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UNITED STATES ATOMIC ENERGY COMMISSION
Research and Development Report

TECHNOLOGY AND USES OF
BERYLLIUM, CESIUM, GERMANIUM,
HAFNIUM, NIOBIUM (COLUMBIUM),
RARE EARTHS (INCLUDING YTTRIUM
AND SCANDIUM), TANTALUM,
TITANIUM AND ZIRCONIUM

by

Karl A. Gschneidner, Jr.

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January, 1968

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TECHNOLOGY AND USES OF BERYLLIUM, CESIUM,
GERMANIUM, HAFNIUM, NIOBIUM (COLUMBIUM),
RARE EARTHS (INCLUDING YTTRIUM AND SCANDIUM),
TANTALUM, TITANIUM AND ZIRCONIUM*

Karl A. Gschneidner, Jr.

ABSTRACT

The chemical, metallurgical and physical properties of beryllium, cesium, germanium, hafnium, niobium, rare-earth, tantalum, titanium and zirconium metals and their principal compounds are reviewed, especially in light of their importance in present day technology and applications. The use of these metals and their compounds in industry, and in basic and applied research, such as space, nuclear energy, and electronics, is discussed. Special problems associated with these materials are noted and commented upon.

* This paper is to be presented at the "Seminar on New Metals and Minerals" sponsored by the United Nations' Economic Commission for Africa at Addis Ababa, Ethiopia, February 5-10, 1968.

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The use of a material will depend upon the chemical and/or metallurgical and/or physical properties of the material as related to a particular problem, the costs of the raw material and its manufacture into the usable form, and the availability of the raw material and/or manufacturing facilities. These factors for a particular material, of course, need to be weighed against the same factors for many other competing materials. In the final analysis it is the material which best meets the criterion or specifications laid down for the particular application that will be utilized.

For example, if reliability or safety is an important requirement, then the properties of the material play the dominant role, and cost and availability play a secondary or negligible role. If low costs are the most important consideration then other factors may be compromised. In some instances the availability of a material in a given country or region of a country may be the deciding factor in choosing material A over material B.

In this paper we will not be concerned with economic and availability problems, since these are discussed by other international experts at this conference. Although these are important considerations in the final analysis, the main emphasis is placed on the chemical, metallurgical and physical properties of beryllium, cesium, germanium, hafnium, niobium, the rare earths, tantalum, titanium and zirconium and their principal compounds and alloys. These properties are reviewed and discussed in relation to their utilization in present day technology. Attention is also given to special problems that may be associated with these metals, and their prominent and more exciting applications are noted.

INTRODUCTION

After all of these elements have been reviewed individually, the outlook for these materials in tomorrow's world is examined in the final chapter.

Introduction

Beryllium's major asset in present day technology stems from its position in the periodic table which gives rise to many of its unique properties. Beryllium has a filled inner level of electrons ($1s^2$) and two outer valence electrons, and a nucleus of four protons and five neutrons.

The low number of nuclear particles (9) and its low nuclear cross-section (ability to absorb neutrons) accounts for beryllium's ability to scatter and slow down neutrons.* Its behavior as a neutron moderator accounts for the great nuclear interest in beryllium and its compounds.

The low number of nuclear particles also accounts for its low mass, which when combined with its moderately good physical properties accounts for the special attention paid this metal by aerospace material engineers. The physical properties are due to the two outer valence electrons, which occupy overlapping s and p bands and give rise to beryllium's high melting point, elastic moduli and mechanical properties (see Table I). The favorable strength-to-density ratio, the high heat capacity and heat of fusion (on a weight basis) and low rate of oxidation up to temperatures of 825°C make this metal very attractive for some space and aircraft applications.

Physical Properties¹⁻¹³

The physical properties of beryllium metal are summarized in

* The rule of thumb is that all things being equal, the material which has a mass closest to that of the particle being scattered (i. e. the neutron) is the most effective in absorbing energy (i. e. slowing the particle down). This is why hydrogen is a better moderator than beryllium and beryllium better than graphite.

Table I. Although many of the physical properties listed appear to be those of a normal metal, it must be remembered that these are given as molar quantities, but for most technological applications it is more important to examine these properties on a weight basis.

The high heats of fusion (391 cal/gm) and vaporization (8630 cal/gm), heat capacity (0.436 cal/gm-deg) and melting and boiling temperatures make beryllium a very competitive material for heat shields and nose cones in space capsules and missiles. The high values of Young's (elastic) and shear moduli and the low temperature dependence of these properties make it a desirable material where maintenance of dimensional stability under heat and stress is important, especially when combined with beryllium's low density. This accounts for the use of beryllium in inertial guidance systems and control compartments in spaceships and rockets, gyroscopes in aircraft and ocean-going ships, and components of jet engines.

The low electrical conductivity and the high Debye temperature combine to make beryllium a better conductor than either aluminum or copper below 200°K (-73°C); this accounts for the use of beryllium in transformers operating at cryogenic temperatures. Although the resistivity of beryllium (3.6 μ ohm-cm) is larger than that of copper (1.6) and aluminum (2.6) at room temperature, the temperature dependence of resistivity, which is approximately proportional to the Debye temperature (1031°K for Be, 310 for Cu, 390 for Al) divided by the absolute temperature, is nearly three times larger for beryllium than for either copper or aluminum.

TABLE I. PHYSICAL PROPERTIES OF BERYLLIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Atomic Number	4	-
Atomic Weight ($^{12}\text{C}=12.00$)	9.0122	1
Atomic Volume (cc/mole)	4.891	2
Lattice Parameter ($\text{\AA}$) α (hcp)	a = 2.286	3
	c = 3.584	3
β (bcc, at $T=1255^\circ\text{C}$)	2.551	3
Density (gm/cm^3)	1.843	-
Metallic Radius ($\text{CN}=12$) ^a ($\text{\AA}$)	1.128	4
α - β Transition Temperature ($^\circ\text{C}$)	1267	5
Heat of Transformation (kcal/g at)	(0.65)	6
Melting Point ($^\circ\text{C}$)	1284	2
Heat of Fusion (kcal/g at)	3.52	2
Vapor Pressure A	16734	7
$\log P_{\text{torr}} = -A/T+B+CT$ B	9.067	7
C $\times 10^4$	-1.454	7
(temp. range $^\circ\text{C}$)	900-1280	7
Boiling Point ($^\circ\text{C}$)	2869	2
Heat of Sublimation at 25°C (kcal/g at)	77.9	2
Heat Capacity, C_p (cal/g at-deg)	3.93	2
Electronic Specific Heat Constant (cal/g at-deg ²) $\times 10^4$	0.533	2
Debye Temperature ($^\circ\text{K}$)	1031	2
Magnetic Susceptibility (emu/mole) $\times 10^6$	-9.01	8
Electrical Resistivity (μ ohm-cm)	3.6	9, 10
Superconducting Transition Temperature	LT films ^b	10
Hall Coefficient (volt-cm/amp-Oe) $\times 10^{12}$	2.44	11
Ionization Potentials (eV)		
I	9.320	12
II	18.206	12
III	153.1	13
IV	216.6	13
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.35	9
Thermal Expansion ($^\circ\text{C}^{-1}$) $\times 10^6$	11.5	2

TABLE I. (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Grüneisen Constant	1.16	2
Compressibility (cm^2/kg) $\times 10^7$	9.772	2
Young's Modulus (kg/cm^2) $\times 10^{-6}$	3.04	2
Shear Modulus (kg/cm^2) $\times 10^{-6}$	1.46	2
Poisson's Ratio	0.039	2
Hardness, Vickers (kg/mm^2)	150	8
Yield Strength (kg/mm^2)	19-27 ^c	9
Ultimate Strength (kg/mm^2)	23-36 ^c	9
Elongation (%)	1-3.5 ^c	9
Nuclear Cross Section (barns)	0.010	9

^aCN means coordination number.

^bObserved only in thin films deposited at low temperatures.

^cVacuum hot pressed powder.

Thus, it is obvious that beryllium's resistivity drops off quite rapidly upon cooling and becomes less than that of copper and aluminum.

Although the yield and ultimate tensile strengths are 2 to 5 times less than that of the stronger steels, the density of beryllium is 4 times less and thus on a strength-to-density basis beryllium is a very strong rival to steels. This accounts for the use of beryllium as disk brakes in aircraft and automobile race cars, as skin panels and extruded tubing in spacecraft, as rotor blades and other parts of gas turbine engines.

The low number of electrons, which allow the passage of x-ray and γ -ray beams with little attenuation,* and the good mechanical properties account for the almost exclusive use of beryllium as windows in x-ray tubes and in industrial and research equipment.

Chemical Properties^{9, 14}

Beryllium is quite resistant to oxidation in air at temperatures below 700°C. At 700°C oxidation is noticeable and occurs quite rapidly at 1000°C and higher. Because highly polished surfaces can be readily produced and maintained for years, beryllium is used as mirrors especially when dimensional stability is required.

Beryllium reacts with air or oxygen to form beryllium oxide, BeO , which is a very stable compound (the heat of formation is -149.0 kcal/mole). Since the finely divided metal powder reacts very readily with

*The scattering cross section of x-rays and γ -rays is directly proportional to the atomic number (number of electrons) of the matter being subjected to the radiation.

air or oxygen, beryllium powder is being used as a fuel for retro-rockets.

At high temperatures, beryllium reacts with nitrogen ($> 900^{\circ}\text{C}$) forming Be_3N_2 and with carbon ($> 1285^{\circ}\text{C}$) forming Be_2C .

Beryllium is attacked quite readily by sulfuric and hydrochloric acids, slowly by dilute nitric acid and not at all by concentrated nitric acid. It reacts with fluorine at room temperature, with the other halides, HCl(g) , HF(g) and CO_2 at elevated temperatures, but not at all with hydrogen at any temperature. The metal is resistant to water and water vapor up to 300°C .

Metallurgical Behavior^{9, 14-21}

One of the biggest drawbacks to greater utilization of beryllium is its inherent brittleness. This is primarily due to its anisotropic nature. When beryllium is worked, it shows good uniaxial properties in the direction of working but a lowering of strength and ductility normal to the working direction.¹⁵ During the past few years there has been much progress in solving this problem, with special attention being paid to texture, grain size, purity and alloying.¹⁵⁻¹⁹

Lowering of oxygen contents below 0.3 wt. % BeO and exclusion of other non-metallic inclusions has permitted direct working of ingots without going through the intermediate powder metallurgy steps. Foils as thin as 0.125 mm (0.005 in)¹⁶ and wire as small as 0.05 mm (0.002 in)¹⁷ have been prepared in this manner. Some mechanical properties of the wire are summarized in Table II. These new techniques have lowered

TABLE II. MECHANICAL PROPERTIES OF DIFFERENT FORMS OF BERYLLIUM
AND SOME BERYLLIUM-BASE ALLOYS^{9, 17, 19}

<u>Alloy or Material</u>	<u>Condition</u>	<u>Yield Strength (kg/mm²)</u>	<u>Ultimate Strength (kg/mm²)</u>	<u>Elongation (%)</u>
pure Be	Vac. hot pressed powder	19-27	23-36	1-3.5
	Cross-rolled powder	28-42	42-63	10-40
Be wire [0.125 mm (0.005in)]	as drawn	62	77	2
	fully annealed	30	44	8
Be-36Al	-	26-42	37-49	-
Be-43Al	-	23-39	31-45	-

the cost of 0.125 mm (0.005 in) beryllium wire from \$10/m (\$3/ft) to \$0.50/m (\$0.15/ft), a cost reduction of twentyfold.¹⁷

Common metallic impurities, such as aluminum, silicon, iron and nickel, have adverse effects on the ductility of beryllium. Lowering of these metal impurities to below the 20 ppm (parts per million) range results in significant improvement in its ductility.²⁰

The development of a 38 wt. % Al-62 wt. % Be alloy (commercially called Lockalloy) and a 43 wt. % Al-57 wt. % Be alloy offers a good compromise between the desirable properties of beryllium and improved ductility and formability. These alloys are expected to bridge the gap between low strength, high ductility magnesium and aluminum and high strength, low ductility titanium and beryllium.^{18, 19} Some of the properties of these alloys along with pure beryllium are given in Table II.

Beryllium may be fabricated by extrusion, forging, rolling and hydrostatic forming. Usually these processes are carried out at high temperatures 800 to 1100°C. Beryllium may be joined to other metals by brazing, welding, electroplating and cladding.^{9, 14}

Beryllium is an important alloying agent. It is added to copper and nickel to form heat treatable alloys which can be easily formed into usable forms and then hardened and strengthened. Beryllium is added to aluminum- and magnesium-base alloys to refine the grain size and improve the oxidation resistance. When added to titanium, beryllium acts as a precipitation hardening agent in α -Ti alloys and reduces the rate of oxidation by a third at 425°C and a half at 540°C. Recently Herchenroeder²¹ pointed out that a small amount of beryllium

(0.8 wt.% is optimum and critical) is an important ingredient in an iron-base chromium (20.5%) nickel (13%) cobalt (12%) high temperature superalloy. The beryllium addition raises the ultimate strength of the alloy from 100 kg/mm^2 for the material without beryllium to 154 kg/mm^2 .

Beryllium-copper alloys are one of the most important materials available today. These alloys are resistant to fatigue and corrosion; exhibit excellent hardness, strength and electrical conductivity, over a wide temperature range; are easy to fabricate while soft; and can be heat treated for maximum strength and hardness. The copper-rich end of the beryllium-copper system is shown in Fig. 1. The useful range of beryllium additions is from 0.5 to 2.0 wt. %. As seen in Fig. 1., all alloys can be obtained in a soft and fabricable state by heat treating at 790°C and rapidly quenching in water. Aging is carried out at 315°C for various periods of time to obtain optimum hardness and strength. The variations of hardness and electrical conductivity as a function of beryllium concentration are given in Table III. These alloys have a wide range of uses as springs, bellows, electrical contacts, switches, non-spark tools and non-magnetic high pressure systems.

Principal Compounds^{3, 9, 13, 14, 22, 23}

Without a doubt beryllium oxide, BeO , is the most important beryllium compound in today's technology, playing a role second only to the pure metal. Beryllium fluoride and chloride are important since they are used in the preparation of the metal. The transition metal beryllides, T_2Be_{17} , TBe_{12} and TBe_{13} , where $\text{T} = \text{Zr, Hf, Mo, Ta and Nb}$ appear

Fig. 1. Copper-rich end of the copper-beryllium system

TABLE III. PROPERTIES OF BERYLLIUM-COPPER ALLOYS

<u>Composition</u> <u>(wt. % Be)</u>	<u>Hardness</u> <u>and</u> <u>Strength</u>	<u>Electrical</u> <u>Conductivity</u>
0.5 + Ag	moderate	highest
0.5	moderate	high
1.6 - 1.8	good	good
2.0	maximum	fair

to have some promise because of their high-temperature strength, low density, oxidation resistance up to 1600°C and good thermal shock resistance.²³

The physical properties of beryllium oxide are listed in Table IV. The most useful properties of BeO are its high melting point, low density, high thermal conductivity, high electrical resistivity, high heat of formation, and good elastic and mechanical properties. Because of its high thermal conductivity, BeO is less desirable as a thermal insulator than many other ceramic oxides. The high heat of formation accounts for the fact that BeO is compatible with many metals at high temperatures. The refractory and stable nature of BeO combined with the low neutron capture cross section make this substance an ideal material for use in high temperature nuclear reactors. Other applications include the utilization of BeO as high temperature electrical insulators, crucible materials and nose cones for re-entry space vehicles.

The high dielectric constant combined with the good refractory properties (high temperature stability, thermal shock resistance, chemical stability and mechanical properties) account for the use of BeO in insulated radomes and microwave windows, and high power vacuum tubes.

One of the biggest drawbacks to widespread use of BeO is its susceptibility to water vapor to form beryllium hydroxide. Because of this, BeO must be used in dry environments.

The chemical stability with respect to most metals, high electrical resistivity and good mechanical properties accounts for the use of BeO

TABLE IV. PHYSICAL PROPERTIES OF BeO AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED^{14, 24, 26, 27}

<u>Property</u>	<u>Value</u>
Lattice Parameter (Å) (ZnS type, hex)	
a =	2.698
c =	4.377
Density (gm/cm ³)	3.010
Melting Point (°C)	2570
Heat of Fusion (kcal/mole)	17.0
Boiling Point (°C)	4260
Heat of Sublimation at 25°C (kcal/mole)	152
Heat Capacity, C _p (cal/g mole)	6.0
Heat of Formation (kcal/mole)	-149.0
Electrical Resistivity at 1000°C (ohm-cm)	8.0 x 10 ⁷
Thermal Conductivity at 200°C (cal-cm/sec-cm ² -deg)	0.190
Thermal Expansion (°C ⁻¹) x 10 ⁶	5.5
Compressibility (cm ² /deg) x 10 ⁷	2.6
Young's Modulus (kg/cm ²) x 10 ⁻⁶	3.9
Shear Modulus (kg/cm ²) x 10 ⁻⁶	1.5
Poisson's Ratio	0.34
Hardness, Knoop (kg/mm ²)	1200
Ultimate Strength (kg/mm ²)	9.8 ^a

^aUltimate strengths as high as 1410 kg/mm² have been reported for BeO whiskers.

as a fine particle dispersent in copper. Beryllia has only a small effect on the electrical conductivity, but greatly increases the strength, ductility and resistance to creep at high temperatures (875°C).²⁵

Composites^{17, 28, 29}

Although the advantages of composites have been known for many years, the last few years have seen a number of technological improvements for obtaining superior properties in a combination of two or more substances over the utilization of only one material. One of the newly-developed composites is a fiber reinforced matrix. Because of their outstanding mechanical and physical properties, beryllium and BeO are both being considered as fiber materials. Combinations of beryllium wire in aluminum, aluminum-titanium alloys, aluminum-silver-germanium alloys, nickel, silver, stainless steels and titanium matrices, and of BeO fibers in a glass matrix have been made into fiber reinforced composites.^{17, 28}

Another type of composite seriously being studied is the eutectic alloy. By proper cooling techniques it is possible to freeze the eutectic mixture such that the lamellar structure of the two phases solidifying are parallel to one another along the entire length of the ingot. One useful beryllium alloy combination is the Be-Ni-B alloys in which Be and Ni-B form the two solidifying phases.²⁸

Coatings or claddings of one material over a second substance is an old, well-known type of composite. This technique permits the protection of a base material by a surface metal or oxide. In general this coating or cladding process is carried out by electrodeposition, vapor deposition

or explosive cladding. However, in mid-1967, the General Electric Company announced a new process²⁹ called "metalliding." In this process a coating material (the anode) such as beryllium is electrolytically deposited on a cathode of a base metal. But since this electrolytic process is carried out between 600 and 1200°C in a molten fluoride salt bath, the beryllium or anode metal diffuses into the base metal to form an alloy coating. It is also possible to use two or more anode metals to form multiple coatings. The metallide technique shows much promise since this method may be the only way to form coatings of beryllium, germanium, hafnium, rare earths, titanium and zirconium on base metals, such as cobalt, copper, iron, molybdenum, nickel, niobium, tantalum, titanium and tungsten.²⁹

Applications

An extensive list of applications and uses of beryllium metal, beryllium-copper and beryllium-nickel alloys, and beryllia is presented in Table V. For the first two categories the uses are subdivided into more narrow fields.

Examination of this list reveals the widespread uses of beryllium in one form or another in today's technology, many of these being in the glamour fields of aerospace, electronics and nuclear energy.

Toxicity^{14, 22}

The toxic nature of beryllium, especially the readily soluble compounds, has been known for many years and most aspects of this problem have been overcome. Careful control has practically eliminated new cases of beryllium-

TABLE V. APPLICATIONS OF BERYLLIUM METALS, ALLOYS AND COMPOUNDS

A. BERYLLIUM AND BERYLLIUM-BASE ALLOYS

1. Aerospace

heat shields
structural tubing
skin panels
antennas
rudders
brakes
powder fuel for retrorockets
solar cell mounting boards

2. Instruments

gyroscope parts
accelerometers
inertial guidance system
parts
mirrors and other optical
parts
cryogenic transformers

3. Nuclear

neutron moderator
canning material
container for radioactive
power sources (e. g. SNAP)^a

4. High Temperature

turbine engine parts -
blades, disks, shafts
coatings on refractory
metals, Mo and W

5. Alloying Agent

aluminum-base alloys
magnesium-base alloys
titanium-base alloys
superalloys

6. Miscellaneous

windows for α - and γ - rays
and subatomic particles
composites

B. BERYLLIUM-COPPER ALLOYS

1. Electrical

contacts
spot welding electrodes
switch parts
circuit breakers
sliding contacts
current carrying terminals
expandable antennas for
space vehicles
electronic connectors
fuse clips
resistance welding electrodes

2. High Strength

non-sparking tools
non-magnetic tools and
parts
springs
bourdon tubing (pressure
gauges)
bellows
diaphragms
aircraft engine parts
plastic molds
marine propellers, pump
and valve parts
gears
bearings
shims
precision castings
rollers
ball and bearing housing

TABLE V. (continued)

fasteners (bolts, etc.)
lock washers
throat for hypersonic
wind tunnels
underwater housings

C. BERYLLIUM-NICKEL ALLOYS

hypodermic needles
surgical instruments
business machine parts
dies
diaphragms
feather valves

matrix for diamond
drill bits
fuel pump parts
switches
springs
bellows

D. BERYLLIUM OXIDE

nuclear reactors
cores for furnaces
crucibles
protective coatings of
refractory metals
glass fibers
composites

electrical insulators
spark plugs
dispersent in Cu for
electrical applications
fluorescent lamps
wave guide windows
low-loss dielectrics

^aSNAP stands for systems nuclear auxiliary power.

associated diseases in the beryllium industry. Since most of the final products are in non-soluble forms, there is little danger from the product. In the beryllium processing and machining industry some of the control measures adapted are central air filtration systems, special enclosures for grinding and machining operations, and standard vacuum systems. Complete physical examinations of workers on a regular basis are an integral part of the control procedure.

Concluding Remarks

A brief survey of the properties of beryllium and some of its alloys and compounds has been presented and discussed with particular emphasis on the utilization of these materials. It is impossible to present much detail here concerning the technology involved, and thus several references have been cited in the text to give the reader sources of more detailed information. In addition to these references, three more volumes are noted (References 30, 31 and 32). They are concerned with a 1963 lecture series on beryllium and its properties and applications³⁰ and the 1964 and 1965 international beryllium metallurgy conferences held in Philadelphia³¹ and Grenoble,³² respectively. These three books contain much detailed information on the technology and metallurgy of beryllium.

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. J. A. Martin and A. Moore, J. Less-Common Metals 1, 85 (1959).
6. K. A. Gschneidner, Jr., estimated value, based on method proposed by D.H. Dennison, K.A. Gschneidner, Jr. and A.H. Daane, J. Chem. Phys. 44, 4278 (1966).
7. R.B. Holder, R. Speiser and H. L. Johnston, J. Am. Chem. Soc. 70, 3897 (1948).
8. C.J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).
9. A.R. Kaufmann, p. 1198 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
10. G.T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
11. C. Kittel, Introduction to Solid State Physics, 2nd Ed., John Wiley & Sons, New York (1965).
12. G.H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Co., New York (1963).

13. Handbook of Chemistry and Physics, 46th ed., p. E-61, R.C. Weast, Ed., The Chemical Rubber Co., Cleveland (1965).
14. B.R.F. Kjellgren, p. 32 in Rare Metals Handbook, 2nd ed., C.A. Hampel, Ed., Reinhold Publishing Corp., New York (1961).
15. S. Gelles, V. Nerses and J. Siergiej, *J. Metals* 15, 343 (1963).
16. Anonymous, *J. Metals* 17, 691 (1965).
17. N.P. Pinto and J.P. Denny, *Metal Progress* 91, [6], 107 (1967).
18. J.A. Van Hamersveld, T.S. Svendsen and W.C. Hayes, *Metal Progress* 91, [2], 91 (1967).
19. J.B. Rittenhouse and J.B. Singletary, *Metal Progress* 89, [2], 57 (1966).
20. C.R. Weymueller, *Metal Progress* 88, [3], 57 (1966).
21. R.B. Herchenroeder, *J. Metals* 18, [1], 33 (1966).
22. L.S. Busch, "Beryllium" in Encyclopedia of the Chemical Elements, C.A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
23. E.G. Kendall, p. 143 in Ceramics for Advanced Technologies, J.E. Hove and W.C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
24. A.J. Rothman, p. 107 in Ceramics for Advanced Technologies, J.E. Hove and W.C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
25. A.S. McDonald, *Metal Progress* 89, [4], 70 (1966).
26. J.F. Lynch, C.G. Ruderer and W.H. Duckworth, Section 5.4.2 in Engineering Properties of Selected Ceramic Materials, Am. Ceram. Soc., Columbus, Ohio (1966).

27. J.I. Slaughter, p. 218 in Ceramics for Advanced Technologies, J. E. Hove and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
28. T. Vasilos and E.G. Wolff, J. Metals 18, 583 (1966).
29. Anonymous, Chem. Eng. News 45, [28], 50 (1967).
30. H.H. Hausner, Ed., Beryllium, Its Metallurgy and Properties, University of California Press, Berkeley (1965).
31. L.M. Schetky and H.A. Johnson, Eds., Beryllium Technology, Vol. 1 and 2, Gordon and Breach Science Publishers, Inc., New York (1966).
32. Conférence Internationale sur la Métallurgie du Beryllium, Grenoble, 1965, Presses Universitaires de France, Paris (1966).

Introduction

Cesium is an unusual metal, having low melting and boiling temperatures, low ionization potential, large mass and volume, and little, if any, strength. These properties limit its usefulness for widespread applications. But at the same time these properties account for some exciting uses in today's technology and potential uses in that of tomorrow's.

The electronic structure of cesium accounts for the properties of this metal. It has a $6s^1$ electron beyond the Xe gas core. Since there are 54 core electrons, which shield the nuclear charge and cause the large separation of the outer electron from the nucleus, the electrostatic attraction between the nucleus and the outer $6s^1$ electron is weak. This accounts for the ease by which the cesium atom is ionized and for the weak metallic bond, which in turn accounts for the low melting and boiling temperatures and strength.

Physical Properties¹⁻¹²

The physical properties of cesium are summarized in Table VI. The atomic volume (and also radius) is the largest of the naturally occurring metals. This limits cesium's usefulness as an alloying agent since it is very unlikely to form solid solution alloys, and is expected to form many immiscible liquid alloys.*

*The heat of sublimation is also an important quantity in determining liquid immiscibility. But since it is much smaller than that of most metals, it goes hand-in-hand with the large volume because the governing parameter is the ratio of the heat sublimation to the atomic volume which is 5 to 10 times smaller for cesium compared to that of normal metals.

TABLE VI. PHYSICAL PROPERTIES OF CESIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Atomic Number	55	-
Atomic Weight ($^{12}\text{C}=12.00$)	132.905	1
Atomic Volume (cc/mole)	69.19	2
Lattice Parameter (Å) (bcc at -100°C)	6.079	3
Density (gm/cm ³)	1.921	-
Metallic Radius (CN=12) ^a (Å)	2.731	4
Melting Point ($^\circ\text{C}$)	28.6	2
Heat of Fusion (kcal/g at)	0.506	2
Vapor Pressure A	3726	5
$\log P_{\text{torr}} = -A/T+B$ B	6.85	5
(temp. range $^\circ\text{C}$)	400-925	5
Boiling Point ($^\circ\text{C}$)	666	2
Heat of Sublimation at 25°C (kcal/g at)	18.84	2
Heat Capacity, C_p (cal/g at-deg)	7.65	2
Electronic Specific Heat Constant (cal/g at-deg ²) $\times 10^4$	8.48	2
Debye Temperature ($^\circ\text{K}$)	43	2
Magnetic Susceptibility (emu/mole) $\times 10^6$	-29	6
Electrical Resistivity (μ ohm-cm)	20	7, 8
Hall Coefficient (volt-cm/amp-Oe) $\times 10^{12}$	-7.8	9
Ionization Potentials (eV)		
I	3.893	10
II	25.1	10
Work Function (eV)	1.89	11
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.044 ^b	12
Thermal Expansion ($^\circ\text{C}^{-1}$) $\times 10^6$	97	2
Grüneisen Constant	1.49	2
Compressibility (cm ² /kg) $\times 10^7$	483.3	2
Young's Modulus (kg/cm ²) $\times 10^{-6}$	(0.0179)	2
Shear Modulus (kg/cm ²) $\times 10^{-6}$	(0.0066)	2
Poisson's Ratio	(0.356)	2
Nuclear Cross Section (barns)	29	12

^aCN means coordination number.

^bLiquid at the melting point.

The melting and boiling points are the second lowest of all the naturally occurring metals, exceeded only by those of mercury.* The fact that cesium melts just above room temperature does not permit this metal to be used in the common metallurgical applications. But it does account in part for its utilization in thermionic power converters, magneto-hydrodynamics, and ion propulsion. The low ionization potential and density are two other factors which are essential in these uses.

The ionization potential and the work function of cesium are by far the lowest of any of the naturally occurring elements. The significance of the former in modern technology was noted above, and that of the latter accounts for the utilization of cesium in photoelectric devices.

Chemical Properties¹²⁻¹⁴

Cesium is the most electropositive element in the periodic table and is very reactive. It reacts explosively with elemental phosphorus and sulfur and vigorously with oxygen and the halogens. Cesium combines with oxygen to form a variety of oxides, peroxides or superoxides. It reacts with water yielding hydrogen which instantaneously ignites. When cesium is brought in contact with hydrogen or nitrogen, the hydride, CsH , or azide, CsN_3 , is formed. Cesium reacts with most glasses displacing elemental silicon. Because of its reactive nature, special care must be taken in handling cesium; dry helium or argon glove boxes and special glass or stainless steel storage containers must be employed. The

* The boiling point of arsenic is lower than that of cesium but arsenic is considered to be a semi-metal.

reactive nature of cesium accounts for its use as a getter in vacuum radio tubes.

Many cesium salts are corrosive and hygroscopic and special care must be taken when working with these materials.

Principal Compounds¹²⁻¹⁴

From a technological point of view the halides are the most important cesium compounds. CsCl is important since it is the primary salt for preparing other cesium compounds. It is sometimes used in analytical chemistry to detect aluminum, chromium and gallium. The iodide, when doped with thallium, is used as a scintillation counter to detect radiation. The iodide is also used for infrared and far-infrared windows since it is transparent to radiation from 24 to 50 μ . As a dopant it is used in ZnS luminescent tubes and screens. CsBr may also be used as a window for infrared radiation, but its upper limit (38 μ) is much less than that of the iodide.

Cesium borohydride, CsBH₄, has been mentioned as a possible solid fuel for rockets because of its high heat of formation. Cesium hydride is a strong reducing agent and has been used to catalyze condensation and polymerization reactions.

Applications¹²⁻¹⁷

An extensive listing of the applications of cesium metal and its compounds is given in Table VII. A brief discussion of the scientific and engineering background of some of the more important or newer and more promising applications are discussed below.

TABLE VII. APPLICATION OF CESIUM METAL AND ITS COMPOUNDS

Cesium

- phototubes
- photomultiplier tubes
- spectrophotometers
- infrared detection devices
- getters
- coatings on tungsten to lower work function
- thermionic power conversion devices
- magneto-hydrodynamic devices
- ion propulsion engines

Cesium Compounds

- transparent windows for infrared radiation
- scintillation counters
- dopant in luminescent tubes and screens
- solid fuel for rockets
- ferroelectrics
- piezoelectrics
- semiconductors
- medicine-sedatives and treatment of epilepsy
- analytical chemistry reagent
- catalyst
- electrolyte in storage batteries
- atomic time standard
- glass and ceramic glazes
- porcelain enamels

The low work function of cesium allows photoelectrons to be emitted when visible or infrared radiation strikes its surface making it useful in photocells. The emitted photoelectrons cause a current to flow when the cell is attached to an external circuit. By monitoring electrical output, the photocell performs a number of useful functions which are utilized in infrared detection devices, spectrophotometers, photosensing devices, photomultipliers, etc. The most important material combinations are Cs-CsO-Ag layered films which are sensitive to visible light and an antimony-cesium alloy of the Cs_3Sb stoichiometry which is sensitive to infrared radiation.

The principle of the cesium thermionic diode is best explained with the aid of Fig. 2a. The diode is made up of a heated cathode and an anode which are 1.0 mm or less apart. The anode must be cooled since it receives radiated heat from the cathode and heat due to electron bombardment. The cesium serves two functions, the first is to lower the work function of the cathode and the second is to reduce the space charge between anode and cathode by the formation of positive cesium ions. By connecting the anode and cathode to an external circuit, the electrons can do useful work. The efficiency of the thermionic converter increases as the temperature difference between the anode and cathode becomes larger. The cathode may be heated in space by solar mirrors. The use of cesium diodes in nuclear reactor piles is being considered since this may be a more efficient way of generating electrical power from reactors. Cesium diodes capable of generating 100 watts have been reported.

(a)

(b)

Fig. 2 a) Cesium thermionic converter diode. b) Cesium-ion propulsion engine.

The ion propulsion engine is schematically illustrated in Fig. 2b. A nuclear reactor provides mechanical and heat energy. The heat is used to vaporize cesium which ionizes when it strikes a hot tungsten surface at 1100°C . These ions are then accelerated to 480,000 km/hr (300,000 miles/hr) by a high voltage field. The loss of positive ions builds up a negative charge which must be neutralized. The mechanical energy from the reactor is used to drive an electric generator which supplies the potential to the accelerator grids and the electrical energy to heat the hot tungsten surface used to ionize the cesium atoms. Ion engines are capable of large specific impulses, up to 20,000 sec , but have very low thrust-to-weight ratios, about 10^{-5} . This compares with specific impulses of 100 to 1000 sec , and thrust-to-weight ratios of 1 to 10 for chemical rockets. Cesium ion engines because of their low thrust-to-weight ratios can only be used to accelerate spacecraft once they are in orbit or free from the earth's gravitational field. They are particularly useful for interplanetary space probes of extended duration.

Cesium appears to play a vital role in magneto-hydrodynamic methods of power generation. A plasma (a high temperature ionized gas) is passed perpendicular to a strong magnetic field to generate a current in the plasma, in much the same manner a current is generated in copper wires as they cut across the magnetic flux lines in the electric generator. The amount of power output depends upon the velocity and degree of ionization of the plasma and the strength of the magnetic field. Cesium is added to the plasma to increase the ionization and thus increase the conductivity of the gas.

Late in 1967 the cesium atomic clock was officially adopted by the 13th General Conference on Weights and Measures, replacing the one based on the earth's motion.¹⁷ The atomic clock is based upon the transition between two hyperfine levels (in zero magnetic field) in cesium-133, the only naturally occurring isotope. The time interval of a second is defined as 9,192,631,770 periods of radiation. The choice of cesium-133 depended in part upon its non-zero nuclear spin, which gives rise to hyperfine levels, and the fact that it has only one naturally occurring isotope (other isotopes especially of nuclear masses near 133 would limit the resolution of the measurement of the transition in cesium-133).

Concluding Remarks

The present day utilization of cesium is of the order of several hundred pounds per year. If the more interesting properties of cesium can be utilized in some of the advanced technological equipment, such as thermionic converters and magneto-hydrodynamic power generators, the demand for cesium will increase significantly. Clearly there is a need for more basic and applied research on the properties of cesium and on new or improved methods for deriving and purifying cesium and its compounds. If advances in these areas can be achieved, the future for cesium will be quite bright.

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. C. F. Bonilla, D. L. Sawhney and M.M. Makansi, Trans. ASM 55, 877 (1962); and J. Bohdanský and H.E.J. Schins, J. Phys, Chem. 71, 215 (1967).
6. C. J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).
7. J.W. Vogt, p. 1200 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
8. G. T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
9. C. Kittel, Introduction to Solid State Physics, 2nd ed., John Wiley & Sons, New York (1965).
10. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
11. G.F. Rouse, p. 9-146 in American Institute of Physics Handbook, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
12. C.A. Hampel, p. 434 in Rare Metals Handbook, 2nd ed., C.A. Hampel, Ed., Reinhold Publishing Co., New York (1961).

13. F.M. Perel'man, Rubidium and Caesium, Pergamon Press, London (1965).
14. C.E. Mosheim, "Cesium" in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
15. R.A. Barney, E.G. Kendall and J.E. Hove, p. 338 in Ceramics for Advanced Technologies, J.E. Hove and W.C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
16. A.J. Rothman, p. 306 in Ceramics for Advanced Technologies, J.E. Hove and W.C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
17. Anonymous, Chem. & Eng. News 45, [48], 51 (1967).

Introduction

Just as for the first two elements discussed (beryllium and cesium), the total number of electrons and especially the outer electronic configurations play an extremely important role in determining germanium's physical, chemical and metallurgical properties and thus its ultimate utilization by society. Germanium has 32 electrons, of these 18 have the argon rare gas core, 10 fill the $3d$ level, and the remaining 4 occupy the outer $5s$ and $4p$ levels. In ground states (i. e. a free gaseous atom) there are two electrons in each of the outer levels, i. e. $5s^2$, $4p^2$, but in the condensed state the outer electronic configuration generally is $5s^1 4p^3$. In this latter configuration the four electrons form hybridized orbitals which are directionally extended in space such that they make an angle of 109° with each other and point to the four corners of a tetrahedron. In the elemental state and in many of its compounds germanium forms covalent bonds with its nearest neighbors. This gives rise to directional bonding and the bonding electrons are restricted to localized spacial positions surrounding the germanium atom. Since these electrons are localized, they do not contribute to electron conduction properties normally found in a metal, and the resistivity of germanium is of the order of 10^6 times larger than that of metals. Furthermore, the temperature dependence of resistivity is of the opposite sign of that of metals. From its electrical behavior and also some other properties germanium is not considered to be a metal but a semiconductor.

Physical Properties¹⁻¹⁷

The physical properties of germanium are summarized in Table VIII. The melting point and heat of sublimation of germanium is significantly lower than those of its preceding congeners, silicon and diamond, indicating a significant decrease in the strength of the covalent bonds compared to those of silicon and diamond. The relative covalent bond strengths for these three elements also account for germanium having the lowest energy gap (to be discussed below).

The electrical resistivity listed in Table VIII is for intrinsic germanium, i. e. for germanium which is as pure as is possible to obtain. Pure or intrinsic germanium, however, is of little commercial interest. Germanium when doped with very small amounts of various impurities shows a wide range of variation in its electrical properties, and it is this doped germanium which is of great importance in the electronic industry. A brief description of the science involved is in order at this time.

In crystalline germanium the sp^3 bonding orbitals are filled by virtue of the covalent bond between neighboring atoms. Each of the four germanium atoms surrounding a given central germanium atom shares a pair of electrons with the central atom, and thus the central atom, by electron sharing, has completely filled its bonding orbitals. In the band model this leads to a complete filling of the valence band with no excess or deficiency of electrons. The next highest band in which electrons are permitted is an antibonding band, commonly called the conduction band,

TABLE VIII. PHYSICAL PROPERTIES OF GERMANIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Atomic Number	32	-
Atomic Weight ($^{12}\text{C}=12.00$)	72.59	1
Atomic Volume (cc/mole)	13.64	2
Lattice Parameter (Å) (diamond)	5.6575	3
Density (gm/cm ³)	5.322	-
Metallic Radius (CN=12) ^a (Å)	1.378	4
Melting Point (°C)	936	2
Heat of Fusion (kcal/g at)	8.83	5
Vapor Pressure A	19120	6
log P _{torr} = -A/T+B-ClnT B	9.94	6
C	0.437	6
(temp. range °C)	1240-1610	6
Boiling Point (°C)	2827	2
Heat of Sublimation at 25°C (kcal/g at)	89.5	2
Heat Capacity, C _p (cal/g at-deg)	5.58	5
Electronic Specific Heat Constant (cal/g at-deg ²) x 10 ⁴	0	2
Debye Temperature (°K)	403	2
Magnetic Susceptibility (emu/mole) x 10 ⁶	-8.7	7
Electrical Resistivity (ohm-cm)	46	8
Superconducting Transition Temperature (°K)	LT films ^b	9
Hall Coefficient (volt-cm/amp-Oe) x 10 ¹²	Varies widely ^c	10
Ionization Potential (eV)		
I	7.88	11
II	15.93	11
III	34.07	12
IV	45.5	12
V	93.0	12
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.14	8
Thermal Expansion (°C ⁻¹) x 10 ⁶	5.75	2
Grüneisen Constant	0.80	2
Compressibility (cm ² /kg) x 10 ⁷	12.70	2

TABLE VIII (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Young's Modulus (kg/cm^2) $\times 10^{-6}$	1.01	2
Shear Modulus (kg/cm^2) $\times 10^{-6}$	0.40	2
Poisson's Ratio	0.27	2
Hardness, Vickers (kg/mm^2)	400	13
Nuclear Cross Section (barns)	2.45	14

^aCN means coordination number.

^bObserved only in thin films deposited at low temperatures.

^cVaries several orders of magnitude and also in sign; it is very dependent upon the kind and amount of impurities.

and it lies 0.75eV above the completely filled valence band. This is shown schematically in Fig. 3. At absolute zero germanium is an insulator since there are no electrons or holes to conduct the current and there is no thermal energy available to excite valence electrons up to the conduction band (Fig. 3a). At higher temperatures there is sufficient energy to excite some electrons into the conduction band. For each electron in the conduction band there is a positive hole in the valence band (Fig. 3b). Both the hole and the electron contribute to the conduction process. The number of electrons excited is proportional to

$$\exp\left(-\frac{\Delta E_{\text{gap}}}{kT}\right) = \exp\left(-\frac{8.7 \times 10^3}{T}\right)$$

where ΔE_{gap} is the gap energy and k is the Boltzmann constant (8.7×10^3 is 0.75eV divided by k).

The effect of impurities is shown in Figs. 3c and d. If a higher valent material, such as P, As, Sb, Bi, is added to germanium, the impurity atom replaces a germanium atom in the lattice and four of its five valence electrons take part in the covalent bonding with the neighboring germanium atoms. The extra electron must go into the conduction band since the valence band is filled (Fig. 3c). These electrons are now available for conduction. This type of semiconductor is called an n-type since the conduction process is carried out by negative particles, i. e. electrons. If a lower valent material (B, Al, Ga, In, Tl) is added to germanium, the impurity atom contributes only three electrons to the covalent bond, leaving one electron pair deficient of an electron, that is a positive hole in the valence band (Fig. 3d). Such material is called a p-type semiconductor since the conduction process is carried out by positive holes.

Fig. 3. The band structure of intrinsic and doped germanium.

The number of impurities added are of the order 10^{-5} to 10^{-3} at. %. The kind and number of impurity atoms have a pronounced influence on the electrical characteristics: i. e. the electrical resistivity, the temperature dependence of resistivity and the Hall effect which may be positive or negative and may vary several orders of magnitude. Because of this wide variation of electrical properties, germanium finds use in the electronic fields as diodes (rectifiers), triodes (transistors), resistance thermometers, magnetometers and photoelectric cells.

Germanium is a very hard and brittle material, which is in line with its covalent nature. The brittleness limits any metallurgical usefulness of germanium or germanium-base alloys. However, it has some application as an additive to other metals.

Germanium transmits infrared radiation and it is used as a detector, window or lens material for this radiation.

Chemical Properties¹⁵⁻¹⁷

Germanium is stable at room temperature with respect to air, water and oxygen. Above 600°C it oxidizes quite rapidly. It reacts with the halogens to form the tetrahalides.

Hydrochloric and sulfuric acid have no effect on germanium, but at 100°C sulfuric attacks it slowly. Germanium is readily dissolved in nitric acid, aqua regia, and molten alkalies, but it is inert to aqueous hydroxides.

Metallurgical Behavior¹⁵⁻¹⁸

Because of its brittle nature germanium has no use as a structural

material. Furthermore, it is almost impossible to fabricate germanium in the form of ribbons, wire, rod or rolled shapes. Germanium is usually grown as single crystals by the Czochralski technique* and then cut into the desired shape. Electrodeposition,¹⁵ vapordeposition¹⁷ and metalliding¹⁸ techniques may be used to form thin coherent coatings of germanium on base metals.

Germanium has some utilization as an alloying agent. It is used to prevent the formation of UAl_4 in canned uranium-aluminum fuel elements because the formation of UAl_4 causes considerable difficulties, such as cracking and disintegration. Small additions are used to increase the hardness and strength of magnesium, aluminum and copper, and to increase the ductility of beryllium-base alloys containing aluminum and silver. Soldering and brazing alloys of germanium with iron, nickel, gold and nickel-chromium are used in special applications. The germanium-gold (12-88 wt. %) alloy is of particular interest as a dental and a jeweler's solder since it melts at 356°C and retains its gold color.

Principal Compounds^{16, 17}

The most important technological compounds of germanium are $GeCl_4$, GeO_2 and synthetic garnets, $M_3^{+2}M_2^{+3}(GeO_4)_3$. The tetrachloride is the most important of these since it is used in the extraction and purification processes for preparing ultra high purity germanium. The dioxide is

* This method employs a seed crystal which is in contact with the surface of the melt, and as the crystal begins to grow it is withdrawn from the melt. The melt is held just above the melting point of the material.

important in germanium glasses which are used as infrared windows and lenses, wide-angle camera lenses and microscopic objectives. The tetragonal (high temperature) modification is quite stable and a thin coating on germanium semiconductors will protect it from atmospheric contaminants. The hexagonal (low temperature) modification, however, is soluble in water, and thus it is possible to form oxide-free germanium surfaces which is quite important in some scientific and technological studies.

The germanium garnets are being used as ferri-magnetics in microwave devices.

Some of the germanium intermetallic compounds are high melting.¹⁹ Zr_5Ge_3 melts at $2300^{\circ}C$, Ti_5Ge_3 at $2100^{\circ}C$ and Nb_5Ge at $1900^{\circ}C$. These are of some interest, but since they are readily oxidized at temperatures greater than $1250^{\circ}C$, their usefulness is limited.

Applications¹⁵⁻¹⁷

The semiconducting properties of germanium have made the greatest impact on the commercial utilization of germanium. The discovery of the rectifying properties of the germanium diode in 1948 opened a whole new vista for germanium and eventually led to the triode or transistor, to terodes and pentodes and many other semiconducting devices.

The advantages of these solid state devices over vacuum tubes are many-fold: low power consumption, light weight, small size, rugged, mechanical stability, long life and immediate start-up. Some

of their disadvantages are: the necessity for very rigid quality control in manufacturing and sensitivity to temperature variations and moisture. A listing of a number of the applications of germanium is given in Table IX.

Concluding Remarks

The outlook for germanium remains excellent with an increasing demand in electronics for the foreseeable future. Today in America almost all new radio, television and high fidelity phonograph sets have solid state circuitry (i. e. transistorized circuits). Much of the new electronic measuring equipment is also being constructed with solid state components. This trend is expected to continue and expand to the entire world.

In view of all of the glamour associated with germanium and other semiconductors, we should not overlook a second important role played by germanium in the modern technological world. The success of the germanium semiconductor devices is a tribute to the modern scientific theory, which enabled scientists to predict the behavior of these devices, putting theoretical solid state physics on very firm ground. Furthermore, the development of germanium semiconductors led to zone refining, the first direct observation of dislocations and the preparation of oxide-free surfaces, and these in turn have led to many new technological and scientific applications. Perhaps modern technology owes more to germanium for these other developments, than to all the germanium devices that have been manufactured.

TABLE IX. APPLICATIONS OF GERMANIUM

Based on Semiconducting Properties

power rectifiers
 photoelectric diodes
 piezoresistive strain gauges
 resistors
 resistance thermometers
 magnetometers
 bolometers
 α -particle counters

Miscellaneous

soldering and brazing alloys
 dental alloys
 alloying agent
 ferrimagnetic microwave devices
 phosphors in fluorescent lights
 lead-acid batteries (lowers
 internal resistance of cells)

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1964).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345rev. (to be published ca. 1968).
5. P. Sommelet and R. L. Orr, J. Chem. Eng. Data 11, 64 (1966).
6. A. W. Searcy, J. Am. Chem. Soc. 74, 4789 (1952).
7. C. J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).
8. W. G. Pfann and C. D. Thurmond, p. 1205 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
9. G. T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
10. H. Y. Fan, Solid State Phys. 1, 283 (1955).
11. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
12. Handbook of Chemistry and Physics, 46th ed., p. E-61, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland (1965).
13. E. M. Savitskii, Influence of Temperature on the Mechanical Properties of Metals and Alloys, Stanford Univ. Press, Stanford, California (1961).

14. J. A. Harvey and D. J. Hughes, p. 8-114 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
15. H. R. Harner, p. 188 in Rare Metals Handbook, C. A. Hampel, Ed. Reinhold Publishing Corp., New York (1961).
16. Anonymous, Germanium, Germanium Information Center, Midwest Research Institute, Kansas City, Missouri (1964).
17. A. F. Witt and H. C. Gatos, "Germanium" in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
18. Anonymous, Chem. & Eng. News 45, [28], 50 (1967).
19. V. I. Bondarev and G. V. Samsonov, Akad. Nauk Ukr. SSR, Porosh. Metal. 1966, [6], 52; English transl. Soviet Powdr. Met. Metal Ceram. 1966, 473.

Introduction

Commercially there has been little utilization of hafnium, but the over-all picture appears to be improving. The largest use for hafnium is in the nuclear energy field, where its high cross section makes it quite useful as a control rod material. Because of its ability to absorb neutrons and because it occurs in nature combined with zirconium (as ZrSiO_4 containing 2 to 5 wt. % HfO_2), hafnium is a by-product from the production of the zirconium which is used as a low cross-section material in nuclear reactors.

Hafnium is one of the three metals which lie in the IV A Group of the periodic table and which are of interest to this Conference. The outer electronic configuration of the ground state for this element is $6s^2 5d^2$. In the metallic state these outer electrons occupy the $6s$ and $5d$ bands with about two electrons each. The high melting point, heat of sublimation and resistivity are in accord with this assignment of electrons. The chemical stability of hafnium is also related to its electronic structure. The high temperature properties and reasonable chemical inertness make hafnium attractive as a refractory-base metal or as an alloying additive.

Physical Properties¹⁻¹²

The physical properties of hafnium are summarized in Table X. The high atomic weight and density limit the usefulness of hafnium and its alloys to applications in which weight is not an important consideration. The atomic volume and radius are slightly smaller than its immediate

TABLE X. PHYSICAL PROPERTIES OF HAFNIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

Property	Value	Ref.
Atomic Number	72	-
Atomic Weight ($^{12}\text{C}=12.00$)	178.49	1
Atomic Volume (cc/mole)	13.45	2
Lattice Parameter (Å)		
α (hcp)	a = 3.1946	3
	c = 5.0511	3
β (bcc at 2000°C)	~3.61	3
Density (gm/cm ³)	13.27	-
Metallic Radius (CN=12) ^a (Å)	1.580	4
α - β Transition Temperature (°C)	1740	5
Heat of Transformation (kcal/g at)	(1.69)	6
Melting Point (°C)	2222	2
Heat of Fusion (kcal/g at)	(4.39)	2
Vapor Pressure	A	7
log $P_{\text{torr}} = -A/T+B$	B	7
(temp. range °C)	1780-2030	7
Boiling Point (°C)	4302	2
Heat of Sublimation at 25°C (kcal/g at)	145.5	2
Heat Capacity, C_p (cal/g at-deg)	6.10	2
Electronic Specific Heat Constant (cal/g at-deg ²) $\times 10^4$	5.74	2
Debye Temperature (°K)	213	2
Magnetic Susceptibility (emu/mole) $\times 10^6$	75	8
Electrical Resistivity (μ ohm-cm)	33.7	9, 10
Superconducting Transition Temperature (°K)	0.16	10
Hall Coefficient (volt-cm/amp-Oe) $\times 10^{12}$	-0.016	8
Ionization Potentials (eV)		
I	7.0	11
II	14.9	11
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.0533	9
Thermal Expansion (°C ⁻¹) $\times 10^6$	6.01	2
Grüneisen Constant	1.07	2
Compressibility (cm ² /kg) $\times 10^7$	8.98	2
Young's Modulus (kg/cm ²) $\times 10^{-6}$	1.40	2

TABLE X (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Shear Modulus (kg/cm^2) $\times 10^{-6}$	0.540	2
Poisson's Ratio	0.30	2
Hardness, Vickers (kg/mm^2)	190 ^b	9
Yield Strength (kg/mm^2)	23.6 ^b	9
Ultimate Strength (kg/mm^2)	45.5 ^b	9
Elongation (%)	23 ^b	9
Nuclear Cross Section (barns)	105	9

^a CN means coordination number.

^b Annealed.

cogener, zirconium ($\sim 4\%$ for the atomic volume and $\sim 1.3\%$ for the radii). This is the opposite of what normally occurs in the periodic table and it is a result of the lanthanide contraction (i. e. the filling of the inner $4f$ level), which occurs just before hafnium as one crosses the sixth period of the periodic table. The similar sizes of zirconium and hafnium account both for the difficulties in separating these elements from each other and for their similar chemical and physical behaviors.

The high melting and boiling points, low vapor pressure, good mechanical properties, and also good chemical properties make hafnium an interesting candidate for high temperature applications. Its low superconducting transition temperature is of little commercial interest. The high nuclear cross section, however, accounts for its major use as nuclear control rods, burnable poisons and neutron flux depressors. Its good mechanical properties, resistance to radiation damage and chemical inertness are also important considerations in nuclear applications.

Chemical Properties^{8, 9}

Hafnium is stable at room temperature with respect to water vapor, oxygen, nitrogen, hydrogen and air. At the respective temperatures of about 350, 350, 850, 650 and 700°C hafnium begins to react with these common gases. Its reactivity at high temperature with these gases accounts for its use as a getter in vacuum tubes. Hafnium is quite resistant to salt solution, aqueous sodium hydroxide, and all dilute

and concentrated acids except concentrated sulfuric, combinations of other acids with sulfuric acid, and hydrofluoric acid. In the presence, however, of even a small amount of ammonium fluoride, the reaction of acids with hafnium is rapid.

Metallurgical Behavior^{8, 9, 12-15}

Hafnium does not deform readily at room temperature and most forming operations, such as forging, rolling and extrusion, are carried out at high temperatures, $\sim 900^{\circ}\text{C}$. Cold rolling, swaging, hammering, drawing and extruding can be performed at room temperature, but intermediate anneals are required after about a 30% reduction. Hafnium can be welded by using inert gas atmosphere techniques and machined by using high speed tools.

Although hafnium oxidizes above 700°C in air, its oxide coating is quite adherent and reduces the rate of oxidation as it grows. Because of this and the refractory nature of the metal, hafnium-tantalum and hafnium-niobium alloys are seriously being considered for very high temperature applications (up to 2200°C) as structural materials and as oxidation resistant coatings and claddings on refractory metals for use as rocket nozzles and thrust inserts on rocket engines. The most promising of these are alloys which contain between 20 and 30 wt. % tantalum.

Hafnium is also used as an alloying agent in tantalum-rich and niobium-rich alloys. Hafnium improves the corrosion and oxidation resistance, and the mechanical properties. The most important of these alloys have the commercial designations T222 (a tantalum-base

alloy containing 9.6 W, 2.4 Hf and 0.01 wt. % C), C129 (a niobium-base alloy containing 10 W and 10 wt. % Hf) and C129Y, which is the same as C129 except that C129Y contains in addition 1 wt. % Y. Recently, a tungsten-rich alloy containing 0.35 wt. % Hf was reported to have a tensile strength of 53 kg/mm^2 at 1930°C . This alloy is expected to see use in die casting machines, rocket and turbine engines, nuclear reactors and re-entry space vehicles.¹⁵

Principal Compounds^{3, 8, 12, 16-18}

The principal compounds are HfCl_4 , HfO_2 , HfB_2 , HfC and HfN . The first is important because it is used in the purification and metal preparation processes of hafnium, the remaining four compounds because of their high temperature refractory nature. The physical properties of HfB_2 , HfC , HfN and HfO_2 are summarized in Table XI. It is noted that all of these compounds have extremely high melting points. That of the carbide is the highest of any known binary compound, and it is reported to be exceeded only by the HfC-TaC solid solution alloy containing 20 mol% HfC .

The high hardness of HfB_2 accounts for its use in cutting tools. The dioxide is used as an insulator for temperatures up to 1760°C and as a coating for tungsten and tungsten-base alloys. These two compounds have also been used as fibers in tungsten matrix fiber reinforced composites for high temperature, high strength applications. Hafnium nitride has been used as heat-and wear-resistant parts. Hafnia is also used as an opacifier in enamels and glazes, and in special optical glasses.

TABLE XI. PHYSICAL PROPERTIES OF SOME REFRACTORY HAFNIUM COMPOUNDS
AT ROOM TEMPERATURE UNLESS OTHERWISE NOTED^{3, 16, 17}

Property		HfB ₂	HfC	HfN	HfO ₂
Lattice Parameter(s) (Å)	<u>a</u> =	3.141	4.640	4.518	a
	<u>c</u> =	3.470	-	-	a
Crystal System		hex	fcc	fcc	monocl.
Structure Type		AlB ₂	NaCl	NaCl	ZrO ₂
Density (gm/cm ³)		11.20	12.67	13.94	9.68
Melting Point (°C)		3250	3900	3300	2840
Heat Capacity, C _p (cal/mole-deg) ^p		12.0	9.2	9.6	17.1
Electrical Resistivity (μ ohm-cm)		12	37-65	-	-
Thermal Conductivity (cal-cm/sec-cm ² -deg)		0.138 ^b	0.053	0.051	-
Thermal Expansion (°C ⁻¹) x 10 ⁶		5.5	6.6	6.5	4.5
Compressibility (cm ² /kg) x 10 ⁷		-	4.3	-	-
Young's Modulus (kg/cm ²) x 10 ⁻⁶		-	4.3	-	-
Shear Modulus (kg/cm ²) x 10 ⁻⁶		-	1.8	-	-
Poisson's Ratio		-	0.17	-	-
Hardness, Knoop (kg/mm ²)		3800	2500	1650 ^c	-
Modulus of Rupture (kg/mm ²)		-	24	-	-

^a Lattice parameters of HfO₂ are: a=5.116, b=5.172, c=5.295Å, β=99.18°.

^b At 1600°C

^c Vickers hardness number.

Applications and Concluding Remarks

The number of applications in which hafnium is used is limited. A listing of its uses is given in Table XII. By far the largest demand is in the nuclear energy field, and since the number of nuclear energy power plants is expected to continue to increase for the foreseeable future, the utilization of hafnium and its refractory compounds in this field is expected to continue to grow. High temperature applications, such as hafnium-base alloys, alloying additives, oxidation resistant coatings, insulators and fibers for composites, appear to hold considerable promise.

The major problems confronting hafnium are its high cost and the lack of scientific and technological information about it and its compounds and alloys. Undoubtedly continued research will lead to many more new developments and commercial applications.

TABLE XII. APPLICATIONS OF HAFNIUM AND ITS ALLOYS AND COMPOUNDS

Nuclear Energy

- control rods
- burnable poisons
- neutron flux depressors

Refractory

- insulators (HfO_2)
- high-temperature-high strength alloys
- oxidation resistance coatings
- filament in electric light bulbs (Hf and HfC)
- electrodes in x-ray, rectifier and high pressure tubes
- fibers in composite materials
- heat-and wear-resistant parts (HfN)

Miscellaneous

- additive to refractory metal-base alloys
- getters in vacuum tubes
- photographic flash bulbs
- detonating caps and ammunition
- cutting tools (HfB_2 and HfC)
- opacifier (HfO_2)
- optical glasses

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. N.H. Krikorian and T.C. Wallace, J. Electrochem. Soc. 111, 1431 (1964).
6. K. A. Gschneidner, Jr., estimated value, based on method proposed by D.H. Dennison, K.A. Gschneidner, Jr. and A.H. Daane, J. Chem. Phys. 44, 4278 (1963).
7. M.B. Panish and L. Reif, J. Chem. Phys. 38, 253 (1963).
8. D.R. Martin and P.J. Pizzolato, p. 198 in Rare Metals Handbook, 2nd ed., C.A. Hampel, Ed., Reinhold Publishing Co., New York (1961).
9. H.P. Roth, p. 1205 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
10. G.T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
11. G.H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
12. D. E. Thomas and E. T. Hayes, The Metallurgy of Hafnium, U.S. Government Printing Office, Washington, D.C. (1960).

13. K. Marnoch, J. Metals 17, 1225 (1965).
14. I. Machlin and C.M. Gilmore, Metal Progress 90 [3], 101 (1966).
15. Anonymous, Metals & Materials Today 40, [12], 3 (1967).
16. E.G. Kendall, p. 143 in Ceramics for Advanced Technologies, J. E. Hove, and W.C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
17. J.F. Lynch, C.G. Ruderer and W.H. Duckworth, Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, Ohio (1966).
18. T. Vasilos and E.G. Wolff, J. Metals 18, 583 (1966).

Introduction

Niobium has a number of useful properties which make it attractive for many applications in advanced technologies, ranging from high-strength high-temperature structural materials to superconducting magnets.

As in the case of all the elements, the electronic configuration plays a most important role in determining the properties and the chemical behavior of niobium. Niobium has 5 electrons beyond the krypton rare gas core. In the ground state these occupy the $5s^2 4d^3$ levels, but in the metallic state the assignment of electrons is not so simple. It is quite likely they occupy $5s$ and $4d$ bands but the relative occupation cannot be uniquely determined. The high melting and boiling points, heat of sublimation, electronic specific heat constant and magnetic susceptibility all indicate that there is a significant number of d -like electrons (3 or more) involved in the bonding. The low electrical resistivity suggests that the $5s$ level is only partially occupied (< 2).

Physical Properties¹⁻¹⁶

The physical properties of niobium are reviewed in Table XIII. The mass of niobium is about ten times larger than that of beryllium, twice that of titanium, 1.3 times larger than that of iron, but half those of tantalum, tungsten and rhenium. Because of its intermediate mass, it cannot hope to replace beryllium, titanium and steels in many applications where weight is critical (except at temperatures higher than 800°C), but it is given a preference over tantalum, tungsten and rhenium as an alloying additive.

TABLE XIII. PHYSICAL PROPERTIES OF NIOBIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Atomic Number	41	-
Atomic Weight ($^{12}\text{C}=12.00$)	92.906	1
Atomic Volume (cc/mole)	10.83	2
Lattice Parameter (Å) (bcc)	3.3066	3
Density (gm/cm ³)	8.579	-
Metallic Radius (CN=12) ^a (Å)	1.468	4
Melting Point (°C)	2468	2
Heat of Fusion (kcal/g at)	(4.82)	2
Vapor Pressure A	39651	5
log P _{torr} = -A/T+B B	11.371	5
(temp. range °C)	1980-2330	5
Boiling Point (°C)	4540	2
Heat of Sublimation at 25°C (kcal/g at)	175.0	2
Heat Capacity, C _p (cal/g at-deg)	5.88	6
Electronic Specific Heat Constant (cal/g at-deg ²) x 10 ⁴	18.3	2
Debye Temperature (°K)	260	2
Magnetic Susceptibility (emu/mole) x 10 ⁶	139	7
Electrical Resistivity (μ ohm-cm)	13.5	8, 9
Superconducting Transition Temperature (°K)	9.09	9
Hall Coefficient (volt-cm/amp-Oe) x 10 ¹²	0.9	8
Ionization Potentials (eV)		
I	6.881	10
II	14.32	10
III	24.2	11
IV	—	-
V	49.3	11
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.125	8
Thermal Expansion (°C ⁻¹) x 10 ⁶	7.07	2
Grüneisen Constant	1.74	2
Compressibility (cm ² /kg) x 10 ⁷	5.761	2
Young's Modulus (kg/cm ²) x 10 ⁻⁶	1.07	2

TABLE XIII (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Shear Modulus (kg/cm^2) $\times 10^{-6}$	0.382	2
Poisson's Ratio	0.35	2
Hardness, Vickers (kg/mm^2)	80 ^b	8
Yield Strength (kg/mm^2)	21 ^b	8
Ultimate Strength (kg/mm^2)	28 ^b	8
Elongation (%)	30 ^b	8
Nuclear Cross Section (barns)	1.1	8

^aCN means coordination number.

^bAnnealed.

Niobium's high melting point and low vapor pressure make it an attractive metal for high temperature applications, especially when combined with its good mechanical properties. The high temperature mechanical properties can be improved by alloying. Shown in Fig. 4 are the strength-to-density ratio of niobium and a number of other aerospace materials as a function of temperature. In the lower portion of the figure are shown the time-temperature requirements of various aerospace vehicles and some of their major components. The poor oxidation resistance of niobium, however, is a serious drawback and until this problem is solved, the number of applications which utilize niobium or niobium-base alloys will be limited.

The superconducting transition temperature is one of the highest of the elemental superconductors. In addition to its high transition temperature, niobium is a type II superconductor, which means that it remains superconducting in the presence of high magnetic fields. This behavior makes it and its alloys leading candidates for high field superconducting magnets (more is discussed in a later section of this chapter).

The very low nuclear cross section accounts for its usefulness in reactor technology.

Chemical Properties ¹²⁻¹⁷

Niobium is stable at room temperature with respect to attack by the common gases hydrogen, nitrogen, oxygen and air. But it begins to react with these gases at relatively low temperatures, e. g., $\sim 100^{\circ}\text{C}$ for hydrogen and $\sim 300^{\circ}\text{C}$ for oxygen. Reaction with hydrogen leads to

Fig. 4. Strength-to-density ratio vs. temperature for some aerospace materials and the time-temperature spectrum for some aerospace applications.

severe embrittlement, but fortunately the hydrogen may be removed by heating in a dynamic vacuum at temperatures of 1500°C or higher.

Niobium is fairly resistant to attack by many common acids and salt solutions. However, its resistance to attack is significantly inferior to that of tantalum, and furthermore, in many cases very slight attack will lead to embrittlement of the niobium. It is attacked rapidly by hydrofluoric acid and concentrated sodium hydroxide, and slowly by concentrated sulfuric acid. Niobium is resistant to attack at high temperature by water and many liquid metals. The liquid metals and the temperatures at which they may be heated to without attacking niobium are: Li, Na, K and Na-K eutectic-1000°C, Ca-1200°C, Ga-400°C, Hg-700°C, Pb-800°C, Bi-560°C and Th-Mg eutectic-1000°C. Niobium, however, is attacked by U, U-Bi, the U eutectics formed with Cr, Mn, Fe and Ni, and Zn. Niobium's resistance to attack by the above mentioned liquid metals and its low nuclear cross section account for its utilization in nuclear reactors.

Metallurgical Behavior^{8, 12-16, 18-25}

Niobium is generally formed at room temperature. Most forming operations, such as forging, swaging and rolling, can be carried out to about 90% reduction before an annealing heat treatment is required. High temperature forming is possible, but protection from the atmosphere is required. Because niobium tends to seize and gall, wire and tube drawing operations are more difficult to carry out than the other forming methods. By the use of special die materials and appropriate lubricants, these problems can be minimized.

Machining operations may be carried out by following normal procedures and by the use of high speed steel tools. Niobium may be joined by resistance, submerged-arc and inert-gas-shielded arc welding techniques. Brazing techniques have recently been developed; today the best brazing alloys are Ti-or V-base alloys.

As pointed out earlier, niobium has favorable strength-to-density properties for space applications and has desirable properties for many nuclear applications. By proper alloying techniques the mechanical properties of niobium may be greatly improved. The effect of alloying elements on the mechanical properties of niobium are as follows (the listing of the elements is in the order of decreasing effectiveness):

- 1.) Improved high temperature strength - Cr,* V, Zr, Re, Al,* W, Mo, Hf, U, Ti and Ta (*limited solid solubility).
- 2.) Improved creep resistance - Mo, W most effective, Ta for $T > 1250^{\circ}\text{C}$, V for $T < 1200^{\circ}\text{C}$, and Ti in pure Nb, but detrimental in complex alloys.
- 3.) Improved high temperature ductility - Ti, V for concentrations $< 12 \text{ wt. } \%$ and W and Mo for concentrations $< 15 \text{ wt. } \%$. Cr and Zr increase brittleness.
- 4.) Lowering of recrystallization temperature - W, Mo, V and Ta.
- 5.) Increased modulus of elasticity - W and Mo.
- 6.) Lowering of ductile-brittle transition temperature - Ta.
Raising of ductile-brittle transition temperature - H, (most effective), O, N and C are the most harmful elements, of the metallic elements the order is Re (most effective), Al, Mo, W, Cr, Zr, V, Hf and Ti.

Some of the more important high strength niobium-base alloys are listed in Table XIV along with some of their properties. A much more extensive summary of Nb-base alloys and their properties is found in

TABLE XIV. SOME HIGH STRENGTH, HIGH TEMPERATURE NIOBIUM-BASE ALLOYS AND SOME OF THEIR PROPERTIES

Alloy Designation	Composition (wt. %)	Ultimate Tensile Strength (kg/mm ²) at Temperature (°C)			General Remarks
		25°	1200°	1370°	
AS-30	Nb-20W-1Zr-0.1C	120	50	39	highest strength alloy developed to date ^a
C-129Y	Nb-10W-10Hf-1Y	92	24	17	readily formable, superior welding properties
F-48	Nb-15W-5Mo-1Zr -0.6C	85	30	22	very difficult to process
FS-85	Nb-28Ta-10W-1Zr	74	22	15	readily formable, good weld ductility
Cb-752	Nb-10W-2.5Zr	63	39	16	can be cold rolled, low resistance to oxidation

^aAs of the information published in the literature 1966-67.

the review by Syre.¹⁵ The strength-to-density ratio of AS-30 is slightly better than that shown in Fig. 4 for the best Cr, Nb, Mo alloys at room temperature, but at 1100°C the ratio for this alloy is about the same as the upper portion of the Ta, W, Re curve.

The biggest draw-back to niobium-base alloys is their low oxidation resistance. The development of Ti-Cr-Si¹⁸ and disilicide¹⁹ coatings have helped to solve this problem, especially for temperatures below 1250°C, and for some alloys up to as high as 1370°C.

Niobium is used extensively as an alloying agent to improve the properties of alloy steels, high temperature superalloys (nickel-base, iron-nickel-base and less extensively cobalt-base), stainless steels, carbon steels, and some tantalum- and titanium-base alloys. Niobium acts as a grain refiner and prevents graphitization in carbon and alloy steels, and it prevents intergranular corrosion by forming carbides, which prevent the carbon from precipitating at the grain boundaries. Niobium also improves the high temperature strength and creep resistance of many of these steels. Niobium's importance in superalloys is due to the formation of Ni_3Nb , which has desirable age hardening characteristics. A listing of many of niobium-containing superalloys and some of their properties and applications is given by Simmons and Wagner.²⁰ Two other recent reviews on superalloys, which deal with the effects of alloying agents, strengthening mechanisms, structural stability, corrosion resistance and applications, were written by Decker and DeWitt²¹ and Sims.²²

Niobium is an important additive to titanium-aluminum (~90 wt. % Ti-~8 Al) alloys which are used in naval vessels, including deep-diving

vehicles and for desalination plants.²³ The 2 wt. % Nb addition acts as a β -stabilizer. These alloys are immune to cracking in sea water and hot saline solutions, have excellent weldability characteristics and have good toughness in thick sections.

Because niobium and some of its compounds (to be discussed shortly) have good high temperature properties, these materials are being used in fiber reinforced composites.^{24, 25} Some of the reported combinations are: NbC fiber in a niobium matrix; niobium fiber in Al_2O_3 +30% Cr and UO_2 - ThO_2 matrices; and 72.5Ti-20Nb-7.5Al fiber in a 90Ti-6Al-4V matrix. Of these the first appears to be the most interesting. It is prepared by proper solidification of the NbC-Nb eutectic composition, in which the NbC fibers occupy a 31% volume fraction of the composite. At room temperature its strength-to-density ratio is only 3% better than that of AS-30 (best high-strength niobium-base alloy, see Table XIV), but at 1100°C the NbC-Nb composite's strength-to-density ratio is 25% better than AS-30. This makes NbC-Nb one of the best high temperature materials available today.

Superconductivity^{9, 16, 26-29}

As noted earlier in this chapter, niobium becomes superconducting at about 9°K. The critical temperature, T_c , however, can be drastically modified by proper choice of alloy additions. For niobium the most important alloying agents are titanium, zirconium and tin. Before we continue to discuss the effects of these three metals on niobium, it is best to discuss some of the basic principles involved.

Shown in Fig. 5a is the behavior of ideal type I and type II superconductors in an applied magnetic field at a temperature below T_c . For a type I superconductor the magnetization increases linearly with field ($-4\pi M = H$) until a point is reached where the magnetization drops sharply to zero. The magnetic field at which the magnetization goes to zero is called the critical field, H_c . At fields greater than H_c the magnetization remains zero, and the material is in its normal state. For a type II superconductor as one increases the field the magnetization also increases linearly with field ($-4\pi M = H$) until a point is reached where the magnetization starts decreasing with increasing field but it does not drop off rapidly to zero. The magnetic field at which this occurs is called the lower critical field, H_{c1} . At fields greater than H_{c1} the magnetization continues to decrease with increasing fields until the magnetization finally becomes zero; this point is known as the upper critical field, H_{c2} . Above H_{c2} the material is in its normal state. In the region between H_{c1} and H_{c2} the material is neither fully superconducting nor fully normal and it is in the so-called mixed state. The difference between H_{c1} and H_{c2} may be several orders of magnitude.

The importance of a superconductor is the fact that it offers no resistance to a current while it is in the superconducting state. But since a current passing through a wire generates a magnetic field and if the current is large enough the magnetic field will exceed H_c or H_{c2} and thus the material is no longer a superconductor. The relationship between the temperature, field and current is shown schematically in Fig. 5a. For many applications superconducting materials must not only have reasonable T_c and H_{c1} and/or H_{c2} values but must also be able to

a)

b)

Fig. 5(a) Magnetization vs. the magnetic field for an ideal type I and an ideal type II superconductor. (b) The critical surface in temperature (T)-field(H)-current (J) space, which separates the superconducting state from the normal state.

carry large currents with little or no resistance. Thus there are three important criteria to be kept in mind when choosing a material for a particular application. These three parameters in turn are dependent upon the metallurgical microstructure, composition and crystal structure. The metallurgical microstructure has the greatest effect on J_c , some effect on H_c and only a little effect on T_c . The composition and crystal structure have the greatest effect on T_c , an intermediate effect on H_c and the smallest effect on J_c . Usually J_c can be increased by plastic deformation, precipitation and radiation damage.

Some of the properties of the more important niobium-base superconductors are given in Table XV. It is immediately obvious that Nb_3Sn is by far the best niobium superconducting material. At the present time it is the most fully-developed material for very high field superconducting magnets. Magnetic fields of 140,000 gauss with a 15 cm (6 in.) bore have been generated in a Nb_3Sn superconducting solenoid. This solenoid used 88 km (55 miles) of Nb_3Sn vapor-deposited stainless steel ribbon.²⁹ Nb_3Sn wire has been prepared by heating a niobium tube containing tin powder to form a layer of the Nb_3Sn compound at the Nb-Sn interface.

Some of the uses of high field superconducting magnets are: maser microwave amplifiers, high energy physics research (bubble chamber analyzer, beam focusing, accelerators), basic research on magnetic behavior of materials, low temperature refrigerators to attain temperatures below 1°K, energy storage (up to one billion joules $\sim$ 1/4 million kcal), and magneto-hydrodynamic power generation. Other superconducting applications include: computer switches, computer storage

TABLE XV. PROPERTIES OF SOME NIOBIUM-BASE SUPERCONDUCTORS^{26, 28}

Material (Alloys in at. %)	T_c (°K)	H_{c1} (kG)	H_{c2} (kG)	$J_c \times 10^{-3}$ at 4.2°K ² (amp/cm ²)	Cold Work Redn. in area (%)
Nb-15Sc	>4.2	-	-	6.8 ^a	85
Nb-33Ti	9.3	-	120 ^b	-	-
Nb-25Zr	10.8	-	65 ^b	20	67
Nb ₃ In	9.2	-	-	-	-
NbC	~14	-	-	-	-
Nb ₃ Ga	14.5	-	-	-	-
NbN	15.6	-	-	-	-
Nb ₃ Al	17.5	0.375	-	-	-
Nb ₃ Sn	18.05	0.17	221 ^b	2000 ^c	-

^aAt 1.2°K.^bAt 0°K.^cAt zero field.

loops, transmission lines, transformers, bearings, motors, magnetic shields, bolometers, galvanometers and flux pumps.

Principal Compounds^{3, 12, 13, 30, 31}

The most important compounds of niobium are NbB_2 , NbC , Nb_2N , NbN , NbH_x and Nb_3Sn . The first four are refractory materials and are suitable for high temperature applications. A summary of their properties is given in Table XVI. All of the compounds have high melting points ($\leq 2200^\circ\text{C}$), reasonable thermal conductivities and coefficients of expansion and good hardness values. The boride and nitrides find use as refractory materials. The carbide in addition to refractory applications is used in cutting tools, a diluent for carbide nuclear fuels (NbC-UC and NbC-PuC solid solution alloys), and as cladding and structural materials in nuclear reactors. NbC (as mentioned earlier) is also used as a fiber in fiber-reinforced composites.

Niobium hydride (NbH_x where x varies from 0 to 0.85) is formed in the preparation and purification of niobium, and it is used as a reducing and alloying agent. Nb_3Sn , as was discussed earlier, is used in superconducting applications. Some niobium intermetallic compounds are also of interest as cladding and refractory materials. The beryllides, NbBe_{12} , $\text{Nb}_2\text{Be}_{17}$ and $\text{Nb}_2\text{Be}_{19}$, have received the most attention to date. Many of niobium's compounds are superconducting (see Table XV) and they may find utilization in this rapidly growing area.

Some inorganic niobates are of interest because of their electrical or optical properties. Lead metaniobate, PbNb_2O_6 , a ferroelectric, is used

TABLE XVI. PHYSICAL PROPERTIES OF SOME REFRACTORY NIOBIUM COMPOUNDS AT ROOM TEMPERATURE UNLESS OTHERWISE NOTED^{3, 30, 31}

Property		<u>NbB₂</u>	<u>NbC</u>	<u>Nb₂N</u>	<u>NbN</u>
Lattice Parameter(s) (Å)	<u>a</u> =	3.110	4.469	3.056	4.388
	<u>b</u> =	3.266	-	4.996	-
Crystal System		hex	fcc	hex	fcc
Structure Type		AlB ₂	NaCl	Fe ₂ N	NaCl
Density (gm/cm ³)		7.20	7.75	8.31	8.36
Melting Point (°C)		3000	3500	2315	2200
Heat Capacity, C _p (cal/mole-deg)		11.4	9.4 ^a	-	10.7
Electrical Resistivity (μ ohm-cm)		32	35-74	-	-
Thermal Conductivity (cal-cm/sec-cm ² -deg)		0.040	0.034	0.019	0.011
Thermal Expansion (°C ⁻¹) x 10 ⁶		6.7	6.2	3.2	-
Young's Modulus (kg/cm ²) x 10 ⁻⁶		2.0-3.1	3.4	-	-
Hardness, Vickers (kg/mm ²)		1820 ^b	2400 ^b	1720	1400
Rupture of Modulus (kg/mm ²)		-	25	-	-

^aAt 230°C

^bKnoop hardness

in capacitors, electromechanical filters and memory devices. Lithium metaniobate, LiNbO_3 , has optical properties that enable one to tune laser light over the range of 9700 to 11,500Å (3.1×10^{14} to 2.6×10^{14} cycles).

Applications

A list of the applications of niobium and its alloys and compounds is given in Table XVII. The largest use of niobium has been as an alloying agent in various steels and superalloys. Its importance in the steels market depends a great deal on the availability of ferrovanadium, which is in short supply especially in the United States. Niobium-base alloys and superconducting materials are coming into their own and should develop good markets. The major use of niobium-base alloys is as high temperature and nuclear structural materials. Some of the refractory niobium compounds will also be important in the same area.

Concluding Remarks

The outlook for niobium is quite bright in the world of expanding technology. It should continue to hold its own and grow with the metallurgical field. Niobium will become more important in high temperature applications to fill in the region between the superalloys and very high temperature refractory metals of tantalum and tungsten.

Superconducting applications involving niobium and especially its alloys should show a rapid growth as these devices become more important. Although some materials are expected to give niobium-base materials competition, enough scientific and technological research has

TABLE XVII. APPLICATIONS OF NIOBIUM AND ITS COMPOUNDS

Metallurgical, Niobium-Base Alloys

- high temperature service alloys
- liquid metal containers
- fiber-reinforced composites
- gas turbine blades and parts
- aerospace structural components
- coinage metal
- chemical processing industry

Alloying Agent

- ferroniobium (substitute for ferrovanadium)
- stainless steels
- alloy steels
- carbon steels
- welding electrodes
- superalloys
- titanium-base alloys
- tantalum-base alloys

Nuclear

- liquid metal containers
- diluent for nuclear fuels
- claddings
- structural materials

Superconductivity

- high field superconducting solenoid
- computer switches and current loops
- transformers
- bearings
- motors
- magnetic shields
- bolometer
- galvanometers
- flux pumps
- transmission lines

Miscellaneous

- cutting tools
- ferroelectrics
- optical tuner for lasers

been carried out on niobium-based alloys to keep them in the forefront.

The low nuclear cross section, the corrosion resistance to liquid metals, and new metallurgical developments on niobium-base alloys and compounds insure niobium's utilization in the nuclear energy field, especially as the number of power reactors and nuclear applications continues to grow.

Continued research, both basic and applied, will guarantee that niobium's role in the world of the future will be as important as it is today.

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. P.F. Woerner and G.F. Wakefield, Rev. Sci. Instr. 33, 1456 (1962).
6. R. Hultgren, R. L. Orr, P.D. Anderson, and K.K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley & Sons (1963).
7. C. J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).
8. E.S. Bartlett, p. 1202 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).

9. G. T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
10. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
11. Handbook of Chemistry and Physics, 46th ed., p. E-61, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland (1965).
12. E. M. Sherwood, p. 149 in Rare Metals Handbook, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (1961).
13. F. T. Sisco and E. Epremian, Eds., Columbium and Niobium, John Wiley and Sons, Inc., New York (1963).
14. N. E. Promisel, Ed., The Science and Technology of Tungsten, Tantalum, Molybdenum, Niobium and Their Alloys, Pergamon Press, London (1964).
15. R. Syre, Handbook on the Properties of Niobium, Molybdenum, Tantalum, Tungsten and Some of Their Alloys (bilingual book in English and French), North Atlantic Treaty Organization (AGARDograph-94), Brussels (1965).
16. F. F. Schmidt, "Niobium" in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
17. L. Rosenblum, J. Metals 15, 637 (1963).
18. I. Machlin and C. M. Gilmore, Metal Progress 90, [3], 101 (1966).
19. R. J. Van Thyne, J. Metals 15, 642 (1963).
20. W. F. Simmons and H. J. Wagner, Metal Progress 91, [6], 86 & 87 (1967).
21. R. F. Decker and R. R. DeWitt, J. Metals 17, 139 (1965).

22. C. T. Sims, J. Metals 18, 1119 (1966).
23. I. R. Lane, Jr., J. Metals 17, 834 (1965).
24. T. Vasilos and E. G. Wolff, J. Metals 18, 583 (1966).
25. S. Abkowitz, Metal Progress 89, [4], 62 (1966).
26. M. G. Benz, "Superconducting Materials," General Electric Co. Report No. 65-RL-4041M (October, 1965).
27. J. D. Livingston, J. Metals 18, 698 (1966).
28. R. R. Hake, T. G. Berlincourt and D. H. Leslie, p. 53 in Superconductors, M. Tanenbaum and W. V. Wright, Eds., Interscience, New York (1962).
29. Anonymous, Chem. & Eng. News 45, [25], 95 (1967).
30. E. G. Kendall, p. 143 in Ceramics for Advanced Technologies, J. E. Hove, and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
31. J. F. Lynch, C. G. Ruderer and W. H. Duckworth, Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, Ohio (1966).

CHAPTER 6. RARE EARTHS (INCLUDING YTTRIUM AND SCANDIUM)

Introduction

The rare earths are the IIIA Group of elements in the periodic table, seventeen in all. They are characterized by their common $d^1 s^2$ outer electronic configuration in their chemical compounds and, in general, the metallic state. The elements which make up the rare-earth group are: scandium, yttrium and the lanthanides, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Because yttrium occurs in nature with the heavy lanthanides (gadolinium to lutetium), it has always been closely associated with the lanthanides and for this reason it is being discussed in this chapter rather than separately.

Although one thinks of these elements as being closely related, one finds as he studies and works with them that they have many differences, some of which are fairly large. For example, the melting points of the lowest (cerium 798°C) and the highest (lutetium 1663°C) vary by a factor of two; the biggest disparity in their vapor pressures at 1000°C is over a billion (4.9×10^2 torr for ytterbium compared with 1.4×10^{-7} torr for lanthanum); one is a ferromagnet at room temperature (gadolinium) and another becomes superconducting at 5°K (lanthanum); and some may be used as a diluent in nuclear fuels (e. g., cerium, whose nuclear cross section is 0.73 barns) while others may be used as control rod materials (e. g., gadolinium, which has the largest known nuclear cross section-46,000 barns). Because of their wide range of properties, the rare earths are used in many different fields. Their utilization can be divided into two

general categories. One, the applications are dependent upon the nature of $4f$ electronic levels and independent of the outer electronic configuration. Two, the applications are dependent on the outer or valence electron configuration and independent of the $4f$ electrons. The first category includes most of the electronic and magnetic applications, and these in general require separated individual high purity rare-earth elements. The second grouping includes most of the metallurgical, ceramic and chemical applications, and in general the mixed unseparated rare-earth elements are the common form of usage.

The electronic structures of the ground states of the lanthanide elements beyond xenon rare gas core are either $4f^n 5d^1 6s^2$ or $4f^{n+1} 6s^2$. The elements La, Ce, Gd, Tb and Lu have the former and thus are quite similar to Sc and Y which have $d^1 s^2$ configurations beyond their respective rare gas cores. The other lanthanides, Pr, Nd, Pm, Sm, Eu, Dy, Ho, Er, Tm and Yb, have the latter electronic ground state configuration. As metals in the condensed state, however, all of the lanthanides have the $4f^n 5d^1 6s^2$ configuration, except europium and ytterbium which have $4f^{n+1} 6s^2$. Scandium and yttrium metals have the $3d^1 4s^2$ and $4d^1 5s^2$ configurations, respectively. Furthermore, in most of their chemical compounds the rare earths behave as if they have three valence electrons, with three notable exceptions, Ce, Eu and Yb. These three elements have two valence states: 3 and 4 for cerium; and 2 and 3 for europium and ytterbium. The dual valence states, especially for cerium, are important for some applications or for making a quick inexpensive separation of one of these three elements from a mixture of the rare earths.

The wide divergent nature of these elements in some instances can be explained on the basis of their electronic configurations, but in other cases the divergent nature may be more subtle.

Physical Properties¹⁻²⁰

The physical properties are presented in Tables XVIII through XXVII. The atomic number, atomic weight, atomic volume, density and metallic radius are given in Table XVIII. It is seen that the lanthanides are heavy and large metallic elements. Although scandium and yttrium are nearly of the same size, their weights and densities are significantly lower and are more likely to be considered for aerospace applications than the lanthanides, at least on a mass or density basis. The crystal structures and lattice parameters are listed in Table XIX. Most of the rare-earth metals exist in a hexagonal form and many of them undergo high temperature transformations to a body-centered cubic structure. The transformation temperatures and the heats of transformation are given in Table XX. The melting points (Table XXI; also includes heats of fusion), which range from ~ 800 to $\sim 1660^\circ\text{C}$, are high enough for some of these metals to be of interest as refractory materials, most notably Sc, Y and Lu. Although Er and Tm have melting points just as high as Sc and Y, they have sufficiently high vapor pressures (Table XXII), especially Tm, to limit their usefulness as high temperature materials. In addition to the vapor pressures, Table XXII includes the heats of sublimation, cohesive energies and boiling points.

The heat capacity at room temperature, the electronic specific heat constant and Debye temperature are listed in Table XXIII. The electronic

TABLE XVIII. ATOMIC NUMBER, ATOMIC WEIGHT,¹ AND ROOM TEMPERATURE VALUES OF THE ATOMIC VOLUME, DENSITY AND METALLIC RADIUS FOR COORDINATION NUMBER 12.

Metal	Atomic Number	Atomic Weight (¹² C=12.00)	Volume (cc/mole)	Density (gm/cm ³)	Radius (Å)
Scandium	21	44.956	15.04	2.989	1.641
Yttrium	39	88.905	19.95	4.457	1.803
Lanthanum (α)	57	138.91	22.53	6.166	1.877
Cerium (γ)	58	140.12	20.69	6.771	1.824
Praseodymium	59	140.907	20.81	6.772	1.828
Neodymium	60	144.24	20.60	7.003	1.822
Promethium	61	147	-	-	-
Samarium	62	150.35	19.95	7.537	1.802
Europium	63	151.96	28.93	5.253	2.041
Gadolinium	64	157.25	19.91	7.898	1.801
Terbium	65	158.924	19.30	8.234	1.783
Dysprosium	66	162.50	19.03	8.540	1.775
Holmium	67	164.930	18.78	8.781	1.767
Erbium	68	167.26	18.49	9.045	1.758
Thulium	69	168.934	18.14	9.314	1.747
Ytterbium	70	173.04	24.82	6.972	1.939
Lutetium	71	174.97	17.79	9.835	1.735

TABLE XIX. LATTICE CONSTANTS OF THE RARE-EARTH METALS^{2, 3, 4}

Metal	Allo- trope	Crystal Type	<u>a</u>	<u>c</u>	Remarks
Scandium	α	hcp	3.309±2	5.268±7	25°C.
	β	-	-	-	Probably bcc, no data available for <u>a</u> .
Yttrium	α	hcp	3.650±4	5.741±9	25°C.
	β	bcc	4.11 ±2	-	Exists between 1479 and 1526°C.
Lanthanum	α	hex	3.722±4	12.144±15	25°C.
	β	fcc	5.305±2	-	Exists between 310 and 861°C; <u>a</u> at 25°C.
	γ	bcc	4.26 ±1	-	Exists between 861 and 920°C.
Cerium	α	fcc	4.85 ±1	-	Forms below -157°C
	β	hex	3.673±1	11.802±5	Forms below -23°C; <u>a</u> at 25°C.
	γ	fcc	5.1606±5	-	25°C.
	δ	bcc	4.11 ±1	-	Exists between 726 and 798°C.
Praseodymium	α	hex	3.672±2	11.834±5	25°C.
	β	bcc	4.13 ±1	-	Exists between 795 and 931°C.
Neodymium	α	hex	3.659±3	11.799±7	25°C.
	β	bcc	4.13 ±1	-	Exists between 855 and 1016°C.
Promethium	-	-	-	-	No data available.
Samarium	α	rhomb.	3.626±5	26.18 ±6	Hex. lattice const., 25°C.
	β	bcc	4.07	-	Exists between 924 and 1073°C.
Europium	-	bcc	4.580±2	-	25°C.
Gadolinium	α	hcp	3.634±3	5.781±5	25°C.
	β	bcc	4.06	-	Exists between 1260 and 1312°C.
Terbium	α	hcp	3.604±4	5.698±3	25°C.

TABLE XIX. (continued)

Terbium	β	bcc	4.02 $\pm$ 2	-	Exists between 1287 and 1357°C; a at 25°C, obtained from a $\bar{a}$ vs. $\bar{X}_{Mg}$ plot by extrapolation.
Dysprosium	α	hcp	3.592 $\pm$ 4	5.655 $\pm$ 2	25°C.
	β	bcc	3.98 $\pm$ 2	-	Exists between 1384 and 1409°C; a at 25°C, obtained from a $\bar{a}$ vs. $\bar{X}_{Mg}$ plot by extrapolation.
Holmium	α	hcp	3.578 $\pm$ 3	5.626 $\pm$ 9	25°C
	β	bcc	3.96 $\pm$ 2	-	Exists between 1428 and 1470°C; a at 25°C, obtained from a $\bar{a}$ vs. $\bar{X}_{Mg}$ plot by extrapolation.
Erbium	-	hcp	3.560 $\pm$ 2	5.595 $\pm$ 6	25°C.
Thulium	-	hcp	3.5374 $\pm$ 2	5.558 $\pm$ 4	25°C.
Ytterbium	α	fcc	5.483 $\pm$ 3	-	25°C.
	β	bcc	4.44 $\pm$ 1	-	Exists between 792 and 816°C.
Lutetium	-	hcp	3.505 $\pm$ 2	5.553 $\pm$ 3	25°C.

TABLE XX. TRANSFORMATION TEMPERATURES² AND
HEATS OF TRANSFORMATION^{3, 5-7}

Metal	Transformation	Temp. (°C)	Heat of Trans. (kcal/g at)	Remarks
Scandium	α - β	1335	0.958	-
Yttrium	α - β	1479±6	1.189	-
Lanthanum	α → β	310 ±5	} (0.095)	Estimated by Ref. 3.
	β → α	220 ±20		
	β - γ	861 ±5	0.753	-
Cerium	α → γ	-94 ±4	} 0.88	-
	γ → α	-157 ±4		
	β → γ	168 ±7	} (0.01)	Estimated by Ref. 7.
	γ → β	-23 ±3		
	γ - δ	726 ±5	0.700	-
Praseodymium	α - β	795 ±3	0.760	-
Neodymium	α - β	855 ±9	0.713	-
Promethium	-	-	-	No information available.
Samarium	α - β	924±7	0.744	-
Europium	-	-	-	No evidence for a trans.
Gadolinium	α - β	1260±2	0.935	-
Terbium	α - β	1287±4	1.203	-
Dysprosium	α - β	1384±8	(0.94)	Estimated by Ref. 5.
Holmium	α - β	1428±14	(1.12)	Estimated by Ref. 5.
Erbium	-	-	-	No evidence for a trans.
Thulium	-	-	-	No evidence for a trans.
Ytterbium	α - β	792 ±5	0.418	-
Lutetium	-	-	-	No evidence for a trans.

TABLE XXI. MELTING POINTS² AND HEAT OF FUSION^{3, 5, 6, 8}

Metal	Temp. (°C)	Heat of Fusion (kcal/g at)	Remarks
Scandium	1539	3.369	-
Yttrium	1526±5	2.732	-
Lanthanum	920±1	1.482	-
Cerium	798±3	1.238	-
Praseodymium	931±4	1.652	-
Neodymium	1016±5	1.705	-
Promethium	1080±10	(1.94)	Estimated by Ref. 8.
Samarium	1073±1	2.061	-
Europium	822±5	2.204	-
Gadolinium	1312±2	2.403	-
Terbium	1357±6	2.583	-
Dysprosium	1409	(2.68)	Estimated by Ref. 5.
Holmium	1470	(2.91)	Estimated by Ref. 5.
Erbium	1522	4.76	-
Thulium	1545±15	4.02	-
Ytterbium	816±2	1.830	-
Lutetium	1663±12	(4.55)	Estimated by author.

TABLE XXII. VAPOR PRESSURES, HEATS OF SUBLIMATION, COHESIVE ENERGIES AND BOILING POINTS²

Metal	$\log P_{\text{torr}} = A/T + B$			ΔH_{298}° (kcal/mole)	ΔH_0° (kcal/mole)	Boil. Pt. (°C)
	-A	B	Temp. Range (°C)			
Scandium	19140 ± 88	9.452 ± 0.052	1248-1540	91.0±0.1	90.6	2832
Yttrium	20268 ± 417	8.65 ± 0.19	1502-1912	99.6±1.2	99.4	3337
Lanthanum	21980 ± 40	8.918 ± 0.042	1392-1909	103.0±0.5	103.1	3454
Cerium	22991 ± 165	8.396 ± 0.079	1588-2019	111.60	111.76	3257
Praseodymium	18083 ± 73	8.069 ± 0.038	1371-1847	89.09	89.36	3212
Neodymium	16320 ± 59	8.102 ± 0.034	1255-1650	77.3±1.0	77.5	3127
Promethium	-	-	-	(64)	(64)	(2460)
Samarium	10656 ± 128	8.58 ± 0.20	612-949	49.3±0.7	49.2	1778
Europium	8982 ± 16	8.160 ± 0.027	460-630	42.5±0.6	42.6	1597
Gadolinium	19600 ± 90	8.517 ± 0.049	1347-1824	95.75±0.2	96.10	3233
Terbium	19147 ± 141	8.657 ± 0.078	1352-1770	93.96	94.39	3041
Dysprosium	15090 ± 52	8.822 ± 0.035	984-1417	71.2±0.3	71.5	2335
Holmium (s)	15137	8.426	674-1470	71.7±2.9	71.9	2720
Holmium (l)	14122	7.849	1470-1782	-	-	-
Erbium	17324 ± 60	9.222 ± 0.037	1119-1507	74.5±7.6	74.7	2510
Thulium	12552 ± 45	9.176 ± 0.046	535-950	58.3±0.8	58.6	1727
Ytterbium	7696 ± 33	8.295 ± 0.043	350-658	38.2±1.9	38.3	1193
Lutetium	21719 ± 173	9.247 ± 0.095	1378-1659	102.16	102.20	3315

TABLE XXIII. HEAT CAPACITY, ELECTRONIC SPECIFIC HEAT CONSTANT AND DEBYE TEMPERATURE^{8, 9}

<u>Metal</u>	<u>C_p (cal/g at-deg)</u>	<u>$\gamma \times 10^4$ (cal/g at-deg²)</u>	<u>θ_D (°K)</u>
Sc	6.09	25.8	470
Y	6.34	24.1	214
La	6.25	24.1	135
γ -Ce	6.47	18.0	138
Pr	6.45	17.4	138
Nd	6.55	20.5	148
Pm	(6.50)	(24)	-
Sm	6.80	27.5	148
Eu	6.48	8.83	121
Gd	6.56	22.0	155
Tb	6.81	29.1	158
Dy	6.58	21.8	158
Ho	6.50	18.9	161
Er	6.72	25.7	163
Tm	6.46	17.1	167
Yb	6.16	6.93	118
Lu	6.46	24.43	166

TABLE XXIV. MAGNETIC SUSCEPTIBILITY,³ ELECTRICAL RESISTIVITY,³
HALL COEFFICIENT^{3, 9} AND IONIZATION POTENTIALS^{3, 10-15}

Metal	$\chi \times 10^6$ (emu/mole)	ρ (μ ohm-cm)	$R_H \times 10^{12}$ $\left(\frac{\text{volt-cm}}{\text{amp-Oe}}\right)$	Ionization Potentials (eV)		
				I	II	III
Sc	8.08	66.6	-0.30	6.54	12.80	24.75
Y	191	57	-0.770	6.38	12.23	20.5
La	101	56.8	-0.8	5.577	11.06	19.176
Ce	2,430	75.3	+1.81	5.65	10.85	-
Pr	5,320	68.0	+0.709	5.42	10.55	-
Nd	5,650	64.3	+0.971	5.49	10.73	-
Pm	-	-	-	5.55	10.90	-
Sm	1,275	90	-0.2	5.63	11.07	-
Eu	33,100	81.3	-	5.68	11.25	-
Gd	a	140.5	-4.48 ^b	5.98	12.1	-
Tb	193,000	116	(-0.11)	5.98	11.52	-
Dy	99,800	91.2	-2.7	5.93	11.67	-
Ho	70,200	94	-(1.5)	6.02	11.80	-
Er	44,100	86	-0.341	6.10	11.93	-
Tm	26,000	90	-1.8	6.18	12.05	-
Yb	71	27.0	+3.77	6.25	12.17	-
Lu	17.9	68	-0.535	6.15	13.9	-

^aGd is ferromagnetic below 16°C; $\chi \times 10^6 = 356,000$ emu/mole at 50°C.

^bMeasured at -195°C.

TABLE XXV. THERMAL CONDUCTIVITY,¹⁶ THERMAL EXPANSION,⁸
GRÜNEISEN CONSTANT⁸ AND NUCLEAR CROSS SECTION¹⁷

Metal	κ $\left(\frac{\text{cal-cm}}{\text{sec-cm}^2\text{-deg}}\right)$	$\alpha \times 10^6$ $(^\circ\text{C}^{-1})$	γ_G	σ (barns)
Sc	0.0375	10.0	(1.17)	24.0
Y	0.0380	12.0	1.13	1.31
La	0.0335	10.4	0.74	8.9
Ce	0.0268	8.5	0.51	0.73
Pr	0.0287	6.79	0.64	11.3
Nd	0.0394	9.98	0.82	46
Pm	-	(9.0)	(0.81)	150 ^a
Sm	0.0320	10.4	0.71	5,600
Eu	(0.0216) ^b	33.1	(1.69)	4,300
Gd	0.0218	8.28	(0.57)	46,000
Tb	0.0248	10.3	0.91	46
Dy	0.0248	10.0	0.87	950
Ho	0.0254	10.7	1.24	65
Er	0.0330	12.3	1.17	173
Tm	0.0335	13.3	1.38	127
Yb	(0.0673) ^b	24.96	1.02	37
Lu	0.0388	8.12	0.75	112

^aNuclear cross section for Pm¹⁴⁷.

^bEstimated by author.

TABLE XXVI. ELASTIC PROPERTIES: COMPRESSIBILITY,⁸ YOUNG'S MODULUS,⁸
SHEAR MODULUS⁸, POISSON'S RATIO⁸

<u>Metal</u>	$\chi \times 10^7$ <u>(cm²/kg)</u>	$Y \times 10^{-6}$ <u>(kg/cm²)</u>	$\mu \times 10^{-6}$ <u>(kg/cm²)</u>	<u>σ</u>
Sc	22.5	0.809	(0.319)	(0.269)
Y	26.79	0.661	0.263	0.258
La	40.37	0.387	0.152	0.288
Ce	40.97	0.306	0.122	0.248
Pr	32.08	0.332	0.138	0.305
Nd	30.02	0.387	0.148	0.306
Pm	(27.8)	(0.43)	(0.17)	(0.278)
Sm	33.36	0.348	0.129	0.352
Eu	66.63	(0.155)	(0.060)	(0.286)
Gd	25.59	0.573	0.227	0.259
Tb	24.6	0.586	0.233	0.261
Dy	25.52	0.644	0.259	0.243
Ho	24.72	0.684	0.272	0.255
Er	23.88	0.748	0.302	0.238
Tm	24.71	(0.77)	(0.31)	(0.235)
Yb	73.93	0.182	0.071	0.284
Lu	23.85	(0.86)	(0.345)	(0.233)

TABLE XXVII. MECHANICAL PROPERTIES: HARDNESS(VICKERS),^{3, 18} YIELD
STRENGTH,^{3, 18} ULTIMATE STRENGTH,^{3, 18} ELONGATION^{3, 18}

<u>Metal</u>	<u>Vickers Hardness (kg/mm²)</u>	<u>Yield Strength (kg/mm²)</u>	<u>Ultimate Strength (kg/mm²)</u>	<u>Elongation (%)</u>
Sc	77	13.8	16.1	1
Y	38	17.5	31.6	34
La	37	11.6	14.0	8.2
Ce	24	8.0	12.3	32.6
Pr	37	10.2	11.4	12.3
Nd	35	16.2	18.7	12.4
Pm	-	-	-	-
Sm	45	11.4	12.6	2.5
Eu	17	-	-	-
Gd	57	18.6	22.0	10.0
Tb	46	-	-	-
Dy	42	19.4	26.8	5.9
Ho	42	21.5	28.6	6.9
Er	44	22.0	29.8	4.6
Tm	48	-	-	-
Yb	21	6.6	7.3	5.7
Lu	77	-	-	-

specific heat constants for these metals are among the highest of the elements in the periodic table. The magnetic susceptibility along with the resistivity, Hall coefficient and ionization potentials are presented in Table XXIV. The magnetic susceptibility is one of the most useful tools in determining directly the number of $4f$ electrons a lanthanide metal has and thus, by difference, the number of valence electrons. The magnetic susceptibility and magnetic moments of these metals, especially the heavy lanthanides, gadolinium to thulium, are the highest of all the elements. Indeed the metals which have at least one unpaired $4f$ electron undergo magnetic ordering to become a ferro- or antiferromagnet below room temperature. These magnetic properties are being intensively investigated for possible applications. The use of holmium* and dysprosium* as pole pieces of a cryogenic magnet for focusing high energy electrons has recently been described.¹⁹ Another recent development is the RCo_5 (where R is a rare earth) permanent magnet, which may become one of the more important type permanent magnets.²⁰

The thermal conductivity, coefficient of thermal expansion, Grüneisen constant and nuclear cross section are found in Table XXV. Of these the latter is the most interesting since the thermal conductivity and expansion are not outstanding, except that the metals are poor thermal conductors. The high nuclear cross sections for Sm, Eu, Gd, Dy and perhaps Er and Tm, account for their nuclear interests as control rods, burnable poisons, and shielding materials. The low cross sections of Y, La and Ce make

* Holmium and dysprosium have the highest known magnetic moments (10.6 Bohr magnetons) of any element. That of iron is 2.2.

these materials useful as diluents for nuclear fuels, and in the case of yttrium, as a container material for liquid alloys, especially some uranium- and thorium-eutectic alloys.

In Table XXVI are listed the elastic properties (compressibility, Young's modulus, shear modulus and Poisson's ratio). In general, these metals have large compressibilities and low moduli. The mechanical properties (hardness, yield and ultimate strengths and elongation) are given in Table XXVII. The mechanical properties indicate that the rare-earth metals will see limited use as structural materials. It is quite possible that Sc and Y may have desirable mechanical properties, especially in view of their low densities. However, a great deal more research is required before we have an understanding of the mechanical behavior of the pure rare-earth metals and the effects of impurities. This paucity of data is evident in Table XXVII, in that the mechanical properties have not yet been determined for three naturally occurring elements (Eu, Tb and Lu).

A close examination of the physical properties indicates that europium and ytterbium are anomalous compared to their neighbors. This is especially evident in the atomic volumes, densities, radii, melting points, vapor pressures, heats of sublimation, boiling points, electronic specific heat constants, Debye temperatures, coefficients of thermal expansion, compressibilities, Young's moduli, shear moduli, and hardnesses. This variation is due to the divalency of europium and ytterbium as compared to the trivalency of the other rare-earth metals. This tendency toward the divalent state in europium and ytterbium is evident in their alloying and chemical behaviors and it has an influence on their utilization.

Cerium is trivalent at normal temperature and pressure, but a higher valence state can be formed in the pure metal by cooling to 115°K (-158°C) or compressing to about 7.5 kilobars. The ease by which a higher valence form can be induced in cerium is evident in many of its metallic and chemical compounds and also in some of its metallurgical and chemical behaviors. In addition to its normal trivalent state, the tetravalent state in cerium (CeO_2) and its ability to change valence states ($\text{Ce}^{+3} \rightleftharpoons \text{Ce}^{+4} + e^-$) are quite important in today's technology.

Chemical Properties²¹⁻²⁵

The light lanthanides (lanthanum to europium) oxidize readily at room temperature, especially in moist air. La, Ce and Eu are the most reactive of these, followed by Pr, Nd and Sm in that order. The heavy lanthanides (gadolinium to lutetium) and scandium and yttrium are stable at room temperature with respect to air oxidation because they form a coherent oxide layer which prevents further oxidation. All of these metals oxidize at high temperatures ($\geq 300^\circ\text{C}$). As a general rule, the relative rate of oxidation is inversely proportional to the atomic number of the lanthanide metal, with scandium and yttrium being among the more resistant elements.

The rare earths are attacked and dissolved by both dilute and concentrated mineral acids, except for hydrofluoric acid which does not appear to effect them. Alkali solutions also attack these metals.

The rare earths react with the halogens to form the corresponding rare-earth trihalide. Above 200°C the reaction proceeds quite rapidly.

At high temperatures the rare-earth metals in contact with hydrogen, boron, carbon, nitrogen and sulfur will react to form a rare-earth metalloid compound. The stoichiometry of the compound depends upon the temperature and the relative amounts of the materials present. The reactive nature of the metals accounts for their use as getters in vacuum tubes and scavengers in refractory metal-base alloys.

Cerium and lanthanum (to a much lesser extent) are pyrophoric, i. e. when they are filed, ground or machined, they emanate a shower of sparks. This pyrophoric nature of cerium accounts for its use in iron-cerium and iron-mischmetal* alloy as lighter flints.

Metallurgical Behavior^{3, 18, 23, 24, 26-33}

Because of their low strengths, poor oxidation and corrosion resistances, and cost there are few if any common metallurgical uses of rare earth-base alloys. Interestingly, however, the biggest demand for pure individual rare-earth metals is for scientific research on the metals and their compounds. Perhaps out of these developments some metallurgical uses will develop. The most promising are scandium, which has a strength-to-density ratio of 5.4×10^5 cm in the annealed state and a value of 10.9×10^5 cm for a 12 wt. % Ti-Sc alloy,¹⁸ yttrium, erbium and lutetium.

Cerium is finding use as a diluent in plutonium reactor fuels. By changing the cerium content relative to plutonium, various power levels can be obtained.

*Mischmetal is a mixture of the light lanthanide metals, having a composition distribution of lanthanides similar to that in monazite: 45-50% Ce, 22-25% La, 15-17% Nd, 8-10% other rare earths.

The rare earths, however, are valuable alloying agents. They are being added to aluminum, magnesium, vanadium, chromium, iron and steels, superalloys, copper, niobium, molybdenum, and tantalum. In most instances the rare earths are added as a mixture rather than as individual elements. They are added to aluminum to enhance the fluidity, inhibit surface oxidation and refine the grain size.

The addition of the rare earths to magnesium is one of the most important metallurgical uses of these metals. The rare earths are added to improve the high temperature strength, creep resistance and oxidation resistance. The addition of yttrium (10.6 wt. %) to magnesium was reported to have produced the highest strength magnesium-base alloy made to date.²⁸

Yttrium additions were found to lower the hardness and improve the ductility of vanadium by tying up the interstitial oxygen in the vanadium as Y_2O_3 .

Yttrium additions of about 1 wt. % to chromium greatly improve the oxidation resistance of high temperature service alloys due to improving adherence of the oxide coating to the surface of the chromium-base alloys. Yttrium additions also lower the ductile-brittle transition of chromium.

Rare-earth additions to ductile iron alloys combat subversive elements, desulfurize and increase the fluidity. Additions to stainless steels increase the oxidation resistance and hot workability. Impact properties and ductility of cast steels are improved by rare-earth additives. The rare earths are also added to precision castings since they improve the castability of these alloys.

The rare earths have been added to some superalloys to improve the adherence of the oxide coatings and thus reduce the rate of oxidation. In the United States yttrium (0.1 to 0.5 wt. % additions) is almost exclusively used as the rare-earth additive, but in Russia cerium (0.01 to 0.02 wt. % additions) appears to be the most popular rare-earth additive.

The rare earths are added to copper-base alloys to deoxidize, reduce high temperature (500°C) oxidation, harden and refine the grain size. The addition of rare-earth metals to lead bronzes inhibits inverse segregation.

Yttrium additions to niobium-base alloys improve the ductility, high temperature strength and fabricability, and reduce the oxygen and nitrogen contents, grain size and the degree of coring.^{29, 30} Cerium is added to niobium which is used as a non-consumable electrode in arc-melting or arc-welding operations. The cerium is said to improve the stability of the arc.³¹

Yttrium additions (0.1 to 0.2 wt. %) to molybdenum greatly increase the strength, hardness and recrystallization temperature of molybdenum.³² For tantalum, yttrium additions (0.0014 to 0.0072 wt. %) raise the recrystallization temperature 500 to 700°C and retard grain growth.³³

Principal Compounds^{3, 23, 26, 27, 34, 35}

The principal compounds of the rare-earth metals are the halides and oxides, and to a much lesser extent the borides, hydrides, mixed oxides (e.g., garnets, ferrites, etc.), sulfides and intermetallic compounds. The halides are important since they are used in the purification and preparation of the rare-earth metals and many other rare-earth compounds.

In many applications the chlorides are used directly, such as for alloying additions and cores in carbon arc electrodes. The non-4f rare-earth fluorides (YF_3 and LaF_3) serve as host materials for doped lasers and phosphors.

The oxides by far are the most important rare-earth product since this is the form which is most commonly used in various applications. These include catalysts, glass and ceramics, electronic devices and glass polishing compounds. A summary of the physical properties of the rare-earth oxides is given in Table XXVIII. It is noted that the oxides are very refractory, electrically insulating compounds with high heats of formations. These properties account for their use in high temperature applications as crucible materials, high temperature insulators, coatings for refractory metals, fiber materials in fiber-reinforced composites, and zirconia stabilizers. The rare-earth oxides are the base products which are used to react with other materials to form garnets, ferrites, titanites, and phosphors for use in the electronics industry and to form glasses and other ceramics in the glass industry. The oxides of Y, La and Ce, because of their low nuclear cross sections, are used as diluents and/or as stabilizers in oxide-base nuclear fuels. The most common form of rare-earth control rods is a stainless steel or aluminum matrix containing a dispersion of a lanthanide oxide. The oxides (which have no 4f or 14 4f electrons) serve as host materials for the other lanthanide dopants which are added for the laser or phosphor action.

The borides, primarily the hexaborides, are of interest because of their refractory nature and electron emission characteristics. LaB_6

TABLE XXVIII. PHYSICAL PROPERTIES OF THE RARE-EARTH OXIDES

Composition	Structure	a (Å)	c (Å)	Density ³ (gm/cm ³)
Sc ₂ O ₃	cubic	9.81	-	3.88
Y ₂ O ₃	cubic	10.603	-	5.03
La ₂ O ₃	hex.	3.934	6.134	6.58
Ce ₂ O ₃	hex. ^a	3.888	6.062	6.87
CeO ₂	cubic	5.411	-	7.22
Pr ₂ O ₃	hex. ^a	3.856	6.008	7.07
Pr ₆ O ₁₁	cubic	5.466	-	6.83
Nd ₂ O ₃	hex. ^{a, b}	3.836	6.000	7.31
Sm ₂ O ₃	cubic ^b	10.924	-	7.11
EuO	cubic	5.144	-	8.13
Eu ₂ O ₃	cubic ^b	10.863	-	7.29
Gd ₂ O ₃	cubic ^b	10.817	-	7.61
Tb ₂ O ₃	cubic	10.729	-	7.87
Dy ₂ O ₃	cubic	10.668	-	8.16
Ho ₂ O ₃	cubic	10.607	-	8.41
Er ₂ O ₃	cubic	10.548	-	8.65
Tm ₂ O ₃	cubic	10.482	-	8.90
Yb ₂ O ₃	cubic	10.435	-	9.21
Lu ₂ O ₃	cubic	10.394	-	9.41

^aMay also be prepared in the cubic modification by decomposing the oxalate, R₂(C₂O₄)₃, at temperatures of 400-600°C. The hexagonal form is thought to be the thermodynamically stable form.

^bMay also be prepared in a monoclinic modification by heating the above forms at 800-1200°C for a long period of time. The monoclinic form is the thermodynamically stable form for Eu₂O₃ and probably for Gd₂O₃ and Sm₂O₃.

TABLE XXVIII (continued)

Composition	Melting Point (°C)	Coefficient of Thermal Expansion $\alpha \times 10^6 (^\circ\text{C})^{-1}$	Electrical Resistivity at 725°C (megohm-cm)	Heat of Formation (Kcal/mole oxide)
Sc ₂ O ₃	2300	9.4	51.6	-455.4
Y ₂ O ₃	2415	9.1	6.48	-455.4
La ₂ O ₃	2250	12.9	0.175	-428.6
Ce ₂ O ₃	2140	-	-	-434.9
CeO ₂	2400	12.6	0.0180	-260.2
Pr ₂ O ₃	2200	12.0	1.20	-435.8
Pr ₆ O ₁₁	2040	20.0	c	-1366
Nd ₂ O ₃	2272	12.3	0.0121	-432.2
Sm ₂ O ₃	2325	7.6	0.0463	-433.9
EuO	1950	-	0.0005 ^d	-
Eu ₂ O ₃	2050	8.5	-	-389.6
Gd ₂ O ₃	2340	9.4	1.19	-433.9
Tb ₂ O ₃	2387	-	-	-436.8
Dy ₂ O ₃	2340	8.5	1.83	-445.8
Ho ₂ O ₃	2405	-	-	-449.6
Er ₂ O ₃	2390	8.5	-	-453.6
Tm ₂ O ₃	2400	-	-	-451.4
Yb ₂ O ₃	2346	8.3	4.14	-433.7
Lu ₂ O ₃	2490	-	-	-452.8

^cThe electrical resistivity of Pr₆O₁₁ at 725°C is 6.42 ohm-cm.

^dAt 25°C.

has been used as a cathode in thermionic emitting devices. The nuclear properties combined with their refractory nature make them of interest in nuclear energy. More details concerning their physical properties can be found in recent reviews.^{3, 23, 34}

The hydrides are of interest, especially yttrium hydride (YH_2), because they contain a large number of hydrogen atoms per cm^3 , nearly equal that of water (5.3×10^{22} for YH_2 compared to 6.7×10^{22} for H_2O). This fact when combined with the fact that YH_2 loses very little hydrogen up to 1200°C makes it an attractive nuclear shield for high temperature operations.³⁵

The sulfides, like the oxides, are also refractory stable compounds and have been used as liquid metal containers.^{3, 23, 34} They are also of great interest as semiconductors, but much more technology needs to be developed before they will be used in this capacity.

The nitrides and carbides are also very refractory materials,^{3, 34} but since they react with the water vapor in the air at room temperature to form ammonia and hydrocarbons, respectively, there is no great interest in these materials at this time.

The rare-earth garnets and ferrites are being used as microwave devices, laser and maser hosts and infrared modulators. The rare-earth-doped barium titanates are used in temperature compensated dielectric capacitors and in other ferroelectric ceramic devices.

Applications^{26, 27, 36, 37}

A list of some of the applications of the rare-earth elements is given in Table XXIX. A much more detailed listing of rare-earth uses

TABLE XXIX. APPLICATIONS OF THE RARE-EARTH METALS^a

Metallurgy

alloying agent
 ferrous-M
 magnesium-M, I
 other-M
 pyrophoric alloys-M, I
 pure metals for research-I

Glass

polishing-I, M
 decolorizer-I, M
 coloring agent-I
 filters-I
 optical glass-I
 photochromic glass-I

Ceramics

enamels and glazes-I, M
 coatings-M, I
 refractories-I
 stabilizers-I, M

Electronics

capacitors-I
 cathodes-I, M
 computer components-I
 electrodes-I, M
 garnets-I
 getters-M, I
 ferrites-I
 insulators-I, M
 magnets-I, M
 resistors-I
 semiconductors-I
 thermistors-I

Illumination

carbon-arc-M
 lasers-I
 phosphors-I, M
 fluorescent lamps-I
 mercury vapor lamps-I
 color television-I

Nuclear

control rods-I
 burnable poisons-I
 diluents-I
 shielding-I
 detectors-I
 radioactive heat and power
 sources-I
 counters-I

Miscellaneous

catalyst-I, M
 pharmaceuticals-I
 photography-I
 analytical-I
 lubricant-I
 chemical processing-I
 thermometers-I

^aThe letter M after an application indicates that the rare earths are used as a mixture and the letter I indicates that individual rare earths are used. If both letters are given it indicates that both forms are used, the first letter indicates that the utilization is greater in that form than it is in the other.

is found in the review chapters by Mandle and Mandle^{26, 27} in which they cite over 1900 references. New developments of actual applications and potential uses of the rare earths are published in the quarterly newsletter of the Rare-Earth Information Center.³⁶

On a volume basis the applications using mixed, unseparated rare earths account for 80% of the United States production, but on a dollar basis this accounts for about 25% of the total amount spent.³⁷ That is, the market for separated individual elements accounts for only 20% of the total volume of rare earths produced but this costs 75% of the total dollar amount spent on the rare earths. The breakdown of the volume and dollar amounts in various categories is given in Table XXX.

One of the most important uses for rare earths to develop in the last few years is color television (TV). The two rare earths involved are europium, which is the dopant that gives rise to the bright red color, and yttrium, which is the host material for the europium. The amount of europium per television tube is small, but the quantity of yttrium is appreciable and thus the most expensive component. The yttrium host is used in the form of the pure oxide or as the vanadate.

The lanthanide elements have very complex spectra due to electronic transitions between various electronic levels. Because there are twelve useful lanthanides, each with its own electronic level scheme, there are numerous transitions which make these elements useful as phosphors and laser materials. Neodymium which has a characteristic laser wavelength of 1.06μ is one of today's most useful laser materials. Because the host material must be free of electronic transitions which might interfere

TABLE XXX. THE AMOUNT OF RARE EARTHS CONSUMED
IN 1966 IN THE VARIOUS APPLICATIONS³⁷

Volume Basis		Dollar Basis		Application
(<u>Millions lbs</u> year)	(Percent)	(<u>Millions \$</u> year)	(Percent)	
2.1	26.2	0.4	2.6	metallurgy
2.0	25.0	1.95	12.9	glass polish
1.45	18.1	0.5	3.3	catalysts
0.7	8.8	0.8	5.3	carbon-arc
0.6	7.5	0.5	3.3	research
0.5	6.2	0.75	5.0	and misc.
				glass and
				ceramics
0.35	4.4	9.7	64.2	phosphors
0.25	3.1	0.2	1.3	capacitors
0.05	0.6	0.3	2.0	microwave
8.00	99.9	15.1	99.9	total

with the phosphor or laser action and since the dopant must be able to be substituted in the host lattice, yttrium oxide or other yttrium compounds are the most important host materials for lanthanide dopants.

As noted earlier several lanthanides have two fairly stable valence states. Among these the $\text{Ce}^{+3}/\text{Ce}^{+4}$ couple is the most important one in several applications. Cerium dioxide is used in glasses which are subject to α, γ , x-ray, light and electron radiation to prevent discoloration of the glass due to the strong oxidizing power of the Ce^{+4} ion. Cerium decreases the rate of discoloration primarily by preventing the lower valent lead and/or iron from forming. This is especially useful in color TV tubes, where electron radiation could cause the glass to discolor and destroy the color quality of the TV picture. The $\text{Ce}^{+3}/\text{Ce}^{+4}$ couple is also important in analytical chemistry and may be used to determine quantitatively iron, copper, uranium, arsenic, antimony, lead and a number of other metals and some organic compounds.

Concluding Remarks

The outlook for the rare earths is indeed quite bright. The majority of new applications will be based on properties which depend upon the 4f electron configurations. An increased demand in electronics, illumination and nuclear fields will continue to grow, especially as increased production will lead to lower costs through increased volume, better efficiency and new innovations. Lower costs will make the rare earths more competitive with other materials and may displace them from their markets. Metallurgical and ceramic uses will increase and probably hold

their share of the market. One pessimistic point is in the glass polishing market, where the new development of producing plate glass without polishing threatens to reduce this application from the 25% of the total volume to a small percentage. Glass polishing of optical lenses, mirrors, etc., however, will not be affected.

There have been several good reviews concerning the rapid technological advances and the rare-earth markets during the last few years.³⁸⁻⁴⁰

Continued research, both basic and applied, will lead to a better understanding of these metals and to many new developments and applications. Furthermore, the use of the rare earths in research accounts for a small but significant share of the rare-earth market. One should not, however, overlook the contribution made by these elements in understanding the nature not only of the rare earths themselves but to materials in general. Because of basic experimental research and theoretical analyses and developments, the rare earths have led to new knowledge concerning magnetism, superconductivity, co-existence of ferromagnetism and superconductivity, alloying theory, chemical complexes, ion exchange processes and solid state chemistry, to cite a few examples.

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., p. 91 in Trans. Vacuum Metallurgy Conference, 1965, L. M. Bianchi, Ed., Am. Vac. Soc., Boston, Mass. (1966).
3. K. A. Gschneidner, Jr., Rare Earth Alloys, D. Van Nostrand Co., Princeton, New Jersey (1961).
4. A. E. Miller and A. H. Daane, Trans. Met. Soc. AIME 230, 568 (1964).
5. D. H. Dennison, K. A. Gschneidner, Jr. and A. H. Daane, J. Chem. Phys. 44, 4273 (1966).
6. J. R. Berg, F. H. Spedding and A. H. Daane, U.S. Atomic Energy Commission Report IS-327 (1961).
7. K. A. Gschneidner, Jr., R. O. Elliott and R. R. McDonald, J. Phys. Chem. Solids 23, 555 (1962).
8. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
9. K. A. Gschneidner, Jr., p. 153 in Rare Earth Research III, L. Eyring, Ed., Gordon and Breach Science Publishers, New York (1965).
10. W. R. S. Garton and M. Wilson, Astrophys. J. 145, 333 (1966).
11. J. Sugar and J. Reader, J. Opt. Soc. Am. 55, 1286 (1965).
12. J. Sugar and V. Kaufman, J. Opt. Soc. Am. 55, 1283 (1965).
13. J. Reader and J. Sugar, J. Opt. Soc. Am. 56, 1189 (1966).
14. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 70, 3014 (1966).
15. N. I. Ionov and M. A. Mittsev, Zh. Ekskl. Teor. Fiz. 40, 741 (1961); Eng. transl. Soviet Phys. -JETP 13, 518 (1961).
16. B. W. Jolliffe, R. P. Tye and R. W. Powell, J. Less-Common Metals 11, 388 (1966).

17. J. A. Harvey and D. J. Hughes, p. 8-114 in American Institute of Physics Handbook, D.E. Gray, Ed., 2nd ed., McGraw-Hill Book Co., New York (1963).
18. D. Geiselman, J. Less-Common Metals 4, 362 (1962).
19. P. Bonjour and A. Septier, Compt. rend. 264B, 747 (1967).
20. K. J. Strnat and G.I. Hoffer, U.S. Air Force Materials Laboratory Report AFML-TR-65-466 (1965).
21. L. Lee and N.D. Green, Corrosion 20, 145t (1964).
22. T. Moeller, The Chemistry of the Lanthanides, Reinhold Publishing Corp., New York (1963).
23. B. Love and V. Kleber, Technology of Scandium, Yttrium and the Rare Earth Metals, The Macmillan Company, New York (1963).
24. F. H. Spedding and A.H. Daane, Eds., The Rare Earths, John Wiley and Sons, Inc., New York (1961).
25. R. C. Vickery, Chemistry of the Lanthanides, Academic Press, Inc., New York (1953).
26. R. M. Mandle and H. H. Mandle, p. 416 in Progress in the Science and Technology of the Rare Earths, Vol. 1, L. Eyring, Ed., Pergamon Press, Oxford (1964).
27. H. H. Mandle and R.M. Mandle, Progress in the Science and Technology of the Rare Earths, Vol. 2, L. Eyring, Ed., Pergamon Press, Oxford (1966).
28. R. V. London, R.E. Edelman and H. Markus, ASM Trans. Quart. 59, 250 (1966).
29. R. T. Torgenson and W. A. Baginski, Trans. Met. Soc. AIME 236, 158 (1966).

30. E. J. Delgrosso and C. E. Carlson, J. Inst. Metals 94, 363 (1966).
31. S. S. Aconsky and J. R. Doyle, Electrochem. Tech. 1, 116 (Mar. - Apr., 1963).
32. E. A. Loria, J. Less-Common Metals 12, 425 (1967).
33. L. D. Kirkbride, J. A. Basmajian, D. R. Stroller, W. E. Ferguson, R. H. Perkins and D. N. Dunning, J. Less-Common Metals 9, 393 (1965).
34. G. V. Samsonov, Tugoplavkie Soedineniya Redkozemel'nykh Metallov s Nemetallami, Metallurgiya, Moscow (1964); Eng. transl. High Temperature Compounds of Rare Earth Metals with Nonmetals, Consultants Bureau, New York (1965).
35. R. Van Houten and W. G. Baxter, J. Spacecraft Rockets, 2, 469 (1965).
36. RIC News, published in March, June, September and December by the Rare-Earth Information Center, Ames Laboratory, Iowa State University, Ames, Iowa 50010.
37. H. E. Kremers, 6th Rare-Earth Research Conference, May 3-5, 1967, Gatlinburg, Tennessee, p. 1 of Conference Preprints.
38. Anonymous, Chem. & Eng. News 43, [19], 78 (1965).
39. P. Farin, Metals Week 37, [52], 5 (1966).
40. Anonymous, Chem. & Eng. News 45, [25], 46 (1967).

CHAPTER 7. TANTALUM

Introduction

Tantalum is a strong, high melting, chemically inert metal. These properties, which account for most of its uses, can be accounted for by tantalum's electronic structure. The ground state of tantalum consists of the xenon rare gas core, the completely filled 4f level and five outer electrons with two electrons in the 6s and three in the 5d levels. Metallic tantalum has the same inner core configuration, but the outer electronic distribution has about one in the 6s and nearly four in the 5d bands. This band configuration would account for the high melting point, heat of sublimation and electronic specific heat constant and the low electrical resistivity.

Tantalum's chemical and metallurgical behaviors are also consistent with this electronic configuration.

Physical Properties¹⁻¹⁵

The physical properties of tantalum are shown in Table XXXI. Because of its large mass, its usefulness is limited in aerospace applications to very high temperatures ($> 1100^{\circ}\text{C}$), where it is one of the few materials which has any reasonable strength (see Fig. 4). Tantalum is slightly smaller than its immediate preceding cogener niobium (0.3% by volume and 0.1% by radius). This is unusual in the periodic table* and is the result of the lanthanide contraction, which occurs just before it in the periodic table (atomic numbers 57 to 71).

*This also occurs for zirconium and hafnium pair for the same reason.

TABLE XXXI. PHYSICAL PROPERTIES OF TANTALUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

Property	Value	Ref.
Atomic Number	73	-
Atomic Weight ($^{12}\text{C}=12.00$)	180.948	1
Atomic Volume (cc/mole)	10.80	2
Lattice Parameter (Å) (bcc)	3.298	3
Density (gm/cm ³)	16.75	-
Metallic Radius (CN=12) ^a (Å)	1.467	4
Melting Point (°C)	2998	2
Heat of Fusion (kcal/g at)	(5.76)	2
Vapor Pressure A	40539	5
$\log P_{\text{torr}} = -A/T + B + CT + DT^2$ B	10.064	5
C x 10 ⁴	0.81	5
D x 10 ⁸	-1.84	5
(temp. range °C)	2350-2670	5
Boiling Point (°C)	5487	2
Heat of Sublimation at 25°C (kcal/g at)	186.8	2
Heat Capacity, C _p (cal/g at-deg)	6.07	2
Electronic Specific Heat Constant (cal/g at-deg ²) x 10 ⁴	14.0	2
Debye Temperature (°K)	225	2
Magnetic Susceptibility (emu/mole) x 10 ⁶	168	6
Electrical Resistivity (μ ohm-cm)	12.9	7, 8
Superconducting Transition Temperature (°K)	4.48	8
Hall Coefficient (volt-cm/amp-Oe) x 10 ¹²	0.95	7
Ionization Potentials (eV)		
I	7.88	9
II	16.2	9
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.130	7
Thermal Expansion (°C ⁻¹) x 10 ⁶	6.55	2
Grüneisen Constant	1.82	2
Compressibility (cm ² /kg) x 10 ⁷	4.89	2
Young's Modulus (kg/cm ²) x 10 ⁻⁶	1.85	2
Shear Modulus (kg/cm ²) x 10 ⁻⁶	0.700	2

TABLE XXXI. (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Poisson's Ratio	0.35	2
Hardness, Vickers (kg/mm ²)	95 ^b	10
Yield Strength (kg/mm ²)	18.5 ^b	10
Ultimate Strength (kg/mm ²)	20.6 ^b	10
Elongation (%)	36 ^b	10
Nuclear Cross Section (barns)	21	11

^aCN means coordination number.

^bAnnealed.

The high melting point and low vapor pressure make tantalum a very attractive metal for high temperature applications. Its melting point makes it the fourth highest melting metal exceeded only by tungsten, rhenium and osmium. The high heat of sublimation (a measure of the binding energy of the solid) is exceeded only by tungsten and osmium.

The low electrical resistivity is useful in some of its electrical and electronic applications. The superconducting transition temperature may be of some usefulness in cryogenic applications. Its reasonably good thermal conductivity accounts, in part, for its use in heat exchange equipment.

Although the tensile strength of annealed tantalum is nothing tremendous, it can be improved by alloying and cold-working. Furthermore, its strength changes little with temperature up to about 850°C, and thus at higher temperatures it becomes one of the more useful structural metals.

Chemical Properties^{7, 10, 12-16}

Tantalum is inert to all acids except hydrofluoric and hot fuming sulfuric acid. It is resistant to attack by dilute or weak alkali solutions. As the concentration and/or temperature is increased, tantalum becomes more susceptible to attack by alkali solutions. Tantalum is not attacked by many molten metals, including alkali metals, alkaline earth metals, magnesium, aluminum, many of the rare-earth metals, plutonium, copper, silver, gold, zinc, mercury and tin.

This chemical inertness accounts for its use in chemical processing

equipment (tanks, pipes, pumps, etc.), container material for the manufacture of metals (rare-earth metals and plutonium), ion propulsion engines, heat exchangers, and as a prosthetic metal (wire used as suture material, wire gauze to repair abdominal walls, and sheets used as skull plates, etc.).¹⁶

The chemical inertness of tantalum is due to the formation of a thin adherent film of Ta_2O_5 on the surface. This thin oxide film because of its dielectric nature is also important in tantalum capacitors and rectifiers.

Tantalum is readily attacked and embrittled by hydrogen at temperatures above 250°C. Fortunately by heating in a dynamic vacuum above 1500°C the hydrogen may be removed.

Tantalum begins to oxidize at approximately 500°C and reacts catastrophically with oxygen above 1250°C. It starts to react with nitrogen at 300°C, carbon dioxide at 500°C and water vapor at 925°C. Thus it is apparent that tantalum needs to be protected for high temperature service. Oxide, silicide and boride coatings have been used to protect tantalum from high temperature oxidation.

Tantalum is attacked by fluorine at room temperature but is inert to chlorine up to 250°C, and bromine and iodine up to 300°C. Sulfur does not react with tantalum except at temperatures above 500°C.

Metallurgical Behavior^{7, 10, 12-15, 17-23}

Tantalum can be readily formed by cold-working into plate, sheet, foil, rod, wire and seamless tubing because it is very ductile and work hardens slowly. Usually after about a 60% reduction the material is vacuum annealed before further working.

Tantalum can be machined if high speed tools are used with sufficient lubrication and cooling.¹⁷ Tantalum is readily welded in an inert gas atmosphere using standard techniques. It also can be brazed by using copper.

A number of tantalum-base alloys have been developed for high temperature applications. Most of these are based on V, Nb, Mo, Hf and W additions, either singly or with a second metal, usually from this group.¹⁵ Tungsten appears to be the most effective in increasing the high temperature strength of tantalum. Hafnium is also a useful strengthener, and it also improves the oxidation resistance. But on a strength-to-density basis niobium-vanadium combinations (32 wt. % Nb-5.1V and 29 wt. % Nb-7.1V) are better than the typical Ta-W-Hf alloys (10 wt. % Hf-5W). Furthermore the Ta-Nb-V alloys have better weldability properties.¹⁸ More details concerning tantalum-base alloys are found in Sayre's review.¹⁵

Protection of tantalum-base alloys from oxidation may be obtained by coating or cladding with HfO_2 , ZrO_2 , silicides, aluminides or ZrB_2 .^{14, 19} Jaffee²⁰ noted that a Sn-Al coating on tantalum-base alloy gave excellent protection up to 1760°C, good protection between 1760 and 1930°C, but failed rapidly above 1930°C.

Tantalum is used as a minor alloying additive to nickel- and cobalt-base superalloys. Tantalum plays much the same role as niobium in that they form carbides and improve the high temperature strength.^{21, 22} Tantalum appears to be an important additive in titanium-base alloys (Ti-8Al-2Nb-1Ta) for use in naval vessels, especially deep diving vehicles and in desalination plants.²³ Tantalum acts as a β -stabilizer

in these alloys. Tantalum is also added to hafnium to improve its strength and high temperature oxidation resistance. In the form of ferrotantalum-niobium it is added to stainless steels to improve the oxidation resistance.

Principal Compounds^{3, 10, 13, 24-27}

The most important tantalum compounds are Ta_2O_5 , K_2TaF_7 and the refractory compounds, TaB_2 , TaC , Ta_2N and TaN . The oxide is important since it forms an adherent coating on the metal's surface and prevents oxidation and corrosion of the metal at room and low ($< 300^\circ C$) temperatures. Furthermore, the dielectric properties of the oxide account for tantalum's major use in capacitors and rectifiers.

The double fluoride, K_2TaF_6 , is important since this is the compound which is used to separate and purify tantalum from niobium and other impurities in its ores. K_2TaF_6 is the salt which is reduced electrolytically or by sodium to give tantalum metal.

The properties of TaB_2 , TaC , Ta_2N and TaN are presented in Table XXXII. These compounds have very high melting points, low resistivities and thermal expansions and good hardness values. These materials are used as refractories, heat resistant parts, crucibles and cutting tools.

One of the standard carbide cutting tools is a complex carbide consisting of WC , TiC , TaC and a Co binder.²⁶ Recent studies show TiB_2 -20% TaC and TaN -40% ZrB_2 to be among the best high speed cutting tool combinations known.²⁷

Some tantalate compounds, such as $KTaO_3$, have found use as ferroelectrics in capacitors, electromechanical filters and memory devices.

TABLE XXXII. PHYSICAL PROPERTIES OF SOME REFRACTORY TANTALUM COMPOUNDS AT ROOM TEMPERATURE UNLESS OTHERWISE NOTED^{3, 24, 25}

Property		TaB ₂	TaC	Ta ₂ N	TaN
Lattice Parameter(s) (Å)	$\frac{a}{c} =$	3.088 3.241	4.456 -	3.048 4.919	5.190 2.911
Crystal System		hex	fcc	hex	hex
Structure Type		AlB ₂	NaCl	Fe ₂ N	CoSn
Density (gm/cm ³)		12.60	14.47	15.86	14.36
Melting Point (°C)		3100	3900	2980	3090
Heat Capacity, C _p (cal/mole-deg)		12.1	8.7	11.3	8.8
Electrical Resistivity (μ ohm-cm)		68	30-41	-	-
Thermal Conductivity (cal-cm/sec-cm ² -deg)		0.276 ^a	0.053	0.024	0.019
Thermal Expansion (°C ⁻¹) x 10 ⁶		5.72	5.5	5.0	3.6
Young's Modulus (kg/cm ²) x 10 ⁻⁶		2.6	2.9	-	-
Hardness, Vickers (kg/mm ²)		2530 ^b	1800 ^b	1220	1060
Ultimate Strength (kg/mm ²)		-	23	-	-
Modulus of Rupture (kg/mm ²)		-	22	-	-

^aAt 260°C

^bKnoop hardness

Applications

A list of tantalum applications is given in Table XXXIII. The electronic industry accounted for 75% of the use of tantalum in 1965. Capacitors constitute the major share of this 75%. Integrated circuits, which are made by depositing tantalum on an inert substrate, partially oxidizing this layer to give a dielectric layer of Ta_2O_5 on the tantalum and finally depositing a gold layer, are one of the new important developments in the electronics industry. This integrated circuit gives the same electrical performance as a conventional thin-film circuit consisting of three resistors and four capacitors.

The large mass, poor oxidation resistance and cost limit the utilization of tantalum in the aerospace field; and its cost and large nuclear cross section limits large scale nuclear applications. In spite of these adverse properties, tantalum has a number of useful properties which make it very competitive in refractory and chemical applications (see Table XXXIII). The good properties of TaC, TaB_2 and TaN make these compounds very attractive as advanced technological materials.

Concluding Remarks

The outlook for tantalum is quite bright, especially in the electronic industry which should continue to hold a very large share of the tantalum market. As the demand for higher operating temperatures in jet turbine and rocket engines increases, the utilization of tantalum in these applications is expected to be appreciable. As an alloying agent the use of tantalum will increase especially for high temperature alloys. The special chemical properties of tantalum metal and the refractory nature of some of its metalloid compounds will play an important part in tomorrow's world.

TABLE XXXIII. APPLICATIONS OF TANTALUM

Electronics

- capacitors
- rectifiers
- resistors
- vacuum tubes
- high voltage surge arrestors
- integrated circuits
- ferroelectrics

Chemical Equipment

- heaters
- heat exchangers
- condensers
- coils
- pipes
- valves
- reactors
- laboratory ware
- rayon spinnerets

Refractory

- high temperature alloys
- jet engine parts
- valve seals and guides
- rocket nozzle coatings
- alloying agents
- crucibles and containers for molten metals
- heat shields
- furnace heating elements
- thermocouple sheaths

Medical

- surgical and dental tools
- prosthetics

Miscellaneous

- catalyst
- high speed cutting tools
- anode baskets for electroplating devices
- special optical glass
- components of vacuum ion pumps

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. J. W. Edwards, H. L. Johnston and P. E. Blackburn, J. Am. Chem. Soc. 73, 172 (1951).
6. C. J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).
7. F. F. Schmidt, p. 1222 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
8. G. T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
9. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
10. C. A. Hampel, p. 469 in Rare Metals Handbook, 2nd ed., C. A. Hampel, Ed., Reinhold Publishing Co., New York (1961).
11. J. A. Harvey and D. J. Hughes, p. 8-114 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
12. R. F. Wehrmann, "Tantalum," in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).

13. F. T. Sisco and E. Epremian, Eds., Columbium and Tantalum
John Wiley & Sons, Inc., New York (1963).
14. N. E. Promisel, Ed., The Science and Technology of Tungsten,
Tantalum, Molybdenum, Niobium and Their Alloys, Pergamon
Press, Oxford (1964).
15. R. Syre, Handbook on the Properties of Niobium, Molybdenum,
Tantalum, Tungsten and Some of Their Alloys, AGARDograph 94,
North Atlantic Treaty Organization, Brussels (1965).
16. D. C. Ludwigson, J. Metals 16, 226 (1964).
17. R. E. Droegkamp, Metal Progress 89, [4], 133 (1966).
18. D. J. Maykuth, G. S. Root and H. R. Ogden, J. Metals 16, 180 (1964).
19. J. E. Eorgan and N. D. Fern, J. Metals 19, [9], 6 (1967).
20. R. I. Jaffee, J. Metals 16, 410 (1964).
21. R. F. Decker and R. R. DeWitt, J. Metals 17, 139 (1965).
22. W. F. Simmons and H. J. Wagner, Metal Progress 91, [6], 86 & 87 (1967).
23. I. R. Lane, Jr., J. Metals 17, 834 (1965).
24. E. G. Kendall, p. 143 in Ceramics for Advanced Technologies, J. E.
Hove, and W. C. Riley, Eds., John Wiley & Sons, Inc., New York
(1965).
25. J. F. Lynch, C. G. Ruderer and W. H. Duckworth, Engineering Properties
of Selected Ceramic Materials, American Ceramic Society, Columbus,
Ohio (1966).
26. E. W. Goliber, Metal Progress 90, [2], 95 (1966).
27. F. C. Holtz and N. M. Parikh, Metal Progress 90, [2], 117 (1966).

Introduction

In the late 1940's and early 1950's titanium, the ninth most abundant element in the world, had one of the most promising technological futures of the known metals, only to fall to a point of almost complete neglect. By the early 1960's, however, the so-called wonder metal came on strong and finally fulfilled the role which many of its backers had hoped for 10 to 15 years earlier.

Titanium's major advantages are its strength, lightness and corrosion resistance. These properties are due to titanium's electronic structure, which consists of eighteen electrons having the argon rare gas core and the remaining four electrons evenly divided between the 4s and 3d levels in the ground state. In the metallic form its outer four electrons occupy the 4s and 3d bands, with the 4s level nearly filled (< 2) as suggested by titanium's high resistivity and moderate heat of sublimation. Although titanium has nine more electrons and is about 50% more dense than aluminum, its strength is 5 to 6 times greater. The tensile strength of unalloyed titanium is about the same as mild steel, but it is 50% less dense than iron. These physical properties plus titanium's good chemical stability make it an outstanding metal in aerospace, chemical processing and cryogenic fields.

Titanium dioxide is also a very important material in today's technological world, especially its use as a pigment in paints, and as a component of many other materials, such as plastics and floor coverings. These uses of titanium dioxide account for about 90 to 95% of the total titanium products marketed in the United States.

Physical Properties¹⁻¹⁶

The physical properties of titanium metal are summarized in Table XXXIV. Titanium's mass and density are in the low-to-intermediate range of the metals in the periodic table. This is quite important in applications where weight and/or density are critical, such as space vehicles and aircraft. Its melting point is about 1000°C above that of aluminum, nearly 400°C higher than beryllium's and more than 100°C above iron's, but significantly below those of Nb, Mo, Ta and W (by 800°C or more). The combination of a high melting point and low vapor pressure make it a useful metal for high temperature applications. The high temperature limit (~600°C) being determined by its strength at temperature.

Titanium has a reasonably high thermal conductivity (about half that of copper) and this is quite useful in some applications, such as heat exchangers in corrosive environments. The mechanical properties shown in Table XXXIV are nothing spectacular, but by proper alloying and heat treatment the strengths can be increased by a factor of five times, however, a fivefold deterioration in the ductility is sacrificed. The thermal neutron cross section is in the low-to-intermediate range. It is not low enough to allow consideration of titanium as a structural material for reactors except under very unusual conditions.

It is noted that titanium undergoes a polymorphic transformation at 882.5°C from hexagonal to body-centered cubic upon heating. This transformation is quite influential on its metallurgical properties and thus on its utilization in various applications. This is discussed in more detail in a later section.

TABLE XXXIV. PHYSICAL PROPERTIES OF TITANIUM AT ROOM TEMPERATURE
UNLESS OTHERWISE NOTED

Property	Value	Ref.
Atomic Number	22	-
Atomic Weight ($^{12}\text{C}=12.00$)	47.90	1
Atomic Volume (cc/mole)	12.01	2
Lattice Parameter (Å)		
α (hcp)	a= 2.9511	3
	c= 4.6843	3
β (bcc at 900°C)	3.3065	3
Density (gm/cm ³)	3.988	-
Metallic Radius (CN=12) ^a (Å)	1.462	4
α - β Transition Temperature (°C)	882.5	5
Heat of Transformation (kcal/g at)	1.01	6
Melting Point (°C)	1668	2
Heat of Fusion (kcal/g at)	(3.42)	2
Vapor Pressure	A 24644	7
$\log P_{\text{torr}} = -A/T+B+CT$	B 10.577	7
C x 10 ⁴	-2.27	7
(temp. range °C)	1315-1490	7
Boiling Point (°C)	3313	2
Heat of Sublimation at 25°C (kcal/g at)	112.7	2
Heat Capacity, C _p (cal/g at-deg)	5.98	2
Electronic Specific Heat Constant (cal/g at-deg ²) x 10 ⁴	8.15	2
Debye Temperature (°K)	380	2
Magnetic Susceptibility (emu/mole) x 10 ⁶	60	8
Electrical Resistivity (μ ohm-cm)	42.5	9, 10
Superconducting Transition Temperature (°K)	0.39	10
Hall Coefficient (volt-cm/amp-Oe) x 10 ¹²	-0.36	11
Ionization Potentials (eV)		
I	6.82	12
II	13.57	12
III	27.6	13
IV	42.98	13
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.48	14
Thermal Expansion (°C ⁻¹) x 10 ⁶	8.35	2

TABLE XXXIV. (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Grüneisen Constant	1.33	2
Compressibility (cm^2/kg) $\times 10^7$	9.328	2
Young's Modulus (kg/cm^2) $\times 10^{-6}$	1.08	2
Shear Modulus (kg/cm^2) $\times 10^{-6}$	0.401	2
Poisson's Ratio	0.345	2
Hardness, Vickers (kg/mm^2)	80-90	15
Yield Strength (kg/mm^2)	14	9
Ultimate Strength (kg/mm^2)	24	9
Elongation (%)	54	9
Nuclear Cross Section (barns)	5.8	16

^a CN means coordination number.

Chemical Properties^{5, 17-28}

Titanium is inert to the common gases hydrogen, nitrogen, oxygen and water vapor at room temperature. But it begins to react at relatively low temperatures with oxygen and hydrogen ($\sim 250^{\circ}\text{C}$) and at much higher temperatures with nitrogen and water vapor ($\sim 700^{\circ}\text{C}$). Titanium reacts with the halogen gases (F_2 , Br_2 and I_2) above room temperature to form the corresponding tetrahalide.

Titanium is resistant to dilute cold hydrochloric acid and nitric acid under all conditions but is readily attacked by sulfuric, phosphoric, dilute hot hydrochloric and concentrated hydrochloric acids. It is resistant to moist chlorine gas, chloride solutions, dilute alkali solutions and many organic acids. This accounts for its use in chemical processing equipment¹⁸ and the paper industry.¹⁹

It is very resistant to salt water solutions, even at elevated temperatures. This behavior accounts for its use in desalination plants* and in naval vessels as parts, such as propellers and hulls.

The addition of 0.2 wt. % Pd to titanium improves its corrosion resistance, especially under reducing conditions.²⁰ Other alloys which have been used in marine environments²¹⁻²⁷ with good success are:

Ti-8Al-2Nb-1Ta,	Ti-7Al-2.5Mo,
Ti 7Al-3Nb,	Ti-7Al-2Nb-1Ta,
Ti-6Al-4V,	Ti 6Al-2Nb-1Ta-0.8Mo and
Ti-4Al-3Mo-1V.	

* Approximately 160 km (100 miles) of 0.71mm (0.028in.) diameter seamless titanium tubing was used in the construction of the multistage flash evaporator desalination plant, which is located at St. Croix, Virgin Islands.²⁰

The chemical inertness also accounts for its use as a prosthetic metal.²⁸ Its utilization in this field, however, is significantly behind that of tantalum.

Metallurgical Behavior^{5, 9, 15, 17, 20-27, 29-37}

Titanium can be worked by the usual methods, such as hot forging at 1040°C, rolling at 870°C and bending and forming operations at 260-315°C. Since titanium has a tendency to seize and gall, special lubricants are required for drawing and extrusion. Titanium is usually machined at slow speeds with heavy cuts and cooling with cutting oils containing chlorinated solvents such as carbon tetrachloride. It can also be chemically milled.

Titanium can be brazed or welded. Welding must be done in an inert atmosphere to avoid oxidation or nitrogen pick-up which will cause embrittlement. Brazing may be accomplished by using Ti-Co-Zr, Ti-Al-Be-Zr and Ti-Be-Ni-Zr brazing alloys, which fuse between 800 and 950°C.

There are a great number of titanium-base alloys available for a variety of applications, ranging from outer space to the bottom of the ocean. Titanium alloys are generally grouped in four categories, alpha, near-alpha, alpha-beta and beta, according to the predominant character of the alloys. Alloying elements such as aluminum, tin, zirconium, carbon and oxygen are alpha stabilizers and solid-solution strengthen titanium while retaining the alpha phase. Alloying elements such as chromium, iron, molybdenum, nickel, niobium, silicon and vanadium are beta stabilizers and also lead to solid solution strengthening. The general

characteristics of alpha, near-alpha, alpha-beta and beta alloys are given in Table XXXV along with some typical alloys for each category. The mechanical properties of some of these alloys are listed in Table XXXVI. More extensive information concerning the mechanical properties of titanium alloys is given in the reviews by Ogden⁵ and Lyman⁶ and more recent journal articles by a number of authors.^{23, 27, 29-32}

These titanium alloys are used as structural parts, panels, tubing, pressure vessels, cryogenic containers and tubing, turboprop and jet engine parts, fasteners, landing gear and wheels in aircraft and space-ships, as propellers and hulls in marine vessels, in desalination plants, and in chemical processing equipment. The greatest amounts of titanium-base alloys are used in aerospace applications.

Some titanium alloys, specifically Nb-Ti, V-Ti and Ti-Ta, have very interesting and useful high field superconducting properties, which make them attractive for some low temperature superconducting applications (see NIOBIUM chapter for more details, especially Table XV for the properties of the Nb-33wt. %Ti alloy). Titanium alloys containing a few weight percent platinum or palladium are used as catalysts. Alloys containing the former are also used as electrodes and those containing the latter are used in gas purification processes.

Titanium is also used in fiber-reinforced composites, primarily as the matrix material, either as pure titanium or as Ti-6Al-4V.^{32, 33} The common fiber materials used are molybdenum, tungsten, boron, Al_2O_3 , SiC, and Ti-20Nb-7.5Al. Several of these composites show a significant improvement in the strength over the pure titanium or Ti-6Al-4V alloy used alone.

TABLE XXXV. CHARACTERISTICS AND TYPICAL EXAMPLES OF THE FOUR CATEGORIES OF TITANIUM-BASE ALLOYS

Type	alpha	near-alpha	alpha-beta	beta
Advantages	High creep strength, maintain strength to 500°C, exceptional strength and ductility to cryogenic temperatures, readily welded.	Heat treatable to greater strengths than alpha alloys.	Can be easily formed in solution-heat-treated-condition, and then aged to high strength.	Same as alpha-beta, but more formable.
Disadvantages	Hard to form, strength limited because alloys cannot be heat-treated.	Hard to form.	Do not have low temperature strength and ductility of alphas, difficult to weld.	Poor notch toughness at low temperature, welds are brittle after aging, high densities.
Typical alloys	Ti-7Al-12Zr Ti-5Al-2.5Sn Ti 5Al-5Sn-5Zr	Ti-8Al-1Mo-1V Ti-8Al-2Nb-1Ta Ti-7Al-2Nb-1Ta Ti-6Al-4Zr-1V Ti-6Al-4Zr-2Mo	Ti-7Al-4Mo Ti-6Al-4V Ti-6Al-4V-2Sn Ti-6Al-2Mo Ti-2Al-11Sn-5Zr-1Mo-0.2Si	Ti-7.5Al-20Nb Ti-3Al-13V-11Cr

TABLE XXXVI. MECHANICAL PROPERTIES OF SOME TYPICAL TITANIUM ALLOYS AND SOME OF THEIR APPLICATIONS

Alloy (wt. % of additives)	Ultimate Strength (kg/mm ²)	Yield Strength (kg/mm ²)	Elongation (%)	Typical Applications
pure Ti	24	14	54	aircraft, chemical resistant equip.
8Al-1Mo-1V	112	109	10	jet engine, cryogenic, sheets for aircraft
7.5Al-20Nb	125	125	0-2	high hot strength, strengthening component in a Ti alloy-Ti alloy composite
7Al-4Mo	130	120	-	aircraft wheels
7Al-2Nb-1Ta	120	113	8	jet engine
6Al-4V	120	112	10	most extensively used Ti alloy, cryogenic, pressure vessels, spacecraft, aqueous environment
6Al-4V-2Sn	127	120	10	high strength applications, structural parts and panels in aircraft
5Al-2.5Sn	84	81	10	cryogenic, pressure vessels, spacecraft
3Al-13V-11Cr	92	88	10	sheet for aircraft
2Al-11Sn-5Zr- 1Mo-0.2Si	98	91	10	high temp., fatigue critical applications

Titanium is an important alloying agent, especially in superalloys.^{34, 35} Titanium is added to iron-base, nickel-iron base, nickel-base and cobalt-base superalloys for its age hardening ability which is due to the precipitation of face-centered cubic Ni_3Ti . In some of the cobalt-base alloys, no nickel is present and in this case the improved properties are due to the formation of TiC . Several of the iron-nickel base superalloys are also known as maraging steels because the precipitation reaction occurs on aging when they are in the martensitic condition. In general these steels have about 18 wt. % nickel. The titanium added increases the strength, within limits, 4.2 to 7.0 kg/mm^2 for each 0.1 wt. % titanium added due to the uniform distribution of the Ni_3Ti precipitate throughout the matrix. Details concerning the aging mechanism, effect of composition, heat treatment, mechanical and fatigue properties, corrosion and embrittlement characteristics and weldability are given by Contractor³⁶ for these maraging steels. Wagner and Prock³⁷ noted that the Russians tend to keep the level of titanium and aluminum below that used in the United States in superalloys. These lower quantities are compensated for by increased use of other alloying additions.

Titanium is also added to aluminum, cast iron, chromium, copper, molybdenum, tantalum and zirconium to improve their properties. Copper alloys containing 10 wt. % Ti, 30 wt. % Ti and 15 wt. % Sn-5 wt. % Ti are useful brazing alloys and may be used as casting alloys (Cu-15Sn-5Ti) and as chemical resistant bronzes (Cu-10Ti).

Principal Compounds^{3, 5, 17, 38-41}

As noted earlier titanium dioxide is the most important form of titanium in today's markets. Some of its important physical properties are listed in Table XXXVII. Titanium dioxide has two polymorphic modifications in addition to its common modification, rutile (see Table XXXVII). The other two are anatase (also tetragonal $a = 3.785$ and $c = 9.514\text{\AA}$) and brookite (orthorhombic, $a = 9.185$, $b = 5.447$ and $c = 5.145\text{\AA}$). Titanium dioxide's most useful properties in relation to its technological applications are its high opacity, chemical inertness, high index of refraction and ability to be produced in a fine particle size. These account for its major use as a pigment. Paints, varnishes and lacquers account for 63% of its use, paper-12%, floor coverings-4%, rubber-4%, plastics-3%, coated fabrics and textiles-2%, roofing granules-2%, printing ink-2% and miscellaneous-8%.

Other important compounds include the tetrachloride, which is the form that is reduced to the metal by magnesium or sodium. The refractory compounds TiB_2 , TiC and TiN are quite useful because of their high melting points and high hardnesses, especially the first two. TiB_2 and TiC are the second and third hardest known materials, exceeded only by diamond, which has a Knoop hardness number of 8000. These properties make them useful as cutting tool materials and abrasives, bearing and heat resistant materials, hard facing alloys, refractories, and strengthening and hardening dispersents for metals and alloys. Some new and greatly improved cutting tools include TiC-Ni , WC-TaC-TiC-Co , WC-TiC-Co and $\text{TiB}_2\text{-TaC}$ combinations.^{40, 41}

TABLE XXXVII. PHYSICAL PROPERTIES OF SOME REFRACTORY TITANIUM COMPOUNDS AT ROOM TEMPERATURE UNLESS OTHERWISE NOTED^{3, 38, 39}

Property		TiB ₂	TiC	TiN	TiO ₂
Lattice Parameter(s) (Å)	<u>a</u> =	3.028	4.329	4.246	4.594
	<u>c</u> =	3.228	-	-	2.962
Crystal System		hex	fcc	fcc	tetr
Structure Type		AlB ₂	NaCl	NaCl	rutile
Density (gm/cm ³)		4.50	4.92	5.44	4.244
Melting Point (°C)		2980	3060	2940	1840
Heat Capacity, C _p (cal/mole-deg)		11.8	7.8	8.8	14.9 ^a
Electrical Resistivity (μ ohm-cm)		10-30	60	22-30	-
Thermal Conductivity (cal-cm/sec-cm ² -deg)		0.141 ^b	0.041	0.060	0.019 ^c
Thermal Expansion (°C ⁻¹) x 10 ⁶		6.4	10.2	8.7	8.8
Compressibility (cm ² /kg) x 10 ⁷		-	2.9	-	4.93
Young's Modulus(kg/cm ²) x 10 ⁻⁶		4.2	4.6	0.8	2.88
Shear Modulus (kg/cm ²) x 10 ⁻⁶		-	1.8	-	1.14
Poisson's Ratio		-	0.18	-	0.26
Hardness, Knoop (kg/mm ²)		3370	3200	1770	1000
Ultimate Strength (kg/mm ²)		-	48	-	-
Modulus of Rupture (kg/mm ²)		25	87	24	-

^aAt 90°C.

^bAt 50°C.

^cAt 150°C.

Titanium dihydride is an interesting compound since it contains more hydrogen atoms per cm^3 than water (9.0×10^{22} for TiH_2 vs. 6.7×10^{22} for water). This compound is of interest as a neutron moderator, especially where weight is critical. Its useful maximum temperature is 600°C compared to about 150°C for water. At higher temperatures both YH_2 and ZrH_2 have higher concentrations of hydrogen atoms per unit volume.

Applications

The applications of titanium and its compounds and alloys are listed in Table XXXVIII. These vary quite widely from pigments to outer space. The largest market for titanium products is the paint industry, followed by the paper, metallurgical, floor covering, rubber and plastics industries, in order of decreasing amounts of titanium consumed. Of these, except for metallurgical uses, the titanium form utilized in the end product is the dioxide.

Titanium metal consumption is roughly divided as 50% jet engines, 25% aircraft, 15% space and missiles, 8% chemical processing equipment and 2% miscellaneous. Titanium metal will become more and more important as aircraft fly faster and faster since titanium is the lightest known metal available with the high temperature strength required for these supersonic aircraft.

Concluding Remarks

The outlook for titanium products is excellent. Titanium dioxide production should increase as the paint, paper, floor covering and rubber

TABLE XXXVIII. APPLICATIONS OF TITANIUM AND ITS COMPOUNDS
AND ALLOYS

Titanium Dioxide

paints	welding rods
varnishes	leather and shoe dressing
lacquers	synthetic fibers
paper	synthetic gems
floor coverings	ceramic refractories
rubber	skin disease ointment
plastics	cosmetics
coated fabrics and textiles	starting material for preparing
roofing granules	titanates and other mixed oxides
printing ink	

Titanium Metal and Titanium-Base Alloys

Aerospace

pressure vessels for
fuels, oxidizers, helium
panels
skirts
structural parts and frames
hydraulic systems
cryogenic vessels
rocket cases
fasteners (bolts, etc.)
wheels
landing gear
jet engine cases and
parts

Marine

deep diving vehicles
hulls
propeller blades
desalination equipment

Chemical Processing

pumps
heat exchangers
valves
retorts & containers
tubing
stirrers

Miscellaneous

alloying agent
superalloys
maraging steels
other
brazes
composites
superconducting alloys
getter
electrodes
electroplating baskets
prosthetic metals

Refractory Compounds

cutting tools
bearings
abrasives
wear resistant parts
heat resistant parts

Miscellaneous

neutron moderator (TiH_2)
electronics (BaTiO_3)

industries continue to grow. The growth is expected to be steady and at about its present rate. The titanium metal industry should see a rapid growth, probably doubling the metal production within ten years. This increase will be due to the need for titanium in the aircraft of tomorrow, the supersonic jets; the continued growth of the chemical industry, which is expected to construct more and more of its processing equipment using titanium; and the new desalination plants which will be increasingly needed in the near future.

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. H. R. Ogden, p. 559 in Rare Metals Handbook, 2nd ed., C.A. Hampel, Ed., Reinhold Publishing Co., New York (1961).
6. R. Hultgren, R.L. Orr, P.D. Anderson, and K.K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley & Sons (1963).
7. J. W. Edwards, H. L. Johnston and W.E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).
8. C. J. Smithells, Metals Reference Book, 3rd ed., Butterworths, Washington (1962).

9. W. S. Lyman, p. 1147 and 1225 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
10. G. T. Meaden, Electrical Resistance of Metals, Plenum Press, New York (1965).
11. T. G. Berlincourt, Phys. Rev. 114, 969 (1959).
12. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
13. Handbook of Chemistry and Physics, 47th ed., p. E-61, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland (1965).
14. R. L. Powell, p. 4-90 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
15. E. M. Savitskii, Influence of Temperature on the Mechanical Properties of Metals and Alloys, Stanford Univ. Press, Stanford, California (1961).
16. J. A. Harvey and D. J. Hughes, p. 8-114 in American Institute of Physics Handbook, 2nd ed., D. E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
17. J. Barksdale, "Titanium" in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
18. F. H. Vorhis, Metal Progress 21, [2], 105 (1967).
19. Anonymous, Metals Week 36, [6], 7 (1965).
20. R. L. Carmichael, Chem. Eng. 73 [24], 109 (1966).
21. R. I. Lane, Jr., J. Metals 17, 834 (1965).
22. D. N. Williams, R. A. Wood, R. H. Ernst and H. R. Ogden, J. Metals 17, 837 (1965).

23. H. Margolin and P. A. Farrar, J. Metals 17, 838 (1965).
24. F. A. Crossley, J. Metals 17, 838 (1965).
25. S. R. Seagle and O. Berteau, J. Metals 17, 839 (1965).
26. A. K. Wolff, L. R. Aronin and S. Abkowitz, J. Metals 17, 840 (1965).
27. R. J. Goode, and R. W. Huber, J. Metals 17, 841 (1965).
28. D. C. Ludwigson, J. Metals 16, 226 (1964).
29. H. L. Martin and A. G. Imgram, J. Metals 17, 735 (1965).
30. V. J. Erdeman, Metal Progress 89, [2], 80 (1966).
31. D. B. Warmuth and H. D. Kessler, Metal Progress 89, [3], 91 (1966).
32. S. Abkowitz, J. Metals 18, 458 (1966), and Metal Progress 89, [4], 62 (1966).
33. T. Vasilos and E. G. Wolff, J. Metals 18, 583 (1966).
34. R. F. Decker and R. R. De Witt, J. Metals 17, 139 (1965).
35. W. F. Simmons and H. J. Wagner, Metal Progress 91, [6], 86 and 87 (1967).
36. G. P. Contractor, J. Metals 18, 939 (1966).
37. H. J. Wagner and J. Prock, Jr., Metal Progress 91, [3], 75 (1967).
38. E. G. Kendall, p. 143 in Ceramics for Advanced Technologies, J. E. Hove, and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
39. J. F. Lynch, C. G. Ruderer and W. H. Duckworth, Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, Ohio (1966).
40. E. W. Goliber, Metal Progress 90, [2], 95 (1966).
41. F. C. Holtz and N. M. Parikh, Metal Progress 90, [2], 117 (1966).

Introduction

Zirconium is the middle member of the IVA Group metals of the periodic table. Like its congeners its electronic ground state configuration consists of a rare gas core (krypton in this case) for its inner core electrons and two electrons each in the $5s$ and $4d$ levels. From the physical properties of the metal, it is quite likely that the $5s$ level is nearly filled (containing less than two electrons) and the $4d$ level has somewhat more than two electrons.

This outer configuration of four electrons accounts for its important chemical property, the formation of many compounds in which zirconium is tetravalent. The two most important compounds are zircon ($ZrSiO_4$) and zirconia (ZrO_2). Technologically these two materials are the most important zirconium products; the metal actually plays a minor, but an important role.

Because of the refractory nature of zirconium and its compounds and its low nuclear cross section, zirconium is of interest in the nuclear energy and space technologies.

Physical Properties¹⁻¹³

The physical properties of zirconium metal are given in Table XXXIX. Zirconium is a hexagonal metal with a high melting point and has a mass and density of intermediate values. Its low vapor pressure makes it an acceptable metal for high temperature applications. The high electrical resistivity and low thermal conductivity are not of any special interest and do not contribute to its present day uses. Its superconducting transition temperature is quite low and not technologically useful.

Property	Value	Ref.
Atomic Number	40	-
Atomic Weight ($^{12}\text{C}=12.00$)	91.22	1
Atomic Volume (cc/mole)	14.02	2
Lattice Parameter (Å) α (hcp) a =	3.2312	3
	5.1477	3
β (bcc at 862°C) c =	3.6090	3
Density (gm/cm ³)	6.506	-
Metallic Radius (CN=12) ^a (Å)	1.602	4
α - β Transition Temperature (°C)	863	5
Heat of Transformation (kcal/g at)	1.04	6
Melting Point (°C)	1850	2
Heat of Fusion (kcal/g at)	(3.74)	2
Vapor Pressure A	31066	7
log P _{torr} = -A/T+B+CT B	10.216	7
C x 10 ⁴	-2.415	7
(temp. range °C)	1675-1780	7
Boiling Point (°C)	4377	2
Heat of Sublimation at 25°C (kcal/g at)	146.0	2
Heat Capacity, C _p (cal/g at-deg)	6.06	2, 6
Electronic Specific Heat Constant (cal/g at-deg ²) x 10 ⁴	6.95	2
Debye Temperature (°K)	250	2
Magnetic Susceptibility (emu/mole) x 10 ⁶	119	8
Electrical Resistivity (μ ohm-cm)	41.4	9, 10
Superconducting Transition Temperature (°K)	0.56	10
Hall Coefficient (volt-cm/amp-Oe) x 10 ¹²	0.18	11
Ionization Potentials (eV)		
I	6.835	12
II	13.13	12
III	24.00	13
IV	33.8	13
Thermal Conductivity (cal-cm/sec-cm ² -deg)	0.0505	9
Thermal Expansion (°C ⁻¹) x 10 ⁶	5.78	2

TABLE XXXIX. (continued)

<u>Property</u>	<u>Value</u>	<u>Ref.</u>
Grüneisen Constant	0.82	2
Compressibility (cm^2/kg) $\times 10^7$	11.77	2
Young's Modulus (kg/cm^2) $\times 10^{-6}$	0.939	2
Shear Modulus (kg/cm^2) $\times 10^{-6}$	0.348	2
Poisson's Ratio	0.34	2
Hardness, Vickers (kg/mm^2)	110	9
Yield Strength (kg/mm^2)	21	9
Ultimate Strength (kg/mm^2)	35	9
Elongation (%)	35	9
Nuclear Cross Section (barns)	0.18	8

^aCN means coordination number.

The mechanical properties of zirconium are reasonably good and can be improved by alloying and heat treatment. The low thermal neutron cross section is of vital interest. This low value and zirconium's resistance to radiation damage account for the major use of zirconium in nuclear reactors as a fuel cladding.

Chemical Properties^{8, 14, 15}

The chemical properties of zirconium metal account for another major share of its present day uses. Zirconium is resistant to attack by many materials, such as urea, most organic acids, most chloride solutions (except cupric and ferric solutions), molten and aqueous alkali hydroxides, and sodium metal. With respect to the common mineral acids it has good corrosion resistance to both hot or cold and concentrated or dilute chromic and nitric acids; to hot or cold dilute hydrochloric, phosphoric and sulfuric acids. Zirconium, however, is readily attacked by hydrofluoric acid and aqua regia. The chemical behavior of zirconium accounts for its use in sulfuric and hydrochloric acid production and in other chemical processing operations, as spinnerettes and crucibles.

Zirconium begins to react with oxygen at 200°C, and the bulk metal ignites at 1000°C giving off a brilliant white light. Zirconium powder ignites at much lower temperatures and care must be taken in handling the powder. This behavior accounts for the use of zirconium in photoflash bulbs. Zirconium reacts slowly with nitrogen at 400°C and rapidly with nitrogen at 800°C, hydrogen at 300°C, CO₂ at 800°C, CO and H₂O at 1000°C,

and the halogen gases at 200°C. This reactive nature accounts for the use of zirconium as a getter material.

The inert nature of zirconium at low temperatures with these common gases accounts for the use of zirconium as a cladding for uranium fuel elements in gas and water cooled reactors. The use of zirconium limits the operation of gas cooled reactors to about 500°C because the zirconium alloy begins to oxidize at this temperature.

Zirconium has had some limited use as a prosthetic metal. Its development is still in the experimental stage. Presently it is being used in animals and to a limited extent in humans.¹⁵

Metallurgy^{8, 14, 16-18}

Zirconium can be both cold-and hot-worked. Rolling and forging operations are usually carried out at 850°C (1000°C for Zircaloy). The surface is cleaned by sandblasting or pickling with HNO₃-HF solution. Extrusion is usually carried out on billets encased with copper or glass between 750 and 1000°C. Drawing operations are carried out at room temperature provided the metal has a thin ZrO₂ coating or still has its copper casing from the extrusion step.

Zirconium is machined using carbide-tipped tools at moderate speeds, heavy cuts and adequate coolant. Care must be taken since zirconium chips will burn if heated during the machining operation. Zirconium can be welded under an inert atmosphere. Pressure welds have been successfully made with aluminum.

The most important zirconium alloys are the Zircaloys, Zircaloy-II and Zircaloy-III. The former is the more extensively used, and it contains

1.5%Sn, 0.12%Fe and 0.10%Cr. Zircaloy-III contains less tin and chromium and more iron (0.25%Sn, 0.25%Fe and 0.05%Cr). The addition of these alloying agents improves the corrosion resistance and increases the yield and ultimate strengths, the elongation and hardness. Zircaloy-II is significantly stronger, more ductile and harder than Zircaloy-III. The major use of zirconium metal is as Zircaloy to clad uranium fuel elements, which are used extensively in the nuclear submarine and commercial reactors. A typical 800 megawatt (electrical) nuclear plant uses about 29.5 metric tons (32.5 short tons) of Zircaloy tubing. About one-fourth to one-third of the Zircaloy tubing must be replaced as the fuel is spent and needs to be reprocessed.

There are no other major zirconium alloys in use today. However, a number of them have interesting properties⁸ and may find some applications in the future. Some of the minor zirconium-base alloys are: 65Zr-35Ti used as a high temperature alloy; 97Zr-3Pd used as a catalyst; 97Zr-3Ag used as a catalyst and brazing alloy; 92.5Zr-7.5W used as a high temperature alloy; and 75Zr-25Pb used as a catalyst.

Zirconium is added to a number of different metals and alloys to impart some improvement in their mechanical and/or corrosion resistant properties. These include magnesium, aluminum, titanium, chromium, iron, cobalt, nickel, copper, niobium, molybdenum, tantalum, tungsten and gold. Zirconium is an important additive to magnesium-base alloys in combination with rare-earth or zinc additions. The magnesium-zirconium-rare earth combinations are used in high temperature applications and the magnesium-zirconium-zinc alloys for room temperature applications. Most of these applications are in aircraft and space vehicles.

Zirconium is added to aluminum-base alloys to increase the strength due to the formation of intermetallic compounds. These alloys are used in structural applications up to 315°C and as a high strength welding filler metal for cryogenic and aircraft parts.

Zirconium additions to steels reduce the oxygen, nitrogen and sulfur contents, help overcome hot shortness in high sulfur steels and improve the mechanical properties of plain carbon steels. These zirconium-containing steels are used as high strength structural steels, tool and speciality steels; in axles, crankshafts and rail and rock drills; and in hydroelectric and pressure vessel construction.

Zirconium is also an important additive to most nickel-base, some cobalt-base and a few iron-nickel-base superalloys.^{17, 18} About 0.03 to 2.3 wt. % Zr is added to help strengthen the alloys by carbide formation. These superalloys have many applications, and since they have been discussed in the NIOBIUM and TITANIUM chapters, there is no need to repeat them here.

Some of the best superconducting alloys are the niobium-zirconium alloys containing between 20 and 40 wt. % zirconium. The superconducting properties of the Nb-25Zr alloy are listed in Table XV of the NIOBIUM chapter. The applications of superconducting materials are also discussed in the same chapter.

Principal Compounds^{3, 14, 19-25}

Zircon, a zirconium silicate of the formula ZrSiO_4 , is the most important compound of zirconium. Zircon is a naturally occurring ore and

usually contains about 2% HfO_2 ; however, some ores may contain as much as 5 and 17% HfO_2 . The use of zircon as the end product accounts for 60 to 75% of the zirconium consumed. It is a high melting (2430°C) refractory compound which is primarily used as foundry sand to make molds and cores. Secondary uses include: abrasives, chemical resistant wares, enamels, electrical insulators, ceramics, glass polishing agents, pigments, gemstones, and porcelains.

The other important compounds are ZrO_2 , ZrC , ZrB_2 , ZrN and ZrCl . The physical properties of the first four are given in Table XL. The dioxide, monocarbide, diboride and mononitride are high melting refractory compounds. The diboride and monocarbide are quite hard materials and the former is a good thermal conductor for a refractory compound. ZrO_2 has good strength which it retains up to about 1200°C ; above this temperature its strength falls quite rapidly.²⁴ This makes ZrO_2 very useful in fiber-reinforced composites, sometimes as the fiber in ZrO_2 -W composites and sometimes as the matrix containing steel, Mo or W as the fibers.²⁶ Zirconia whiskers which have tensile strengths as high as 420 kg/mm^2 , 20 times that of ordinary zirconia, have been grown.²³ However, no practical applications have been developed employing ZrO_2 whiskers due to technological problems in growing useful whiskers. Zirconia is used as a ceramic refractory material; hardener for metals; opacifier for glazes, enamels and x-ray photography; phosphor activator; glass additive; tundish (funnel) nozzle for continuous steel casting; insulator; bearing; in fluorescent lamps, rocket nozzles, nose cones, and electric-lamp filaments to prevent recrystallization; and in the production of the metal

TABLE XL. PHYSICAL PROPERTIES OF SOME REFRACTORY ZIRCONIUM COMPOUNDS AT ROOM TEMPERATURE UNLESS OTHERWISE NOTED^{3, 20-24}

Property		ZrB ₂	ZrC	ZrN	ZrO ₂
Lattice Parameter(s) (Å)	<u>a</u> =	3.169	4.699	4.577	a
	<u>c</u> =	3.529	-	-	a
Crystal System		hex	fcc	fcc	monocl
Structure Type		AlB ₂	NaCl	NaCl	ZrO ₂
Density (gm/cm ³)		6.10	6.56	7.35	5.56
Melting Point (°C)		3060	3400	2980	2765
Heat Capacity, C _p (cal/mole-deg)		12.4	8.8 ^b	10.0	13.9
Electrical Resistivity (μ ohm-cm)		9-16	42-67	-	-
Thermal Conductivity (cal-cm/sec-cm ² -deg)		0.104 ^c	0.049	0.050	0.0045
Thermal Expansion (°C ⁻¹) x 10 ⁶		7.5	9.1	7.0	7.5
Compressibility (cm ² /kg) x 10 ⁷		4.4	3.0	-	5.7
Young's Modulus (kg/cm ²) x 10 ⁻⁶		5.2	4.8	-	2.48
Shear Modulus (kg/cm ²) x 10 ⁻⁶		2.2	1.9	-	0.98
Poisson's Ratio		0.15	0.26	-	0.27
Hardness, Knoop (kg/mm ²)		2300	2600	1500	-
Ultimate Strength (kg/mm ²)		-	20	-	21 ^d
Modulus of Rupture (kg/mm ²)		20	21	-	-

^aThe lattice parameters of ZrO₂ are: a=5.169, b=5.232, c=5.341Å, β=99.25°.

^bAt 230°C.

^cAt 260°C.

^dThe maximum value for the ultimate strength obtained for ZrO₂ whiskers was 420 kg/mm².

as a starting material. The hydrated form is used as a medicine and deodorant. Doped ZrO_2 is used as a high temperature resistor. Zirconia has been produced as a foamed insulator for application up to 1760°C . The foamed ZrO_2 has a low density, fast response time to temperature changes and can be outgassed since the pores are interconnected. Zirconia has several polymorphic transformations and for some high temperature applications it is useless if it undergoes a transformation because of cracking and disintegration. However, ZrO_2 may be stabilized by the addition of other refractory oxides, such as TiO_2 , CaO and Y_2O_3 , making it useful for high temperature applications.

ZrB_2 is quite resistant to oxidation and chemical attack by molten aluminum and cryolite. It has been used to protect tantalum in such environments.²⁷ Combined with 13% MoSi_2 -1%B and with 48% graphite-9%Si it forms good oxidation and thermal shock-resistant ceramics which are useful to 1980°C . A TaN-40% ZrB_2 is one of the best known cutting tool materials developed to date.²⁸

ZrC is used as a cladding and structural material in nuclear reactors and as a component in cutting tools. ZrCl_4 is used as an intermediate step in the production of zirconium metal and as a catalyst. ZrH_2 is used as a moderator in reactors because it has as many hydrogen atoms per cm^3 as does water, and it can be used at temperatures as high as 800°C . Alkaline zirconates are used as catalysts, rust inhibitors, ink stabilizers, water repellants for leather and textiles, and coatings on stainless steels.

Applications

A summary of applications involving zirconium and its compounds is given in Table XII. Fifty percent of the zirconium production is used in foundries as zircon, 25% as zircon and zirconia refractories, 15% as miscellaneous zircon products, 8% as miscellaneous zirconia products and 2% as zirconium metal.

The applications of zirconium products vary quite widely because of the diverse nature of zircon, zirconia and zirconium metal. Space and electronics employ only small amounts of zirconium products. The metal industry utilizes most of the zirconium production primarily as zircon foundry sands for making molds and cores. Zirconium metal has quite important markets in the nuclear and chemical industries.

Concluding Remarks

The future of zirconium is quite glowing. The utilization of zircon and zirconia should continue to grow at a steady pace. Presently, once the zircon has been used as foundry sand, it is discarded. If, however, attempts are made to recover it, there may be an appreciable drop in the demand for raw zircon for a few years before the utilization of raw zircon starts to climb again.

The need for zircaloy should rise very rapidly over the next five years with about a fivefold increase expected, as new commercial power reactors are being built. Large scale breeder reactors will cut into the demand for zirconium once they become technologically feasible. However, the day when breeder reactors become competitive is 10 to 20 years away. By that time new developments should open new markets for zirconium-base alloys.

TABLE XLI. APPLICATIONS OF ZIRCONIUM METAL AND ITS COMPOUNDS AND ALLOYS

Zircon (ZrSiO_4)

foundry sand
 abrasives
 chemical resistant wares
 enamels
 electrical insulators
 glass polishing agents
 gem stones
 pigments
 porcelains
 ceramics

Zirconia (ZrO_2)

refractory ceramics
 fiber-reinforced composites
 hardner
 opacifer
 glass additive
 phosphor activator
 bearings
 insulators
 rocket nozzles
 nose cones
 fluorescent lamps
 medicine
 deodorant
 high temperature resistor

Zirconium Metals and Alloys

cladding for nuclear fuels
 chemical processing equipment
 photoflash bulbs
 alloying agent
 magnesium
 steels
 others
 high temperature alloys
 brazing alloys
 welding flux
 catalyst
 superconducting devices
 getter
 glass-to-metal seals
 explosive primers
 pyrotechnics and fireworks

Other Zirconium Compounds

protective coatings
 cutting tools
 catalysts
 neutron moderator
 claddings and structural components
 in nuclear reactors
 rust inhibitor
 ink stabilizer
 water repellants

References

1. A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962).
2. K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
3. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press, New York (1967).
4. E. Teatum, K. Gschneidner, Jr. and J. Waber, U.S. Atomic Energy Commission Report LA-2345 (1960).
5. T. B. Douglas, J. Res., Natl. Bur. Stand. 67A, 403 (1963).
6. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley & Sons (1963).
7. G. B. Skinner, J. W. Edwards and H. L. Johnston, J. Am. Chem. Soc. 73, 174 (1951).
8. A. W. Schlechten, p. 667 in Rare Metals Handbook, 2nd ed., C.A. Hampel, Ed., Reinhold Publishing Co., New York (1961).
9. J. Hino, p. 1228 in Metals Handbook, Vol. 1, Properties and Selection of Metals, T. Lyman, Ed., American Society for Metals, Novelty, Ohio (1961).
10. G. T. Meaden, Electrical Resistance of Metals, Plenum Press New York (1965).
11. T. G. Berlincourt, Phys. Rev. 114, 969 (1959).
12. G. H. Dieke, p. 7-14 in American Institute of Physics Handbook, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Co., New York (1963).
13. Handbook of Chemistry and Physics, 46th ed., p. E-61, R.C. Weast, Ed., The Chemical Rubber Co., Cleveland, (1965).

14. J.H. McClain, "Zirconium" in Encyclopedia of the Chemical Elements, C. A. Hampel, Ed., Reinhold Publishing Corp., New York (to be published, 1968).
15. D. C. Ludwigson, J. Metals 16, 226 (1964).
16. Anonymous, Chem. & Eng. News 45, [30], 22 (1967).
17. W. F. Simmons and H. J. Wagner, Metal Progress 91, [6] 86 and 87 (1967).
18. C. T. Sims, J. Metals 18, 1119 (1966).
19. D. E. Eilertsen, p. 1105 in Mineral Facts and Problems, 1965 ed., U.S. Bureau of Mines Bull. 630, U.S. Government Printing Office, Washington, D.C. (1965).
20. E. G. Kendall, p. 143 in Ceramics for Advanced Technologies, J. E. Hove and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
21. J. F. Lynch, C. G. Ruderer and W. H. Duckworth, Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, Ohio (1966).
22. J. E. Eorgan and N. D. Fern, J. Metals 19, [9], 6 (1967).
23. J. I. Slaughter, p. 218 in Ceramics for Advanced Technologies, J. E. Hove, and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
24. A. J. Rothman, p. 306 in Ceramics for Advanced Technologies, J. E. Hove, and W. C. Riley, Eds., John Wiley & Sons, Inc., New York (1965).
25. B. C. Weber, An Annotated Bibliography of Research on the Structural and Physical Properties of Zirconia, U.S. Air Force, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio (1964).

26. T. Vasilos and E. G. Wolff, J. Metals 18, 583 (1966).
27. J. E. Eorgan and N.D. Fern, J. Metals 19, [9], 6 (1967).
28. F. C. Holtz and N. M. Parikh, Metal Progress 20, [2], 117 (1966).

The need for continued basic and applied research on beryllium, cesium, hafnium, niobium, rare earths, tantalum, titanium and zirconium and their compounds, cannot be emphasized too strongly since research is the fountainhead for all new technological developments. And it is these developments which lead to the utilization of materials by society.

To get a better idea of the future demands for these "new metals and minerals" we shall examine the present and near future problems facing the world. These problems are concerned with conservation, power production, communication and transportation.

Conservation deals with the better utilization of raw materials, elimination of waste and recovery of spent or used products. This will be a major concern for various metals and minerals, but the biggest problem is water. Not only do we need to convert ocean water into fresh water, but we must prevent polluting present fresh water supplies. Another problem brought about by modern industry is pollution of the air we breathe. Fossil fuel-burning power plants, metallurgical, chemical and other types of manufacturing plants, and automobiles in many densely populated areas are today causing critical pollution of the air. To solve many of these problems engineers and scientists will be turning to the "new metals and minerals" for assistance. From what we have discussed in the previous chapters, it is not too difficult to visualize what some of the uses might be, but other uses not visible in the crystal ball today will appear with time.

Power production will certainly be a major challenge of the future, not only for electrical power production, but also power generated for locomotion, i. e. turbine, jet and rocket engines. There is no doubt that there is a

one-to-one relationship between power consumption and society's development. The need for materials which will withstand very high temperatures will be great since the efficiency of power production increases as the temperature is increased. Since nuclear power will become the main source of electrical power, materials with the required nuclear properties will be in demand.

Communication from one corner of the globe to another is quite rapid and in some places instantaneous, via television and radio-telephone communication satellites, and non-space communication systems. Communication systems of the future will be about as advanced at the turn of the century as we are today compared to Bell's first telephone and Marconi's first "wireless." Computers, lasers, superconducting devices, transistors—will all play a major role in these advanced systems.

Global transportation accomplished in hours and space travel by average persons will pose many interesting and serious challenges to the "new metals and minerals," and in many instances they will meet them with no difficulty. The need for low mass, high strength and high temperature materials will be most pressing and probably never ending.

Clearly there are many opportunities for beryllium, cesium, germanium, hafnium, niobium, rare earths, tantalum, titanium and zirconium in the immediate and also far future. The question is, will the technologies of these materials be sufficiently advanced so that the material will meet this need?

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