic with sodium hydroxide and the liberated ammonia absorbed in a two per cent boric acid solution. Titrations of ammonium ion are then carried out with 0.1 N sulfuric acid. The accuracy of the method is ± 0.005 per cent nitrogen.

Vacuum Fusion for Oxygen and Nitrogen in Yttrium Metal(62)

A 0.2 gram sample of metal is placed in a graphite crucible which resides in a platinum bath under vacuum and maintained at 1950°C. Carbon dioxide (plus CO) and nitrogen are evolved and pumped into a sample measuring volume. Carbon monoxide is converted to CO_2 by passage through a copper oxide trap. Carbon dioxide is frozen out in a bulb immersed in liquid nitrogen and the gas pressure measured. The two measured readings give the amounts of oxygen and nitrogen present. The method was found to have an accuracy of ± 5 per cent relative to the sample.

Bromine Insoluble Residue in Yttrium Metal(63)

One gram of metal is placed in 125 mils of anhydrous methanol. Ten mils of bromine is added in 2 mil portions to the mixture without stirring, allowing the solution to clear between each addition. A slight excess of bromine should be left in the bottom of the solution after the reaction ceases. Dilute with 100 mils of anhydrous methanol and filter the solution through a Selos crucible (series #3000 XF). The insoluble material is washed with five 20 mil portions of anhydrous methanol and then dried at 110°C for 30 minutes.

Lanthanide and Other Impurities in Yttrium Oxide by Emission Spectrograph(6

Small amounts of lanthanide elements and other impurities can be determined by emission spectrographic technique. A 20 mgm. sample is placed in a graphite crater-type electrode and excited in a sustained AC arc at 17 to 18 amperes. The photographic plates are developed and the line intensities measured on a comparative densitometer. The following emission limits have been set:

Element	Limit, ppm	Element	Limit, ppm
Gd	10	Ca	1
Sm	50	Cr	1
Eu	1	Ni	0.1
Dy	1	Bi	1
Lu	1	Al	0.1
B	10	Ti	1
Si	10	Be	0.1
Hg	10	Zr	5
Co	50	Mo	0.5
Ta	5	Nb	5
As	100	Na	100
Sn	1	Cu	10
Mg	1	Li	1

Yttrium Oxide in Mixture with Lanthanide Oxides by X-Ray Fluorescence(65)

The x-ray fluorescence technique involves mixing the RE_2O_3 with $SrCl_2$ x 6 H_2O to altenuate KB x-rays, cold pressing this into a pellet (20,000 psi), and measuring the x-ray fluorescence of the pellet. A Strontium line is used as an internal standard. The accuracy of the method was found to be ± 0.25 per cent yttrium oxide. Principal interfering elements are uranium, columbium, molybdenum, and thorium.

Metallographic Techniques for Yttrium Metal

The methods of mounting, polishing, and etching yttrium metal specimens at General Electric-ANPD(66) for microstructure examination are described separately below.

MOUNTING

Yttrium metal specimens may be rough cut from ingots by the most appropriate method. If by machine saw, water or mineral oil may be used as a lubricant-coolant although it may then be necessary to saw at a slow speed to mimimize heating and subsequent oxidation. The specimens are generally sectioned for mounting using standard cut-off wheels, taking necessary precautions so that the specimen does not become overheated. The sectioned pieces are then mounted in bakelite for ease of handling in polishing.

POLISHING

The rough polishing of yttrium is accomplished by using a series of 80, 280, 400, and 600 grit papers. It apparently makes little difference in the end polish whether a lubricant-coolant is used during grinding; the only critical limitations being that the specimen should not be allowed to overheat on dry grinding.

Two procedures are used for the final polishing depending upon whether the specimen is to be examined under a bright-field illumination or polarized light. The best procedure for polishing

POLISHING
(continued)

for bright field illumination is to polish with a 3, 1, and 1/2 micron diamond paste using a Mira Cloth. For polarized light, the specimen is polished with Linde A using a billiard cloth and then with Linde B using a Gamal Cloth. A blue tint develops on the surface of specimens during polishing which is apparently dependent on heating during grinding. This tint should be kept at a minimum so that there will be a neglible effect when examining under polarized light.

ETCHING

There have been a large number of etchants investigated to try and find a satisfactory one for the metal. Among these have been concentrated nitric-acid and vacuum-cathodic etch neither of which was entirely satisfactory. The most simple to prepare and best etchant encountered to date is a "swab" etch with a solution consisting of 10 parts lactic acid, 10 parts ethyl alcohol, and 1 part phosphoric acid.

Toxicity of Yttrium and Hazards in Handling

Most of the previous toxicological studies on yttrium and yttrium compounds have dealt with the radioactive fission product, Y-91. The small amount of information that has been obtained by various investigators on the biological effects of natural yttrium and its compounds has indicated that yttrium is not an industrial poison. It must be stated, however, that most of this information has been obtained by means of oral or subcutaneous introduction of yttrium compounds to experimental animals. Practically no studies have been carried out of an inhalative nature.

As far as hazards involved in handling or storing yttrium are concerned, there have been indications that finely divided yttrium powder or turnings are pyrophoric, producing an intense heat and a bright glare when ignited. This ignition can occur readily if the dry metal is sawed or turned in a lathe in such a manner as to produce sparking. Common practice during metal working operations is to isolate any fine yttrium particles produced under excess water. At GE-ANPD, most of the machining of yttrium is done dry because of chance contamination from lubricants. Under these conditions, a slow cutting speed and a minimum chip load of 0.010 per revolution or greater is used.

Y-91, one of the common radioactive fission products, is a pure beta emitter with an energy of 1.5 mev and a half-life of 57 days*. Studies of the retention of this isotope by rats were made by Dobson, et al and Hamilton(67). Their studies indicated that radio-yttrium was essentially not absorbed following oral administration, but intraperitoneal

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*Measurements on Y-91 at the Argonne National Laboratory have indicated that the half-life is more nearly 58 days.

injection resulted in retention of yttrium to substantial amounts in the bone marrow, liver and spleen. By far the highest percentage of yttrium injected was localized in the vicinity of the bone marrow (approximately 60%) from which natural elimination was very slow.

Schubert(68) investigated the effect of zirconium citrate injections on the elimination of Y-91 and Pu-239. He found that if injections of citrat were made early following intraperitoneal introduction of the isotopes, the amount of Pu and Y deposited in the skeleton of rats was remarkedly reduced. However, the isotopic content in liver and spleen was seemingly not affected. Cohn, <u>et al</u>(69) reported that administration of Na-EDTA (Sodium salt of ethylenediamine tetra acetic acid) and Ca-EDTA salts respectively resulted in a similar decrease in the skeletal content of Y-91. Moreover, these salts gave evidence that radio-yttrium which had become more firmly fixed in the bone could also be eliminated due to a solvent action of the organic anion grouping.

Liscoe, <u>et al</u>(70) determined that radio-yttrium given orally to rats resided longer in the colon than in any other portion of the intestinal tract. In order to study the damage caused in this region, two groups of rats were given feedings ranging from 1.0 to 31.2 mc of Y-91. Thirty-three animals were given a single feeding of 1.0 to 6.9 mc. Four died with adenocarcinoma of the colon while several exhibited acute and chronic ulceration of the colon. Three groups of animals were fed 31.20, 15.60, and 4.68 mc of Y-91 respectively accumalative over a period of three months. Six of the eight animals in the higher dosage levels died with carcinoma of the colon in 304 to 548 days following the first feeding. At the lower level, several animals displayed superficial ulcerative lesions of the colon.

A study was carried out on the toxicity of yttrium oxide, chloride and nitrate by Cochran, et al(71). These workers administered the individual compounds both orally and by intraperitoneal injection to rats. The compounds exhibited low absorption and toxicity when administered orally and a relatively low intraperitoneal toxicity. On the basis of yttrium content, the insoluble oxide was less than half as toxic as the chloride or nitrate.

Due to the scarcity of information, rather low exposure limits have arbitrarily been set on airborne yttrium and yttrium compounds at the present time. Some of the inhalation limits on more commonly handled compounds are given in Table XV. As knowledge increases on the toxicity characteristics of yttrium, these tentative limits will most certainly be readjusted to more accurate values.

TABLE XV

Tentative Exposure Limits on Airborne Yttrium and Yttrium Compounds

Material	Maximum Allowable Concentration, mgm/cu meter
Yttrium	5
Yttrium Oxide	5
Yttrium Fluoride	1
Yttrium Chloride, Nitrate	∼ 1

PROCESSING AND FABRICATION OF YTTRIUM METAL

Introduction

This section has been included for the purpose of discussing the procedures which have been utilized in processing the yttrium metal reduction product and in fabrication of yttrium metal shapes. By way of explanation, the term "processing" encompasses the arc-melting, casting, or melting techniques used to form solid metal ingots, while the term "fabrication" means the machining, extrusion, rolling or swaging operations which are necessary in forming various yttrium shapes. All of the procedures which have been formulated originate from studies either at General Electric-ANPD or at other laboratories conducting such investigations under the direction of General Electric. It should be emphasized that the processing or fabrication techniques which have been found to be most suitable for sponge process yttrium may not be completely representative of the methods necessary for a "high purity" yttrium which has a minimum of inclusions.

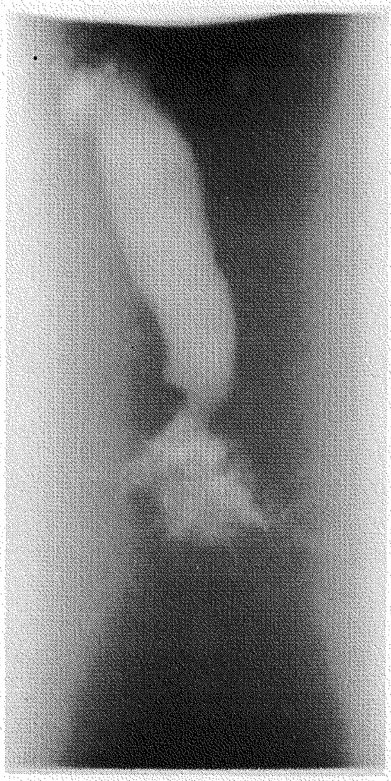
The method used with most success in forming yttrium ingots of maximum purity and massive integrity has been consumable arc-melts of sponge electrodes under a high vacuum. However, the workability of yttrium in general has been poor except at elevated temperatures. Metal forming studies since 1954 have indicated only a gradual improvement in the room temperature ductility and workability, this improvement believed primarily to be due to a gradual increase in metal purity.

Processing of the Yttrium Metal Reduction Products

Early in the yttrium program, it was evident that ingots or billets of yttrium prepared by an "in place" melt sometimes contained voids principally in the center and top. Likewise, the yttrium ingots prepared by drip or pour casting of molten yttrium from tantalum or molybdenum crucibles into cooled copper molds either in a vacuum or an inert atmosphere generally contained voids. There was also some contamination of the yttrium coatings by the crucible materials particularily in the case of molybdenum.

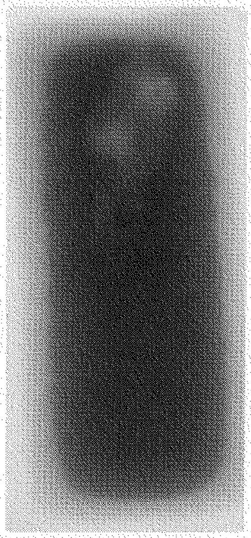
With the development of the sponge reduction method, studies on forming solid yttrium ingots from the sponge by non-consumable arc-melting and by "in place" melting under vacuum or inert atmosphere indicated that the arc-melting technique was the most satisfactory. For comparative purposes, Figure 18 shows a series of x-ray pictures taken on yttrium ingots prepared by the different melting procedures. In these photographs, voids are shown as light-colored areas.

The arc-melting technique was further refined at the Ames Laboratory by employing a consumable method of melting. Since the sponge lends itself readily to cold-pressing operations, electrodes approximately 1-1/4 inch square and 12 inches long are fabricated in suitable dies. The general practice is to weld three of these electrodes together with a short piece of scrap yttrium metal on one end as an adaptor. Tungsten screws are then used to attach the adaptor to the copper arc-electrode. The resulting electrode is then melted consumably under argon to either 3



Yttrium ingot cast into cooled copper direct from $Ca-YF_3$ reduction charge

Yttrium ingot vacuum melted in molybdenum crucible and cast into cooled copper mold



In place melt of yttrium sponge in tantalum crucible under a helium atmosphere

Figure 19 Radiographic Analyses of Yttrium Melts by Various Methods.

or 4 inch diameter ingots. These ingots are then welded together into larger electrodes and arc-melted again into larger diameter ingots.

Recently, the final arc-melting on large 6 inch diameter ingots has been conducted in a vacuum with some success in lowering the calcium and magnesium content (see Table VI). However, the oxygen content continues to be high and variable. Some of the Ames ingots were double arc-melted in a vacuum at the Oregon Metallurgical Corporation, Albany, Oregon(72). The resultant metal was reportedly very soft but would not extrude cold. Calcium and magnesium contents were down but the oxygen content increased slightly in nearly every melt attempted. More comprehensive studies are now underway at GE-ANPD, Oregon Metallurgical, and the Ames Laboratory on the suitability of vacuum arc-melting as a process step for gaining ductile, high purity yttrium in ingot form.

Fabrication of Yttrium Metal

Machining

Machine shop operations (turning, milling, grinding) at General Electric-ANPD(73) indicate that yttrium metal free machines similarily to cast iron. Experience has shown the minimum feed to be a 0.010 inch chip per revolution. If the feed is less, or if the cutting tool is dull, there is a tendency for the chips to catch fire. For machine cutting, the surface speed can be in the order of 150-200 feet per minute for tool steel and 500-700 feet per minute for carbide tool. No unusual problems have been encountered in milling, shaping or grinding the metal. However, as mentioned in the section on toxicity, yttrium turnings or chips appear to be more pyrophoric than zirconium and large quantities should not be allowed to accumulate.

Extrusion, Rolling or Swaging

Considerable success has been achieved in forming yttrium rods of various diameters by a combination of extrusion, rolling or swaging operations. In general, extrusions have been carried out on arc-melted yttrium metal ingots heated to various temperatures. This necessitated either cladding the yttrium ingot in copper or heating it in an inert atmosphere and exposing it for short working times. Likewise, extruded yttrium rods have been hot rolled to various diameters both with and without an external protective cladding. Some cold swaging of extruded rods has been attempte with partial success although attempts to form yttrium flats by both hot and cold rolling have, in general, been unsuccessful. Excessive work-hardening generally occurs during cold operations which results in disintegration of the yttrium piece before appreciable reduction can be realized.

Extrusions at Elevated Temperatures

A number of hot extrusions have been performed on arc-melted yttrium ingots from the sponge process. The ingots were of various diameters and lengths and were usually clad with a layer of aluminum oxide and copper prior to heating for extrusion. Yttrium rods have been successfully extruded ranging from 0.6 inches to 2 inches in diameter at temperatures

1050 to 1450°F. The ease with which yttrium extrudes apparently depends on its chemical purity and the amount of reduction required. Extrusion constants which were calculated from the extrusion data taken during several extrusions of yttrium at Nuclear Metals, Inc., Cambridge, Massachusetts(74) are shown in Table XVI. The constants are irregular but indicate that yttrium has hot extrusion characteristics similar to zirconium. The changes in the grain structure of arc-melted yttrium by hot extrusion at 1400°F are shown in Figure 19. From a scrutiny of the microstructure of the extruded rod it is difficult to tell whether recrystallization of yttrium has commenced under the high temperature conditions of the extrusion operation, although the grain structure of the original arc-melted material has most certainly been destroyed. More will be mentioned of the recrystallization characteristics of yttrium in a succeeding paragraph.

Hot-Rolling of Extruded Yttrium Rods

Several extruded rods of yttrium have been successfully hot-rolled, unclad to smaller diameters at 1300 to 1400°F. This temperature range was selected because good working results are obtained with a minimum of oxidation to the metal. Nevertheless, the working times are necessarily as short as possible, since a heavy oxide coat is formed. The actual procedure followed was to heat the extruded rod under an inert atmosphere, roll for two to three passes, heat again in an inert atmosphere, and roll some more, repeating this process until the desired reduction was achieved. Several rods have been produced in this manner, the greatest reduction in cross-sectional area being approximately 90 per cent.

TABLE XVI

Extrusion of Yttrium Metal[1]

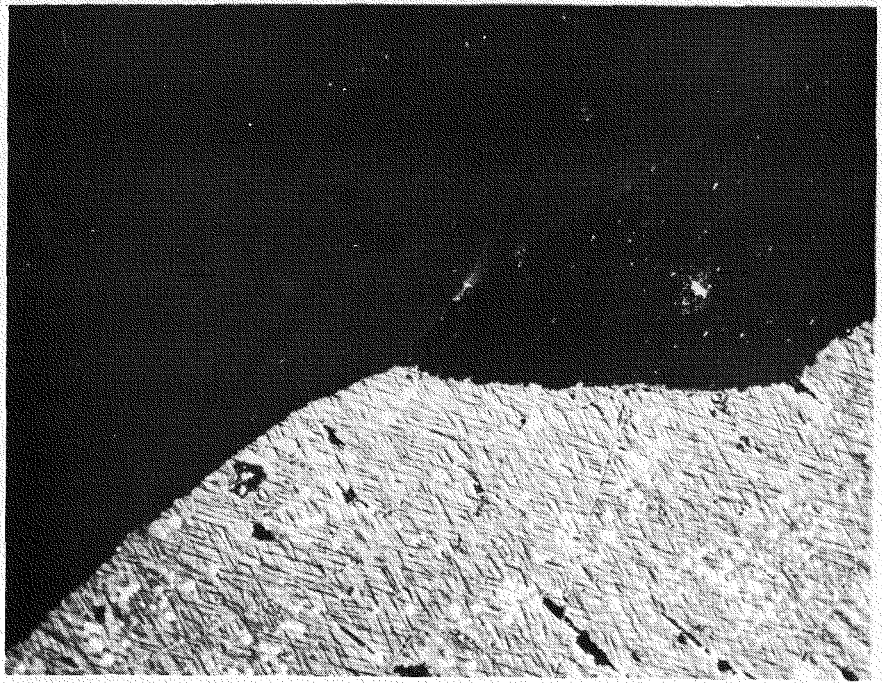
Billet No.	Diameter, inches			Preheat Temp., °F	Reduction	Ram Speed in/min	Extrusion[2] Constant, psi
	Ingot	Liner	Die				
ANP-4	2	2.04	0.60	1200	11.5X	52	39,500
ANP-5	3.45	3.6	2.10	1400	3 X	35	57,000
ANP-6	2.60	2.8	0.60	1040[3]	22 X	60	36,000
ANP-12	3.4	3.6	1.67	1400	4.7 X	35	46,000
ANP-13	3.4	3.6	0.64	1650	32 X	35	36,500
ANP-14	3.87	4.6	1.19	1350	15 X	35	54,000

1. Extrusions carried out on yttrium ingots coated with Al_2O_3 and clad with 16 gauge copper. All extrusions resulted in good rod except ANP-13, which had a rought surface and some interaction with copper clad.

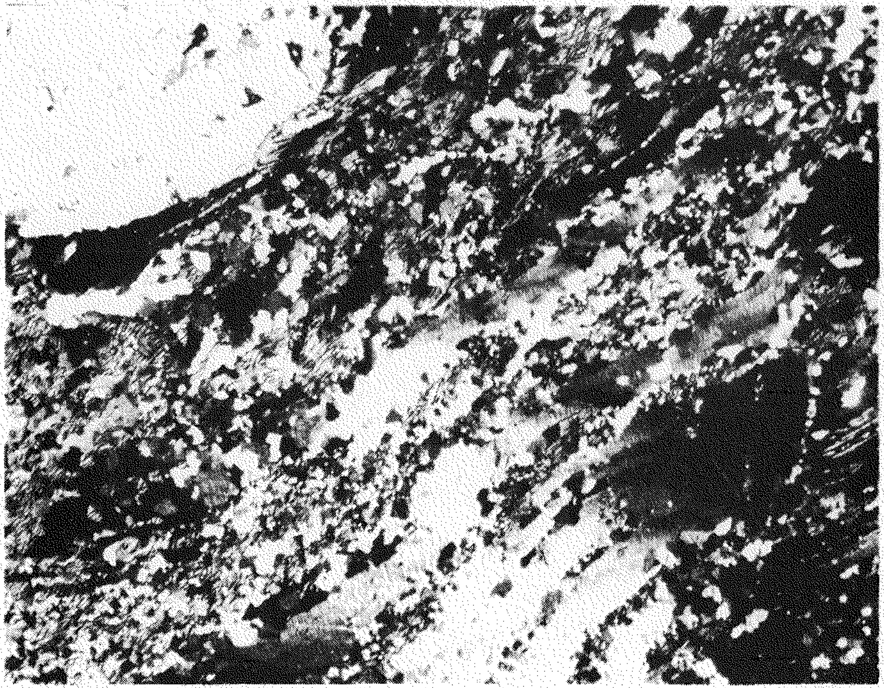
2. Calculated from extrusion data by following formula:

   Extrusion Constant = extrusion force/(liner area)($\log_e$ reduction)

3. This ingot was extruded unclad.



Double Arc-Melt



Extruded through 11X reduction
at 1400°F

Figure 19. Comparison of the Arc-Melted and Extruded Microstructure of Yttrium Metal. Magnified 250X, shown in polarized light.

Cold Flat Rolling, Rod Rolling, and Swaging of Extruded Yttrium

A study was recently made at General Electric-ANPD(75) on the maximum reduction possible on extruded yttrium by cold working. To carry out the testing, a one inch diameter rod of extruded metal (Ames sponge process metal, XC-104) was sectioned and then machined into flats and rods. The test pieces were all annealed to a constant minimum hardness number before working.

Yttrium rods were rolled and swaged parallel to the direction of extrusion and the Rockwell A hardness of the surface (longitudinal) and center (transverse) measured as a function of per cent reduction in rod diameter. The results of the rod roll and swage are shown in Table XVII and indicate that approximately three times more reduction is possible by swaging on this particular metal. Yttrium XC-104 is more or less representative of the sponge metal produced at the Ames Laboratory but for convenience the chemical analyses of this metal is included in Table XVII.

Flat yttrium specimens from XC-104 were cold rolled both across and with the extruded metal grain. The Rockwell A hardness for each method was measured as a function of per cent reduction in thickness. The results of this study are shown in Table XVIII. It is evident that on this particular yttrium metal the highest per cent reduction is achieved by flat rolling in a direction parallel with the extruded metal grains.

The recovery of cold worked yttrium metal by annealing was investigated

TABLE XVII

Maximum Reduction and Hardness Relationships in Cold Rod-Rolling and Swaging of Extruded Yttrium*

Rod-Rolling

Pass	Initial Diameter, inches	Final Diameter, inches	Reduction %	Total Reduction	Hardness Rockwell A Transverse	Hardness Rockwell A Long.
1	0.925	0.915	1.08	1.08	20	25
2	0.915	0.878	4.00	5.08	26	27
3	0.878	0.845	3.75	8.83	28	30
4	0.845	0.824	2.48	11.31	29	31
5	0.824	0.810	1.69	13.00	30	35
6	0.810	0.783	2.09	15.09	31	42 (Cracked)
7	0.783	0.762	2.66	17.75	32	39 (Cracked)

Swaging

Pass	Initial Diameter, inches	Final Diameter, inches	Reduction %	Total Reduction	Hardness Rockwell A Transverse	Hardness Rockwell A Long.
1	0.925	0.900	2.78	2.78	24	32
2	0.900	0.870	3.33	6.11	28	36
3	0.870	0.840	3.45	9.56	31	37
4	0.840	0.810	3.57	13.13	33	41
5	0.810	0.783	3.33	16.46	36	40
6	0.783	0.753	3.84	20.30	37	44
7	0.753	0.736	2.25	22.55	37	41
8	0.736	0.722	1.90	23.45	38	42
9	0.722	0.697	3.46	26.91	38	43
10	0.697	0.661	3.32	32.23	39	43
11	0.611	0.647	2.26	34.49	40	44
12	0.647	0.630	2.78	37.27	42	44
13	0.630	0.596	5.39	43.66	43	44
14	0.596	0.563	5.53	49.19	44	45
15	0.563	0.535	4.97	54.16	46	47 (Cracked)

*Rod specimens for cold work from 1 inch diameter extrusion of Ames ingot XC-104, annealed to constant hardness at 1800-2000°F. GE-ANPD analyses for XC-104 were: C - 210 ppm; N - 400 ppm; Fe - 360 ppm; Zr - 1.1%; Ca - 500 ppm; Mg - 500 ppm; and O - 3000 ppm.

TABLE XVIII

Maximum Reduction and Hardness Relationships in Cold Flat Rolling of Extruded Yttrium*

Longitudinal Flat-Roll**

Pass	Initial Thickness, inches	Final Thickness inches	Reduction %	Total Reduction	Hardness Rockwell A
1	0.500	0.482	3.6	3.6	27
2	0.482	0.470	2.4	6.0	33
3	0.470	0.458	2.5	8.5	35
4	0.458	0.445	2.8	11.3	37
5	0.445	0.433	2.6	13.9	37
6	0.433	0.420	3.0	16.9	29
7	0.420	0.409	2.5	19.4	42
8	0.409	0.397	2.9	22.3	42
9	0.397	0.386	2.7	25.0	44
10	0.386	0.375	2.8	27.8	45 (Slight Crack)
11	0.375	0.364	2.9	30.7	46 (Cracked)
			Cross Flat-Roll***		
1	0.500	0.482	3.0	3.0	32
2	0.482	0.473	1.1	4.1	35
3	0.473	0.458	3.1	7.2	37
4	0.458	0.448	2.1	9.3	39
5	0.448	0.432	3.6	12.9	41
6	0.432	0.424	1.8	14.7	42
7	0.424	0.408	3.7	18.4	43
8	0.408	0.401	1.7	20.1	45 (Cracked)

* 1/2 inch specimens cut from center of 1 inch extrusion, XC-104
** Cold rolled in direction of extrusion
*** Cold rolled across extrusion grains

on specimens cut from the longitudinal flat rolled test piece. The hardness variations were measured on both quenched and slow-cooled specimens annealed at various temperatures and times. The results are shown in Figure 20. It is evident that recrystallization and recovery in this cold-worked yttrium is negligible at temperatures below 1000°F, most efficient annealing being at 2200°F for one hour and at 1800°F for three hours. Of importance, is the apparent constancy of a higher hardness number in cold-worked yttrium which is quenched from annealing temperatures of 1400°F and above. The microstructure of these quenched specimens have not yet been examined but the results intimate that microscopic impurities may be stabilized within the metal grains by quenching at these temperatures. Previous observations in slow-cooled yttrium has revealed that impurities customarily precipitate along the grain boundaries.

Recrystallization Temperature Studies on Yttrium

A series of extruded yttrium rod specimens (extruded at 1400°F) were heated at various temperatures for 24 hours in an attempt to determine the recrystallization temperature of yttrium metal. The results of a microstructure study of these specimens are shown in Figure 21. There is a good deal of uncertainty in selecting a recrystallization temperature from these studies since the hot extruded metal may already have started to recrystallize during cooling from the extrusion operation. However, from the hardness relationships obtained in annealing cold-worked yttrium (see previous section on Cold-Flat Rolling) and the microstructure evidence in Figure 21, it is probable that the recrystallization temperature of yttrium is probably between 1000° and 1200°F.

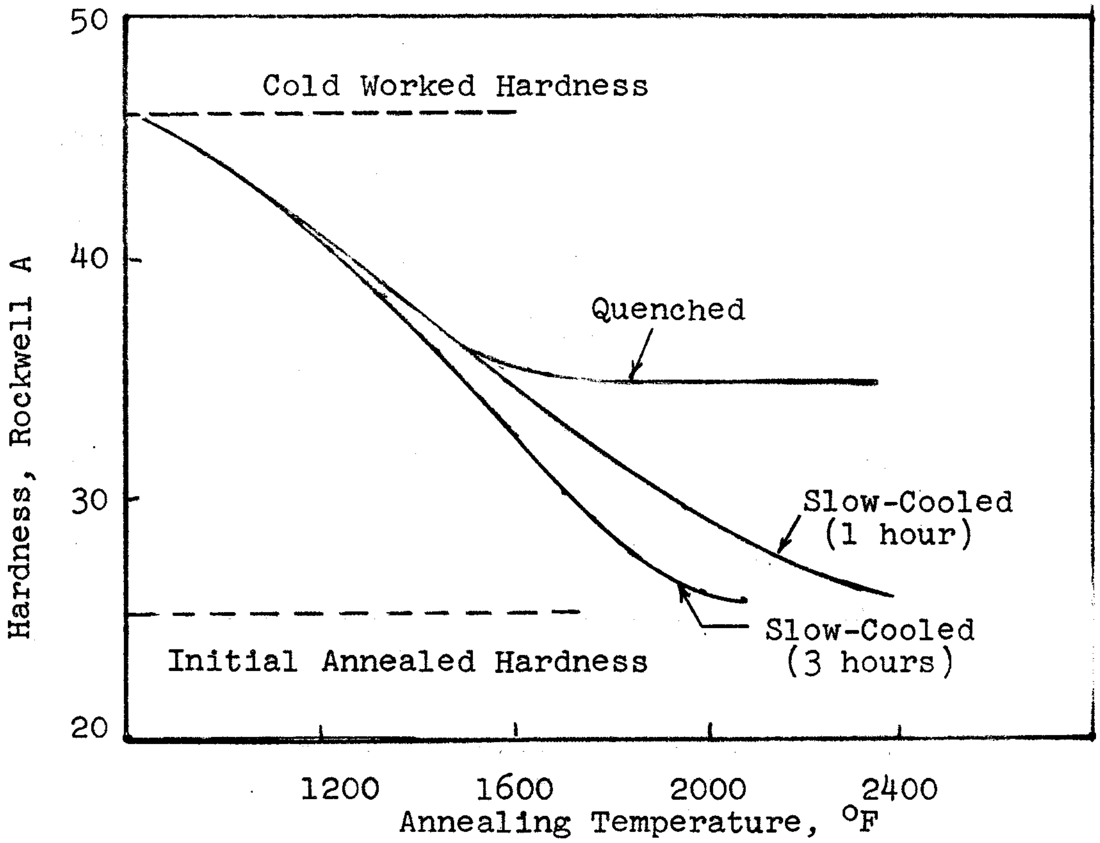


Figure 20 Hardness Variations in Cold-Worked Yttrium as a Function Of Temperature, Time and Method of Cooling

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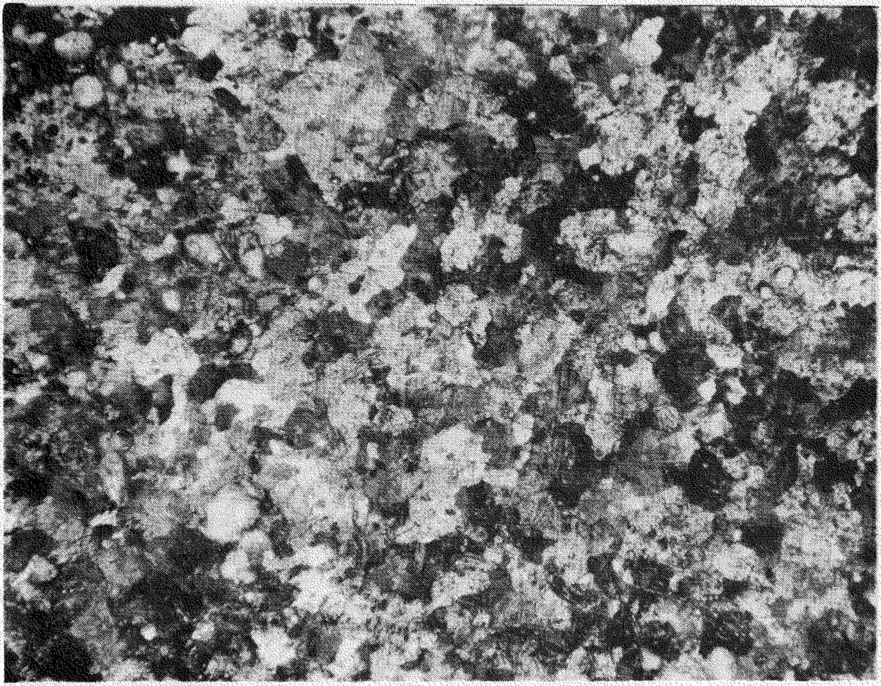
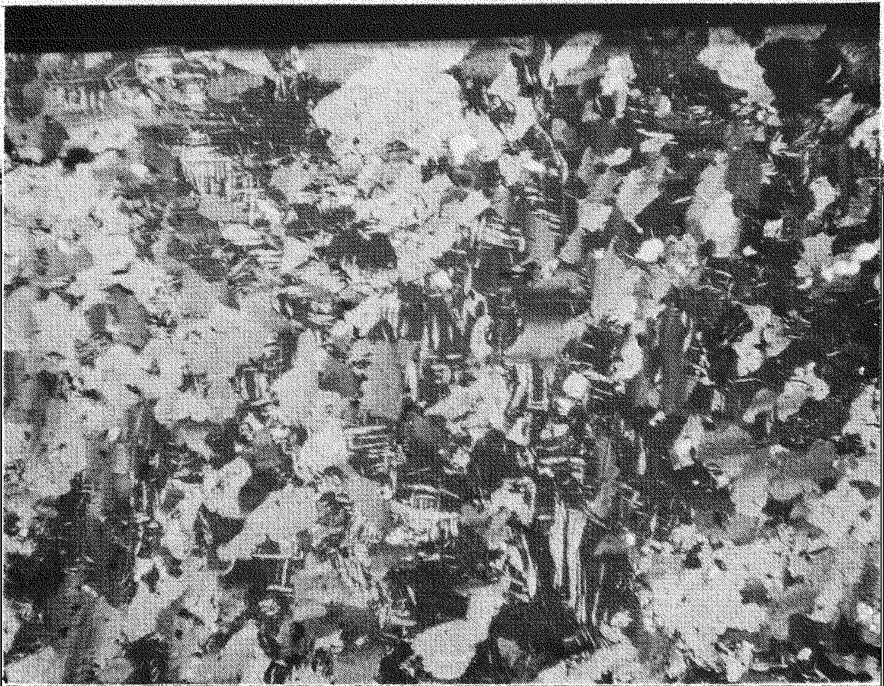


120 X

Polarized Light, Structure of 1400°F
Extruded Yttrium, 4X Reduction



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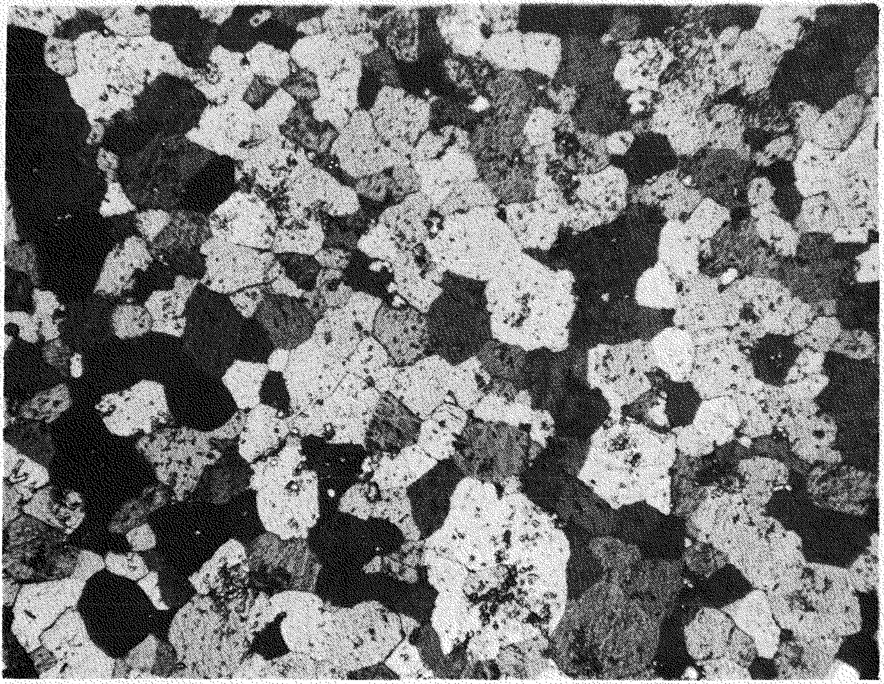
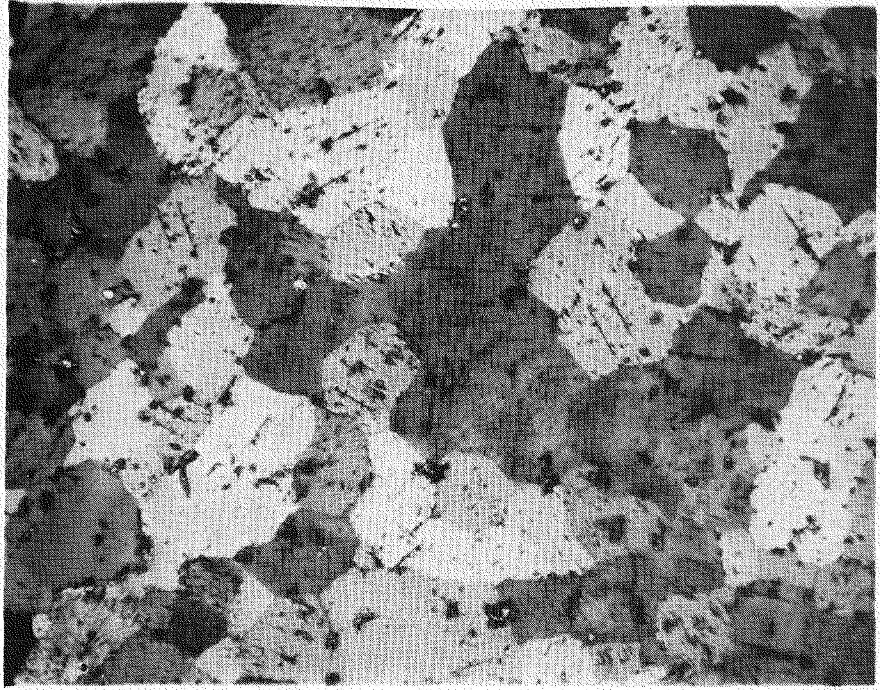


120 X

Vacuum-Cathodic Etch, Extruded Yttrium after 24 hours at 1800°F



120 X

Vacuum Cathodic Etch, Extruded Yttrium after 24 hours at 2100°F, dark bodies are inclusions

Figure 21 Continued

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