

= Zirconium =

Zirconium is a chemical element with symbol Zr and atomic number 40 . The name of zirconium is taken from the name of the mineral zircon , the most important source of zirconium . The word zircon comes from the Persian word *zargun* , meaning " gold @-@ colored " . It is a lustrous , grey @-@ white , strong transition metal that resembles hafnium and , to a lesser extent , titanium . Zirconium is mainly used as a refractory and opacifier , although small amounts are used as an alloying agent for its strong resistance to corrosion . Zirconium forms a variety of inorganic and organometallic compounds such as zirconium dioxide and zirconocene dichloride , respectively . Five isotopes occur naturally , three of which are stable . Zirconium compounds have no known biological role .

= = Characteristics = =

Zirconium is a lustrous , greyish @-@ white , soft , ductile and malleable metal that is solid at room temperature , though it is hard and brittle at lesser purities . In powder form , zirconium is highly flammable , but the solid form is much less prone to ignition . Zirconium is highly resistant to corrosion by alkalis , acids , salt water and other agents . However , it will dissolve in hydrochloric and sulfuric acid , especially when fluorine is present . Alloys with zinc are magnetic at less than 35 K.

The melting point of zirconium is 1855°C (3371°F) , and the boiling point is 4371°C (7900°F) . Zirconium has an electronegativity of 1 @.@ 33 on the Pauling scale . Of the elements within d @-@ block , zirconium has the fourth lowest electronegativity after yttrium , lutetium and hafnium .

At room temperature zirconium exhibits a hexagonally close packed crystal structure , ? @-@ Zr , which changes to ? @-@ Zr a body @-@ centered cubic crystal structure at 863°C . Zirconium exists in the ? @-@ phase until the melting point .

= = = Isotopes = = =

Naturally occurring zirconium is composed of five isotopes . ^{90}Zr , ^{91}Zr , ^{92}Zr and ^{94}Zr are stable , although ^{94}Zr is predicted to undergo double beta decay (not observed experimentally) with a half @-@ life of more than $1 @.@ 10 \times 10^{17}$ years . ^{96}Zr has a half @-@ life of $2 @.@ 4 \times 10^{19}$ years , and is the longest @-@ lived radioisotope of zirconium . Of these natural isotopes , ^{90}Zr is the most common , making up 51 @.@ 45 % of all zirconium . ^{96}Zr is the least common , comprising only 2 @.@ 80 % of zirconium .

Twenty @-@ eight artificial isotopes of zirconium have been synthesized , ranging in atomic mass from 78 to 110 . ^{93}Zr is the longest @-@ lived artificial isotope , with a half @-@ life of $1 @.@ 53 \times 10^6$ years . ^{110}Zr , the heaviest isotope of zirconium , is the most radioactive , with an estimated half @-@ life of 30 milliseconds . Radioactive isotopes at or above mass number 93 decay by ? ? , whereas those at or below 89 decay by ? + . The only exception is ^{88}Zr , which decays by ? .

Five isotopes of zirconium also exist as metastable isomers : $^{83\text{m}}\text{Zr}$, $^{85\text{m}}\text{Zr}$, $^{89\text{m}}\text{Zr}$, $^{90\text{m1}}\text{Zr}$, $^{90\text{m2}}\text{Zr}$ and $^{91\text{m}}\text{Zr}$. Of these , $^{90\text{m2}}\text{Zr}$ has the shortest half @-@ life at 131 nanoseconds . $^{89\text{m}}\text{Zr}$ is the longest lived with a half @-@ life of 4 @.@ 161 minutes .

= = = Occurrence = = =

Zirconium has a concentration of about 130 mg / kg within the Earth 's crust and about 0 @.@ 026 ?g / L in sea water . It is not found in nature as a native metal , reflecting its intrinsic instability with respect to water . The principal commercial source of zirconium is zircon (ZrSiO_4) , a silicate mineral , which is found primarily in Australia , Brazil , India , Russia , South Africa and the United States , as well as in smaller deposits around the world . As of 2013 , two @-@ thirds of zircon mining occurs in Australia and South Africa . Zircon resources exceed 60 million tonnes worldwide and annual worldwide zirconium production is approximately 900 @, @ 000 tonnes . Zirconium also

occurs in more than 140 other minerals , including the commercially useful ores baddeleyite and kosnarite .

Zr is relatively abundant in S @-@ type stars , and it has been detected in the sun and in meteorites . Lunar rock samples brought back from several Apollo missions to the moon have a high zirconium oxide content relative to terrestrial rocks .

= = Production = =

Zirconium is a by @-@ product of the mining and processing of the titanium minerals ilmenite and rutile , as well as tin mining . From 2003 to 2007 , while prices for the mineral zircon steadily increased from \$ 360 to \$ 840 per tonne , the price for unwrought zirconium metal decreased from \$ 39 @,@ 900 to \$ 22 @,@ 700 per ton . Zirconium metal is much higher priced than zircon because the reduction processes are expensive .

Collected from coastal waters , zircon @-@ bearing sand is purified by spiral concentrators to remove lighter materials , which are then returned to the water because they are natural components of beach sand . Using magnetic separation , the titanium ores ilmenite and rutile are removed .

Most zircon is used directly in commercial applications , but a small percentage is converted to the metal . Most Zr metal is produced by the reduction of the zirconium (IV) chloride with magnesium metal in the Kroll process . Commercial @-@ quality zirconium for most uses still has a content of 1 % to 3 % hafnium . This contaminant is important only in nuclear applications . The resulting metal is sintered until sufficiently ductile for metalworking .

= = Separation of zirconium and hafnium = =

Commercial zirconium metal typically contains 1 ? 2 @.@ 5 % of hafnium , which is not problematic because the chemical properties of hafnium and zirconium are very similar . Their neutron @-@ absorbing properties differ strongly , however , necessitating the separation of hafnium from zirconium for nuclear reactors . Several separation schemes are in use . The liquid @-@ liquid extraction of the thiocyanate @-@ oxide derivatives exploits the fact that the hafnium derivative is slightly more soluble in methyl isobutyl ketone than in water . This method is used mainly in United States .

Zr and Hf can also be separated by fractional crystallization of potassium hexafluorozirconate (K_2ZrF_6) , which is less soluble in water than the analogous hafnium derivative .

Fractional distillation of the tetrachlorides , also called extractive distillation , is used primarily in Europe .

The product of a quadruple VAM (vacuum arc melting) process , combined with hot extruding and different rolling applications is cured using high @-@ pressure , high @-@ temperature gas autoclaving . This produces reactor @-@ grade zirconium that is about 10 times more expensive than the hafnium @-@ contaminated commercial grade .

Hafnium must be removed from zirconium for nuclear applications because hafnium has a neutron absorption cross @-@ section 600 times greater than zirconium . The separated hafnium can be used for reactor control rods .

= = Compounds = =

Like other transition metals , zirconium forms a wide range of inorganic compounds and coordination complexes . In general , these compounds are colourless diamagnetic solids wherein Zr has the oxidation state IV + . Far fewer Zr (III) compounds are known , and Zr (II) is very rare .

= = Oxides , nitrides and carbides = =

The most common oxide is zirconium dioxide , ZrO_2 , also known as zirconia . This colourless solid

has exceptional fracture toughness and chemical resistance, especially in its cubic form. These properties make zirconia useful as a thermal barrier coating, although it is also a common diamond substitute. Zirconium monoxide, ZrO , is also known and S @-@ type stars are recognised by detection of its emission lines in the visual spectrum.

Zirconium tungstate has the unusual property of shrinking in all dimensions when heated, whereas most other substances expand when heated. Zirconyl chloride is a rare water @-@ soluble zirconium complex with the relatively complicated formula $[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{16}]\text{Cl}_8$.

Zirconium carbide and zirconium nitride are refractory solids. The carbide is used for drilling tools and cutting edges. Zirconium hydride phases are also known.

== Halides and pseudohalides ==

All four common halides are known, ZrF_4 , ZrCl_4 , ZrBr_4 , ZrI_4 . All have polymeric structures and are far less volatile than the corresponding monomeric titanium tetrahalides. All tend to hydrolyse to give the so @-@ called oxyhalides and dioxides.

The corresponding tetraalkoxides are also known. Unlike the halides, the alkoxides dissolve in nonpolar solvents. Dihydrogen hexafluorozirconate is used in the metal finishing industry as an etching agent to promote paint adhesion.

== Organic derivatives ==

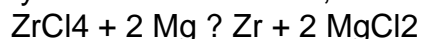
Organozirconium chemistry is the study of compounds containing a carbon @-@ zirconium bond. The first such compound was zirconocene dibromide ($(\text{C}_5\text{H}_5)_2\text{ZrBr}_2$), reported in 1952 by Birmingham and Wilkinson. Schwartz's reagent, prepared in 1970 by P. C. Wailes and H. Weigold, is a metallocene used in organic synthesis for transformations of alkenes and alkynes.

Zirconium is also a component of some Ziegler @-@ Natta catalysts, used to produce polypropylene. This application exploits the ability of zirconium to reversibly form bonds to carbon. Most complexes of $\text{Zr}(\text{II})$ are derivatives of zirconocene, one example being $(\text{C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$.

== History ==

The zirconium @-@ containing mineral zircon and related minerals (jargoon, hyacinth, jacinth, ligure) were mentioned in biblical writings. The mineral was not known to contain a new element until 1789, when Klaproth analyzed a jargoon from the island of Ceylon (now Sri Lanka). He named the new element Zirkonerde (zirconia). Humphry Davy attempted to isolate this new element in 1808 through electrolysis, but failed. Zirconium metal was first obtained in an impure form in 1824 by Berzelius by heating a mixture of potassium and potassium zirconium fluoride in an iron tube.

The crystal bar process (also known as the Iodide Process), discovered by Anton Eduard van Arkel and Jan Hendrik de Boer in 1925, was the first industrial process for the commercial production of metallic zirconium. It involves the formation and subsequent thermal decomposition of zirconium tetraiodide, and was superseded in 1945 by the much cheaper Kroll process developed by William Justin Kroll, in which zirconium tetrachloride is reduced by magnesium:



== Applications ==

Approximately 900 @, @ 000 tonnes of Zr ores were mined in 1995, mostly as zircon.

== Compounds ==

Most zircon is used directly in high temperature applications. This material is refractory, hard, and

resistant to chemical attack . Because of these properties , zircon finds many applications , few of which are highly publicized . Its main use is as an opacifier , conferring a white , opaque appearance to ceramic materials . Because of its chemical resistance , zircon is also used in aggressive environments , such as moulds for molten metals .

Zirconium dioxide (ZrO_2) is used in laboratory crucibles , in metallurgical furnaces , and as a refractory material . Because it is mechanically strong and flexible , it can be sintered into ceramic knives and other blades . Zircon (ZrSiO_4) and the cubic zirconia (ZrO_2) are cut into gemstones for use in jewelry .

Zirconia is a component in some abrasives , such as grinding wheels and sandpaper .

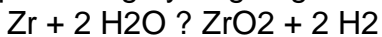
== Metal ==

A small fraction of the zircon is converted to the metal , which finds various niche applications . Because of zirconium 's excellent resistance to corrosion , it is often used as an alloying agent in materials that are exposed to aggressive environments , such as surgical appliances , light filaments , and watch cases . The high reactivity of zirconium with oxygen at high temperatures is exploited in some specialised applications such as explosive primers and as getters in vacuum tubes . The same property is (probably) the purpose of including Zr nano @-@ particles as pyrophoric material in explosive weapons such as the BLU @-@ 97 / B Combined Effects Bomb .

=== Nuclear applications ===

Cladding for nuclear reactor fuels consumes about 1 % of the zirconium supply , mainly in the form of zircalloys . The desired properties of these alloys are a low neutron @-@ capture cross @-@ section and resistance to corrosion under normal service conditions . Efficient methods for removing the hafnium impurities were developed to serve this purpose .

One disadvantage of zirconium alloys is that zirconium reacts with water at high temperatures , producing hydrogen gas and accelerated degradation of the fuel rod cladding :



This exothermic reaction is very slow below 100°C , but at temperature above 900°C the reaction is rapid . Most metals undergo similar reactions . The redox reaction is relevant to the instability of fuel assemblies at high temperatures . This reaction was responsible for a small hydrogen explosion first observed inside the reactor building of Three Mile Island nuclear power plant in 1979 , but at that time , the containment building was not damaged . The same reaction occurred in the reactors 1 , 2 and 3 of the Fukushima I Nuclear Power Plant (Japan) after the reactor cooling was interrupted by the earthquake and tsunami disaster of March 11 , 2011 leading to the Fukushima I nuclear accidents . After venting the hydrogen in the maintenance hall of those three reactors , the mixture of hydrogen with atmospheric oxygen exploded , severely damaging the installations and at least one of the containment buildings . To avoid explosion , the direct venting of hydrogen to the open atmosphere would have been a preferred design option . Now , to prevent the risk of explosion in many pressurized water reactor (PWR) containment buildings , a catalyst @-@ based recombinator is installed that converts hydrogen and oxygen into water at room temperature before the hazard arises .

=== Space and aeronautic industries ===

Materials fabricated from zirconium metal and ZrO_2 are used in space vehicles where resistance to heat is needed .

High temperature parts such as combustors , blades , and vanes in jet engines and stationary gas turbines are increasingly being protected by thin ceramic layers , usually composed of a mixture of zirconia and yttria .

=== Positron emission tomography cameras ===

The isotope ^{89}Zr has been applied to the tracking and quantification of molecular antibodies with positron emission tomography (PET) cameras (a method called " immuno @-@ PET ") . Immuno @-@ PET has reached a maturity of technical development and is now entering the phase of wide @-@ scale clinical applications . Until recently , radiolabeling with ^{89}Zr was a complicated procedure requiring multiple steps . In 2001 ? 2003 an improved multistep procedure was developed using a succinylated derivative of desferrioxamine B (N @-@ sucDf) as a bifunctional chelate , and a better way of binding ^{89}Zr to mAbs was reported in 2009 . The new method is fast , consists of only two steps , and uses two widely available ingredients : ^{89}Zr and the appropriate chelate .

= = = Biomedical applications = = =

Zirconium @-@ bearing compounds are used in many biomedical applications , including dental implants , knee and hip replacements , middle @-@ ear ossicular chain reconstruction , and other restorative and prosthetic devices .

Zirconium binds urea , a property that has been utilized extensively to the benefit of patients with chronic kidney disease . For example , zirconium is a primary component of the sorbent column dependent dialysate regeneration and recirculation system known as the REDY system , which was first introduced in 1973 . More than 2 @,@ 000 @,@ 000 dialysis treatments have been performed using the sorbent column in the REDY system . Although the REDY system was superseded in the 1990s by less expensive alternatives , new sorbent @-@ based dialysis systems are being evaluated and approved by the U.S. Food and Drug Administration (FDA) . Renal Solutions developed the DIALISORB technology , a portable , low water dialysis system . Also , developmental versions of a Wearable Artificial Kidney have incorporated sorbent @-@ based technologies .

Zirconium cyclosilicate is under investigation for oral therapy in the treatment of hyperkalemia . It is a highly selective oral sorbent designed specifically to trap potassium ions in preference to other ions throughout the gastrointestinal tract .

= = = Defunct applications = = =

Zirconium carbonate ($3\text{ZrO}_2 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$) was used in lotions to treat poison ivy but was discontinued because it occasionally caused skin reactions .

= = Safety = =

Although zirconium has no known biological role , the human body contains , on average , 250 milligrams of zirconium , and daily intake is approximately 4 @.@ 15 milligrams (3 @.@ 5 milligrams from food and 0 @.@ 65 milligrams from water) , depending on dietary habits . Zirconium is widely distributed in nature and is found in all biological systems , for example : 2 @.@ 86 ?g / g in whole wheat , 3 @.@ 09 ?g / g in brown rice , 0 @.@ 55 ?g / g in spinach , 1 @.@ 23 ?g / g in eggs , and 0 @.@ 86 ?g / g in ground beef . Further , zirconium is commonly used in commercial products (e.g. deodorant sticks , aerosol antiperspirants) and also in water purification (e.g. control of phosphorus pollution , bacteria- and pyrogen @-@ contaminated water) .

Short @-@ term exposure to zirconium powder can cause irritation , but only contact with the eyes requires medical attention . Persistent exposure to zirconium tetrachloride results in increased mortality in rats and guinea pigs and a decrease of blood hemoglobin and red blood cells in dogs . However , in a study of 20 rats given a standard diet containing ~ 4 % zirconium oxide , there were no adverse effects on growth rate , blood and urine parameters , or mortality . The U.S. Occupational Safety and Health Administration (OSHA) legal limit (permissible exposure limit) for zirconium exposure is 5 mg / m³ over an 8 @-@ hour workday . The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 5 mg / m³ over an 8 @-@ hour workday and a short term limit of 10 mg / m³ . At levels of 25 mg / m³ , zirconium is

immediately dangerous to life and health . However , zirconium is not considered an industrial health hazard . Furthermore , reports of zirconium @-@ related adverse reactions are rare and , in general , rigorous cause @-@ and @-@ effect relationships have not been established . No evidence has been validated that zirconium is carcinogenic or genotoxic .

Among the numerous radioactive isotopes of zirconium , ^{93}Zr is among the most common . It is released as a product of ^{235}U , mainly in nuclear plants and during nuclear weapons tests in the 1950s and 1960s . It has a very long half @-@ life (1 @.@ 53 million years) , its decay emits only low energy radiations , and it is not considered as highly hazardous .