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ZIRCONIUM

A STRUCTURAL MATERIAL FOR THERMAL REACTORS

by

Samuel Untermyer

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ZIRCONIUM

A STRUCTURAL MATERIAL FOR THERMAL REACTORS

A B S T R A C T

A number of references on, and some discussion of, the properties of zirconium are given.

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<u>Note:</u> All reference appearing in this report with the exception of number 283 are unclassified.

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ZIRCONIUM

A STRUCTURAL MATERIAL FOR THERMAL REACTORS

Design of thermal reactors has been difficult because of the poor structural properties of those materials having low absorption cross-sections for thermal neutrons. Among all the elements, only the following solids were considered to have low enough absorption for use in thermal piles:

Beryllium (Metal, Oxide, Carbide)
Carbon
Magnesium
Aluminum
Silicon
Tin
Lead
Bismuth

Of these materials, only carbon and beryllium can be used at elevated temperatures for the efficient production of power. Carbon is a very weak material and has proven to be seriously affected by neutron and fission fragment bombardment damage.

Beryllium metal is very brittle, non-homogeneous, expensive and hard to fabricate. Beryllium compounds are quite brittle and are affected by radiation though to a lesser extent than carbon.

It is obvious, therefore, that any material having good strength, corrosion resistance and ductility in addition to low thermal absorption

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would be of the greatest interest in the construction of thermal piles. Recent measurements by Pomerance and Hoover indicated that the thermal absorption cross-section of pure zirconium (no hafnium present) is definitely less than .4 barns. The most probable value at the present time seems to be less than .2 barns. If these measurements are verified, hafnium free zirconium appears to be one of the most attractive known structural materials for thermal energy piles.

The desirability of a structural material for use in a thermal reactor can be estimated from the product of the strength (F) and the absorption mean free path for thermal neutrons (λa). This criterion (strength per unit absorption) breaks down for brittle materials in which the strength cannot be fully utilized for structural purposes due to thermal stresses. Stiffness of plates, which may also be important, is not indicated by this criterion.

	Density (GMS/cc)	F (PSI)	σa (Barns)	λa Cm	λa In	F λa(Lbs/In)	Remarks
Zirconium	6.4	75,000	.4	62	24	1,800,000	Ductile
Steel	7.8	60,000	2.5	4.2	1.7	100,000	Ductile
Cb	8.4	50,000	1.2	15.	5.9	300,000	Ductile
Al	2.7	6,000	.2	80	32	180,000	Very Ductile
Be	1.8	11,000	.01	720	290	3,200,000	Brittle
C	1.6	1,000	.005	2500	1000	1,000,000	Brittle
BeO	2.0	14,000	.01	2000	800	11,000,000	Very Brittle

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Properties of Zirconium (3)

Zirconium metal is strong and ductile (40,000 PSI with 30% elongation, 56,000 PSI with 12% elongation, 115,000 PSI with 2% elongation, 142,000 PSI with 1% elongation) (3). Strength and elongation depend on heat treatment and on cold working. Zirconium is a relatively light metal and has an atomic volume of 14.3 CC/Gr atomic weight. The density of the pure metal is probably about 6.49 GMS/cc but measured values of metal contaminated with small amounts of hafnium average 6.56 (value from Foote Mineral Co., Philadelphia, Pa.) The modulus of elasticity is reported to be 10,700,000 PSI (3). Zirconium in the alpha phase is hexagonal close packed (a = 3.228 c = 5.140). The beta phase of the metal occurs above 861° C (1584° F). The crystal arrangment in the beta phase is body-centered cubic (3.61).

thermal conductivity?

The coefficient of expansion of zirconium metal is $3.5 \times 10^{-6}/^{\circ}C$ (about 1/2 that of steel). The electrical resistance is $.41 \times 10^{-4}$ OHMS/CM^3 at 0° C, rising in the beta phase at 1150° C to 1.26×10^{-4} OHMS/CM^3. Although zirconium probably melts at about 2130° C it cannot ordinarily be considered for use at any such temperatures, as it combines rapidly with most gases at a much lower temperature. At about 800° C zirconium reacts with oxygen in air to form first; a brittle solution of oxide in metal, later white oxide. Zirconium also reacts with hydrogen (at about 800° C), nitrogen, and with chlorine (at a dull red heat).

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Zirconium can easily be spot welded. Heliarc welding is possible if a good purity of helium or argon is used. Zirconium is easily rolled, extruded, formed, forged or swaged.

Corrosion Resistance of Zirconium (Data From Foote Mineral Co.)

Reagent	Inches Penetration Per Yr. Room Temp.	100°C
Sulfuric Acid, conc.	(1)	(2)
Aque Regia	(3)	(4)
50% Ferric Chloride Sol.	(5)	(6)
Bromine Water	(7)	-
Phosphoric Acid, Conc.	0.0004	(8)
10% Sodium Fluoride, Sol.	0.0003	(9)
10% Sulfuric Acid, Sol.	0.0002	0.0007
Hydrochloric Acid, Conc.	0.0001	0.0002
5% Hydrochloric Acid, Sol.	No Attack	No Attack
Nitric Acid, Conc.	0.00001	0.00005
10% Nitric Acid	0.00001	0.00003
Phosphoric Acid, 10%	0.00002	0.00005
10% Citric Acid	No Attack	0.00002
10% Oxalic Acid	No Attack	0.00004
10% Sodium Hydroxide	No Attack	0.00002
10% Potassium Hydroxide	0.00002	No Attack
Strong Ammonia Water	0.00003	Gained Wgt.
Sat. Mercuric Chloride	No Attack	No Attack
1/10 N Iodine Sol.	No Attack	-
Chlorine Water	(10)	-

Remarks

(1) Sample completely dissolved in 24 hours.
(2) Hard protective film of sulfate prevented solution of strip for 2 days.
(3) Completely dissolved in 24 hours.
(4) Completely dissolved within a few hours.
(5) Strip disintegrated into flakes in two days.
(6) Strip completely disintegrated into flakes in one day.
(7) Strip disintegrated in 2 days.
(8) Lost 30% in weight in 2 weeks.
(9) Completely disintegrated in 1 day.
(10) Lost 50% in weight in two weeks.

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<u>Effect of Hot Water</u> (Verbal communication from A. Kaufman)

A.Kaufman (M.I.T.) has tested zirconium in contact with high pressure water for several days at about 300° C. The only noticeable effect was a slight bluish surface coloration.

<u>Occurrence and Hafnium Contamination</u>

The zirconium content of the Earth's crust is estimated to be about 0.028% (47). The most abundant mineral is zircon ($Zr\ Si\ O_4$). Zirconium also occurs as the oxide, baddeleyite. Zirconium ores occur commercially in Ceylon, Australia, Brazil, Colorado, Canada and Norway. The cost of the oxide is about $0.2250 per pound.

As predicted by Bohr, von Hevesy found that zirconium ores contain varying amounts of hafnium. Hafnium is an element which is almost identical to zirconium in all its chemical properties but has a very high neutron absorption cross-section (about 100 barns), a high atomic weight and a high density. Various zirconium ores contain widely varying amounts of hafnium. Scandinavian ores contain as much as 54% as much hafnium as zirconium while the "average" hafnium content of zirconium ores seems to be about 3%. von Hevesy measured hafnium concentration by X-ray emission spectography, comparing the intensity of the hafnium line with the intensity of the line due to known additions of tantalum (47).

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Analysis of Zirconium and Hafnium in Minerals (47 - 78)

Mineral	Location	ZrO_2 (Percent by Wt.)	Hf/Zr (Percent by Wt.)
Baddeleyite	Brazil	97.1	2.0
Zircon. Oxide Favas	Brazil	91.12	2.5
Zircon. Oxide Favas	Brazil	74	1.5
Zircon (White)	Austria	65	7.1
Zircon (Brown)	Norway	60	6.7
Syenite (Gray)	Norway	-	6.2
Zircon (Brown)	Norway	64	5.0
Zircon (Brown)	Langesund	-	3.1
Zircon (Brown)	Larvik	-	11.0
Zircon (Brown)	North Carolina	-	2.3
Zircon (Brown)	Ceylon	-	3.5
Zircon (Grey)	Madagascar	-	5.4
Hyacinth	Espouilly (LePuy)	64	3.2
Hyacinth	Vicenza	-	3.2
Zircon (Monazite)	Brazil	64	2.3
Zircon (Monazite)	India	62	5.0
Cyrtolite	U.S.A.	34	54
Alvite	Kraero	34	54
Naegite	Japan	48	17
Eudialyte	Greenland	14.3	1.5
Eucocyte	Norway	14.5	5.7
Catapleite	Greenland	30.6	.7
Polymignite (78)	Norway	30	-0

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As it has been reported that certain zirconium ores contain less than 1% hafnium, samples of ore from various parts of the world have been obtained from the American Museum of Natural History and these specimens are being analysed to locate an ore containing small amounts of hafnium. Identification of hafnium in zirconium complicated by the fact that the half lives of one of the principal zirconium activities is easily confused with a hafnium activity: (Zr 95, 12% abundant 65 days; .24, .4, .75 Mev gammas is easily confused with Hf 181 46 days; .07, .30, .52 Mev gammas) (283). Even in consideration of electro-magnetic separation or mass spectography care must be taken not to confuse doubly charged Hf ions with Zr ions since the atomic weight of Hf 180 is just twice that of Zr 90.

S. De Benedetti and F. K. McGowan (283) have developed a quantitative method of determing hafnium in zirconium. This method counts each gamma, if and only if, it is preceeded within a given time period by a beta.

Ta^{181} (daughter of Hf^{181}) exhibits a short lived isomeric state of 22 micro-seconds, which is detectable though observation of delayed coincidences from Hf^{181} sources. The number of delayed coincidences is proportional to the number of Hf^{181} atoms present. If the Hf^{181} is produced under known conditions of irradiation this method can be used to measure the hafnium content of a given sample.

Because of the Lanthanide contraction the ionic diameters of Hf and Zr are almost the same (probably with1%). Consequently, chemical purification by ion exchange would seem difficult. B. Ketelle at

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Clinton National Laboratories is attempting to make 10 Mg of pure Zr by ion exchange. Selective precipitation of phosphates out of sulfuric acid can be used to remove much of the Hf from the Zr (63) (68). Wickers at the Bureau of Standards will try to remove the hafnium from about five pounds of zirconium by precipitation.

Such isotope separation methods as thermal or gaseous diffusion should give good separation because of the large mass differences. Hoover has suggested zirconium boro-hydride as a suitable gas to use in a thermal diffusion process. Zirconium boro-hydride has recently been prepared by J. J. Katz at the Argonne National Laboratory.

Preparation of Zirconium Metal

Zirconium is made in small quantities by decomposition of the iodide. (56, 60-66, 100, 109). Foote Mineral Co. of Philadelphia make about 100 pounds per month by this method. Pure zirconium metal on the bottom of an evacuated bulb is transported by means of the tetra-iodide to the surface of an electrically heated filament and there deposited as the metal. The filament must be heated to 1400 - 1500° to decompose the iodide.

At M. I. T., A. Kaufman is using this method to deposit thin zirconium coatings on various materials.

A large scale separation method (82, 103) is being developed by the Northwestern Electro-Development Laboratory of the Bureau of Mines at Albany, Oregon. This method consists of:

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(1) Production of zirconium carbide from zircon.

(2) Chlorination of the carbide.

(3) Purification of the chloride.

(4) Reduction to metal with magnesium.

(5) Elimination of residual salts by vacuum treatment.

(6) Melting of ingots.

This method seems to make possible production of large amounts of pure metal at low cost, probably less than $10.00 per pound. At present, 10 pound ingots of malleable zirconium are being produced. About 60 pounds of metal is produced in the furnace per charge.

Zirconium Alloys (137)

Zirconium alloys with Al, Pb, Bi, Fe, Hf, C, Cu, Mg, Ni, P, Hg, S, Se, Ag, Si, N, Ti, H, W, SN, Zn. The low-zirconium alloys have been studied principally. The following may be of interest: (values given are atomic percent)

Al-Zr (114, 130, 126, 134)

The solid solubility of Zr in Al is .28% atomic at 660° C and only .05% at 500° C. Zr with a small amount of Al is malleable. Alloys of about 3% Zr in Al and Mg have been proposed for corrosion resistance.

Mg-Zr (160, 173, 185, 153, 172, 113, 116)

Since Zr is a powerful neutralizer for iron, these alloys are quite corrosion resistant. Zr also improves the mechanical properties of Mg.

The solubility of Zr in Mg is .8% at 700°C, .3% at 300°C. There are difficulties in introducing the Zr into the Mg.

Si-Zr (187, 146, 184, 119, 168, 124, 146)

This alloy is used to introduce Zr into steel. Commercially it contains about 38% Zr, 1% Al, 5% Fe, remainder Si.

Fe-Zr (114, 181, 182, 183, 188)

$Fe_3 Zr_2$ forms an eutectic with Fe at 16% Zr and 1,300°C. C or S present goes with the Zr. Eutectic compositions might be used as brazing material for pure Zr.

Zr-C

Zr has a strong affinity for carbon and can be surface hardened by carbonization.

The Bureau of Mines found that molten Zr dropped onto a piece of carbon in an inert atmosphere formed a solid bond. The molten metal appeared to penetrate thru the pores of the carbon and traces of metal passed through as much as 1/2 inch of carbon.

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Production of Zirconium Metal

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Production of Zirconium Metal

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Zirconium chloride and hydrogen introduced into an arc.

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Production of Zirconium Metal

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The action of oxygen on the transformation point.

Zirconium Alloys

112. ALEXANDER, P. P. (Zirconium Magnetic Alloy) U. S. Patent 2,184,769 (1939)

Fe-Ni-Co-Zr magnets heat-treated at 345° C.

113. ALLIAGES AUTOPROTEGES. (Aluminum-Magnesium Alloys) British Patent 503,953 (1939)

Corrosion resistant alloys of magnesium, zirconium, and aluminum, with 0.05 to 3 percent zirconium and 10 to 96 percent magnesium.

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Reference book on magnesium alloys.

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Zirconium-iron-silicon alloy.

119. BECKET, F. M. (Process for Producing Zirconium Alloys) U. S. Patent 1,966,037 (1935), British Patent 427,076 (1935)

React ZrC with Fresh ore rich in silica or with silicon.

Zirconium Alloys

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Fusion electrolysis with metal cathode which dissolves through eutectic formation; a chloride-fluoride bath used.

121. BOEHLER, GEBR. (Steel for Objects with High Resistance Against Dynamic Stress) Austrian Patent 154,648 (1938)

Carbon steels for shells and armor plates.

122. BOEKER, J. G. (Hard Alloys) British Patent 499,763 (1939)

Carbides and nitrides with a binder.

123. BOSCH, R. (Electrode for Electric Discharge) Swiss Patent 197,-919 (1938)

Spark-plug metal with 0.01-0.2 percent Zr, 0.01-10 percent Mn, and the remainder Ni.

124. BOZEL-MALETRA, SOC. IND. PROD. CHIM. (Making Zirconium Alloys) French Patent 818,473 (1937)

Calcium carbide added in making zirconium-silicon. Alloys made that are higher in zirconium than in silicon; iron-zirconium alloys also made.

125. BRAID, M. (Dental Alloy) U. S. Patent 2,246,288 (1941)

Alloy of Cr-Mo-Co-W-Zr with 0.25 to 3 percent zirconium.

126. CANAC, L. H. Alloy. U. S. Patents 2,228,513 (1942), 2,310,214 (1943)

Corrosion-resistant alloys: Mg-Al-Zr-Ti and Mg-Zr-Al.

127. COMSTOCK, G. F., and BANNON, R. E. (Heat-Treated Copper Castings Alloyed with Zirconium and Beryllium. Metals and Alloys, Vol. 8 (1937) 106-109 pp; French Patent 836,017 (1939)

Properties of copper-zirconium-beryllium alloys.

Zirconium Alloys

128. COOPER, H. S. Alloy. U. S. Patent 1,221,769 (1916); 1,277,046 (1918); 1,278,304 (1918); Canadian Patent 179,121 (1917)

Nickel-zirconium combinations with other metals as a cutting alloy.

129. DE BOER, J. H., and JONAS, C. B. (Nickel-Alloy Electrode) Canadian Patent 405,674 (1942)

Alloy for electrodes in vacuum tubes containing 0.05 to 3 per-cent zirconium; the remainder nickel; gas-free and with a tensile strength of 24 kg. per sq. mm.

130. FINK, W. L., and WILLEY, L. A. (Equilibrium Relation in Aluminum-Zirconium Alloys of High Purity) Trans. Am. Inst. Min, and Met. Eng., Vol. 133 (1939) 69-80 pp.

Aluminum side of the aluminum-zirconium equilibrium diagram.

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Zirconium carbide made from ZrO_2 and carbon under hydrogen at 1,900°C.

132. GAUTHIER, G. (SOC. ALAIS FROGES ET CAMARGUE). Aliages du magnesium. French Patent 829,316 (1938); Beryllium-Containing Magnesium Alloys U. S. Patent 2,224,151 (1940)

Grain-refining action of zirconium.

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Equilibrium diagram of zirconium-zinc.

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136. COYLER, A. G. Alloy U. S. Patent 2,213,207 (1940)

A centrifugal casting alloy of W-Mo-U-Cr-Zr, containing 0.25 to 7 percent Zr.

137. HANSEN, M. Der Aufbau der Zweistofflegierungen, J. Springer, Berlin (1936)

138. HARRINGTON, R. H. (Double-Aged Copper-Base Alloys) U. S. Patent 2,275,188 (1942)

Double aging of alloys after cold work.

139. HARTMANN, M. L. Zirconium Carbide U. S. Patent 1,576,275 (1926)

Zirconium carbide produced from zircon in an arc furnace under reducing conditions.

140. HENSEL, F. R. Contact. U. S. Patent 2,195,307 (1940)

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141. HENSEL, F. R. (Welding Electrode) U. S. Patent 2,097,816 (1937)

Copper-zirconium alloy with 0.1 to 5 percent Zr; mechanical properties of the aged alloy given.

142. HENSEL, F. R., and LARSEN, E. J. Alloys. U. S. Patents 2,268,940 (1942); 2,161,468 (1939); 2,137,281 (1938) Copper-Base Alloy. British Patent 503,753 (1939)

Copper-zirconium-beryllium welding electrodes with lithium added and with iron group metals added.

143. HENSEL, F. R., LARSEN, E. J., and DOTY, A. S. (Beneficial Effects of Zirconium in Cast Nickel-Silicon Bronzes) Trans. Am. Inst. Min. and Met. Eng., Vol. 143 (1941) 212-215 pp.

Nickel castings degassed with zirconium.

Zirconium Alloys

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Ternary copper-zirconium alloys; Cd-Li-Si-Mg.

145. I.G. FARBEN, A. G. Magnesium Alloys (British Patent 511,137 (1940) SOCETI. GENERALE DU MAGNESIUM (Magnesium Alloys) French Patent 845,843 (1939)

Use of Pb, Ca, Zn, Cd, Ce, Ag, Tl, Th, Cu, and Bi and avoidance of Al, Si, Sn, Mn, Co, Ni, and Sb.

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Zirconium-silicon alloy made by reduction with carbon, aluminum and carbon plus silicon; lime was added.

147. KAMISHIMA, Y. (Alloy Containing Zr and W for Principal Constituents) U. S. Patent 1,926,775 (1933); (Hard Metal Alloy Made by Fusion) French Patent 721,267 (1932)

Zirconium-tungsten alloys with other metal additions.

148. KELLEY, M. Copper-Base Alloy. U. S. Patent 2,169,187 (1939)

Precipitation of hardened copper-zirconium-cobalt alloy for electrical purposes.

149. KOESTER, W., and MULFINGER, W. (The Systems of Cobalt with Boron, Arsenic, Zirconium, Columbium, and Tantalum) Ztschr. Metallkunde, Vol. 30 (1938) 348-350 pp.

Magnetic compound, Co_4Zr, found in the cobalt-zirconium system.

150. KROLL, W. Titanium Alloys, German Patent 718,822 (1942)

Ta-Zr alloy for light reflectors; also Ti, Mo and W.

151. KRUPP, F. Permanent Magnet Alloys. British Patent 524,420 (1941)

Fe-Co-Ni-Zr. magnet alloys with Al or Ti present.

Zirconium Alloys

152. LENTZ, D., and WOEKEL, E. (Solder for Parts of Vacuum Containers, Expecially for Light Bulbs, Discharge Lamps, and Rectifiers) German Patents 665,005 and 665,006 (1938)

Zirconium alloyed with iron or nickel for a welding metal; 16 percent zirconium.

153. MAGNESIUM ELECTRON. Magnesium-Base Alloys. British Patent 533,264 (1941)

Use of molded pieces of $ZrCl_4$ with a density of 2 to 2.3.

154. MCELROY, L. A. Cutting Tool. U. S. Patent 2,235,232 (1940)

Alloy of chromium, cobalt, and tungsten with 0.25 to 3 percent zirconium.

155. MEJERSSON, G. A. Carbide schwerschmelzbarer Metalle. Seltene Metalle (Russ.), Vol. 4, No. 4 (1935) 6-20 pp.; Chem. Zentral., I (1936) 2520 p.

Properties of zirconium carbide.

156. MISCH, L. (Crystal Structure Examination of Some Beryllium Alloys) Metallwirtschaft, Vol. 15 (1936) 163-166 pp.

Structure of ZrB_2 as shown by X-rays.

157. MOISSAN, H., and LENGFELD, F. (A New Carbide of Zirconium) Compt. rend., Vol. 122 (1896) 651-654 pp.

Zirconium carbide made from zircon and carbon in an arc furnace.

158. MOTT, W. R. (Volatilities of Refractory Material) Trans. Am. Electrochem. Soc., Vol. 34, (1919) 275-295 pp.

Volatility of zirconium carbide.

159. NIPPES, E. F. (Copper-Nickel-Zirconium Alloys) Metals and Alloys, Vol. 13 (1941) 294-300 pp.

Copper, nickel, and zirconium alloys.

Zirconium Alloys

160. NOWOTNY, H., WORMNES, E., and MORNHEIM, A. Untersuchunger der Systems, Al-Ca, Mg-Ca, and Mg-Zr, Ztschr. Metallkunde, Vol. 32, (1940) 39-42 pp.

Magnesium-zirconium equilibrium diagram.

161. OBINATA, I., and HAYASI, S. (Researches on the Complex Alloys of Magnesium Based on the Magnesium-Cadmium System) Tetsu- to - Hagane, Vol. 24 (1938) 34-42 pp.; Chem. Abs. Vol. 33 (1939) 4943 p.

Corrosion resistance of cadmium-magnesium-zirconium and magnesium-zirconium alloys.

162. PHILIPS, N. V. Gloeilampenfabrieken. Copper Alloys. French Patent 836,017 (1939); Belgian Patent 427,304, (1938); British Patent 508,330 (1940); German Patent 691,138 (1940)

Copper-zirconium electrical conductors with 0.02 to 5 percent zirconium.

163. PHILIPS, N. V., Gloeilampenfabrieken. Resistance Wires. British Patent 330,280 (1930)

Alloy of 1.5 to 2 percent zirconium with aluminum to be used for cathods vacuum tubes.

164. PILLING, N. B. and TALBOT, A. M. A.S.M. Symposium of Age Hardening (1939) 231-257 pp.

Ni Zr age hardening.

165. POGODIN, S. A., and OTHERS (Constitution and Properties of Copper Zirconium Alloys) Compt. rend. acad. sci. U.S.S.R., Vol. 27 (1940) 670-672 pp.; Chem. Abs. Vol 35 (1941) 1745 p.

Equilibrium diagram of copper-zirconium.

166. POGODIN, S. A. and SCHUMOVA, I. S. (Alloys of Copper with Zirconium) Ann. secteur anal. phys.-chim., Inst. chim. gen. (U.S.S.R.), Vol. 13 (1940) 225-232 pp.; C em. Abs., Vol. 37 (1943) 4350 p.

Equilibrium diagram of copper-zirconium.

166. PRESCOTT, C. H., JR. (The Equilibrium Between ZrO_2 and C and Their Reaction Products at Incandescent Temperatures) Jour. Am. Chem. Soc., Vol. 48 (1926) 2536-2550 pp.

Dissociation pressure of ZrO_2-C established as 1 atmosphere at 1,930°K; crystal structure discussed.

167. RAFFLES, F. (Permanent Magnet) Belgian Patent 428,870 (1938)

Magnetic alloys; 10 percent Zr, 5 to 40 percent Ni, 5 to 20 percent Al.

168. RENAUX, L. Contribution a l'étude de la zircone. Diss. Univ. Paris-Vincennes (Pharmacy) (1910)

Calcium carbide as a reducing agent.

169. ROHN, W. (Valve Made of Co-Ni-Fe-Cr Alloy) U. S. Patent 2,246,078 (1941)

Co-Ni-Fe-Cr alloy plus Zr or Ti for exhaust valves in combustion engines.

170. RUTHARDT, K. (Platinum Alloys) German Patent 670,897 (1939)

Platinum alloys with 0.05 to 5 percent zirconium that are corrosion resistant, stick well to porcelain, and can be used for electrical contacts.

171. SARBEY, M. D. Flashlamp. U. S. Patent 2,272,779 (1941)

Flashlamp alloy of aluminum, magnesium and zirconium containing 0.5 to 15 percent zirconium.

172. SAUERWALD, F. (heat Treatment of Magnesium Alloys Containing Zirconium) U. S. Patent 2,212,130 (1940)

Heat treatment of a magnesium-zirconium alloy at 450°C.

173. SAUERWALD, F. Magnesium-Zirconium Alloys U. S. Patent 2,286,311, (1942) Process for the Production of Zirconium-Magnesium Alloys U. S. Patent 2,228,781 (1941)

Magnesium-zirconium alloys with 2.1 to 5 percent zirconium and a method of introducing zirconium powder into magnesium by stirring.

Zirconium Alloys

174. SCHAEFER, C., Tool Alloys. U. S. Patents 2,307,960 (1943) and 2,301,082 (1942)

Alloys of Fe-Cb-Ta-Zr and W-Ta-Cb-Ti-Zr with 10 to 40 percent zirconium used for cutting tools.

175. SERI. SOCIETA ANNON. PROC. PRIV. IND. ALLOYS. British Patent 517,083 (1940)

Alloys of copper, zirconium, and beryllium.

176. THUM, E. E. (The Book of Stainless Steel) Am. Soc. Metals (1935) 261, 441 pp.

Free-cutting sulfur steels and zirconium as a carbon neutralizer and an alloying element.

177. TROOST, L. Sur la préparation du zirconium et du thorium. Compt. rend., Vol. 116 (1893) 1227-1230 pp.

Zirconium carbide made in the arc furnace from zircon plus carbon.

178. VAN ARKEL, A. E. Reine Metalle. J. Springer, Berlin (1939)

179. VAN ARKEL, A. E., and DE BOER, J. H., Darstellung von reinem Titanium, Zirkonium, Hafnium and Thoriummetall, Ztschr. anorg. Chem., Vol. 148 (1925) 345-350 pp.

$ZrCl_4$ reacted with carbon and hydrogen.

180. VAN LIEMPT, J. A. (The Light of Combustion of Some Metals and Alloys) Rec. trav. chim. Pays-Bas, Vol. 58 (1939) 423-431 pp.

Flashlight powders of magnesium aluminum and zirconium.

181. VOGEL, R., and HARTUNG, A. (Ternary Diagram Fe-Zr-S) Arch. Eisen., Vol. 15 (1942) 413-418 pp.

Ternary diagram of Fe-Zr-S, showing the melting point of ZrS_2 as 1550°C.

Zirconium Alloys

182. VOGEL, R., and LOEHBERG, K. Das System $Fe-Fe_3C-ZrC-Fe_3Zr_2$. Arch. Eisen., Vol. 7 (1934) 473-478 pp.

Ternary diagram, Fe-Zr-C.

183. VOGEL, R., and TONN. W. Das Zustandsschaubild Eisen-Zirkon. Arch. Eisen., Vol. 5 (1931-32) 387-389 pp.

Equilibrium diagram of iron-zirconium.

184. VOLKERT, G. Experimente über die Metallurgie der Zirkonium Legierungen. Metall. Erz, Vol. 40 (1943) 246-252 pp.

Zirconium-silicon alloys produced by reduction with carbon; also with CaC_2.

185. VON ZEPPELIN, H. (Manufacture of Alloys) U. S. Patent 2,235,508, (1941)

Zirconium dispersed in a flux.

186. ______ Manufacture of Alloys. U. S. Patent 2,250,687 (1941)

$ZrCl_4$ with magnesium in a copper container reacted in a salt bath.

187. WAINSTEIN, G. M. Versuch zur Gewinnung von Kohlenstoffhaltigem und kohlenstoff-freiem Ferrosilicozirkonium. Metallurg. (Russ.), Vol. 13, No. 9 (1938) 17-23 pp. Chem. Zentralb., Vol. 110, Pt. I (1939) 1640 p.

Zirconium-silicon alloy produced by carbon and silicon reduction.

188. WALLBAUM, H. J. (The Systems of Iron-Group Metals with Titanium, Zirconium, Columbium, Tantalum) Arch. Eisen., Vol. 14 (1941) 521-526 pp.

Equilibrium diagram of iron-zirconium with manganese, cobalt, and nickel.

Zirconium Alloys

189. WARTENBURG, Von Hv., BROY, J., REINICKE, R. (The Reduction of Difficult Reducible Metal Oxides with Hydrogen) Ztschr. Elekrochem., Vol. 29 (1923) 214-217 pp.

ZrO_2 reduced with hydrogen under pressure in presence of tungsten.

190. WEDEKIND, E. (Zirconium Carbide from Natural Zirconium Oxide) Chem. Ztg., Vol. 31 (1907) 654-655 pp. über kolloides Zirkon silizid. Ztschr. Chem. Ind. Koll., Vol. 7 (1910) 249-251 pp.

Zirconium carbide made in the arc, and the combination of ZrO_2 and silicon to give ZrOSi.

191. ______ Zur Kenntnis der Darstellung von Zirkonerde. Ztschr. anorg. Chem., Vol. 33 (1903) 81-86 pp.

ZrO_2 and carbon treated in the arc furnace.

192. WEISS, L. Untersuchungen über natürliches Zirkondioxyd. Ztschr. anorg. Chem., Vol. 65 (1910) 178-227 pp.

Zirconium carbide produced from zircon.

193. WILKINS, R. A., and BUNN, E. S. (Copper and Copper-Base Alloys) McGraw Hill Book Co., New York (1943) 291-293 pp. DELMONTE, J. (Beryllium and Its Alloys) Metals and Alloys, Vol. 7 (1936) 211-215 pp.

Master alloys containing zirconium.

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