Hafnium

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Overview

For many years Hafnium was a metal element that eluded chemists. By 1920, all but a handful of the elements had been discovered and based upon three empty spaces in Henry Moseley's version of the periodic table; chemists knew that elements 43, 61, and 72 had still yet to be identified. They understood that element 72 would be quite different from the rare earth elements that precede it in the periodic table, and quite similar to zirconium, the element above it in the table.

In June 1923, element number 72 was finally discovered by Dutch physicist Dirk Coster (1889-1950) and Hungarian chemist George Charles de Hevesy (1889-1966), whilst they were examining a zirconium ore from Norway, using the methods of X-ray analysis developed by Moseley. They observed a set of spectral lines that they had never seen before in the mineral and attributed the lines to the missing element. They named the element *hafnium* after the ancient Latin name for the Danish capital city Copenhagen – “Hafnia”. Today, The Faculty of Science of the University of Copenhagen uses in its seal a stylized image of hafnium.

Hevesy later analyzed many other zirconium minerals and found hafnium in all of them. The element is actually more abundant than gold, silver, and some other better known elements. However, hafnium is so similar to zirconium that the two metals are very difficult to physically separate.

Hafnium was separated from zirconium through repeated crystallization of soluble ammonium or potassium fluorides by Jantzen and von Hevesey. Metallic hafnium was first prepared by Anton Eduard van Arkel and Jan Hendrik de Boer by passing hafnium tetra iodide vapour over a heated tungsten filament. This process for differential purification of Zr and Hf is still in use today.

Tangible quantities of Hafnium oxide and metal powder were not produced until the 1940’s. Commercial production of Hafnium arose from the need to produce Hafnium –free Zirconium metal for use in nuclear reactors.

In 1950, zirconium was selected for use in the prototype land-based Nautilus reactor for future use in submarines and in 1951 Hafnium was selected as the material to be used in the reactor’s control rods.

Today, Hafnium's main uses are in nuclear fuel rods and as an alloy addition in superalloys, although demand in new electronics applications is increasing.

In 2007, two major computer chip manufacturers announced that Hafnium would replace Silicon in their next generation products, with Intel citing it as the industry's biggest advancement since silicon-based transistors in the 1960s. This new application has incited new interest in the metal and will no doubt alter the equilibrium of the supply/demand situation and its associated commercial value.

Physical & chemical properties

Hafnium is chemically similar to zirconium. Both transition metals have similar electronic configurations, and their ionic radii and atomic radii are nearly identical because of the influence of the lanthanide contraction. The density of zirconium however, is about half that of hafnium.

Hafnium is a lustrous, ductile silvery metal. Its atomic symbol is Hf and its atomic number is 72. It has a high melting point of 4,051.4 ± 68°F (2,233 ± 20°C), its boiling point, 8,317.4°F (4,603°C), and it has an atomic weight of 178.49.

Reports of its physical properties sometimes differ, probably due to the presence of zirconium as an impurity in the sample.

The physical property of greatest interest for hafnium is its response to neutrons. A neutron is a very small particle found in the nucleus (centre) of an atom. Neutrons are used to make nuclear fission reactions occur. Nuclear fission reactions take place when a neutron strikes a large atom, such as an atom of uranium. The neutron makes the atom break apart. In the process, a large amount of energy is released, which can in turn be converted to electricity.

In order to make electricity from nuclear fission, the fission reaction must be carefully controlled. To achieve this, the number of neutrons must also be regulated. Hafnium, similar to Cadmium in its ability to absorb neutrons very easily, is used in rods that control how fast a fission reaction takes place.

This property is one of the few ways in which hafnium differs from zirconium. Whilst hafnium is very good at absorbing neutrons, zirconium hardly absorbs neutrons at all, allowing them to pass right through it.

Hafnium has six naturally occurring isotopes: hafnium-174, hafnium-176, hafnium-177, hafnium-178, hafnium-179, and hafnium-180. The first of these is radioactive. It has a half life of an astounding two quadrillion years. (That's 2 followed by 15 zeroes!).

Like zirconium, hafnium is not very reactive. It does not combine easily with oxygen in the air or react with water or cold acids. It may be more active with hot acids, however.

At 700ºC hafnium rapidly absorbs hydrogen to form the composition HfH1.86. Hafnium is resistant to concentrated alkalis, but at elevated temperatures reacts with oxygen, nitrogen, carbon, boron, sulfur, and silicon.

Mode of occurrence in nature

Hafnium is the 45th most abundant element in the Earth's crust with an average abundance of 3 ppm (parts per million).

It is present in ocean water in very small amounts, specifically 0.008 ppb (parts per billion) by weight.

Zirconium and hafnium occur most commonly in nature as the mineral zircon and less commonly as baddeleyite. Zircon is used both for its properties as a mineral, and as an ore of zirconium and hafnium. Zircon is a byproduct from the mining and processing of heavy mineral sands for rutile and ilmenite. Hafnium is normally present at 1.5-3.0% by weight in zircon sand and baddeleyite.

Hafnium vapour has been identified in the Sun's atmosphere.

Mining & extraction techniques

Hafnium is retrieved as a by-product from zirconium ore minerals. In a typical zirconium ore, there is a Zr:Hf ratio of about 50:1. The mineral *zircon* is the primary ore source of hafnium. Most zircon (and, therefore, hafnium) is mined from titanium-rich, heavy-mineral sand deposits.

Hafnium ores are rare, but two are known: hafnon and alvite. World reserves are not recorded, but can be estimated from those of zirconium.

Hafnium extraction is always associated with its difficult separation from zirconium, as it is a contaminant of all zirconium minerals. Hafnium was originally separated from zirconium by repeated re-crystallization of the double ammonium or potassium fluorides by von Hevesey and Jantzen. Today, ion-exchange and solvent-extraction techniques have supplanted fractional crystallization and distillation as the preferred methods of separating hafnium from zirconium. Chemists know that compounds of hafnium dissolve more easily in some solvents than do compounds of zirconium, but the separation process is not easy and exploits the differential solubilities of the metal thiocyanates in methyl isobutyl ketone. Of all the elements, zirconium and hafnium are two of the most difficult to separate.

Metallic hafnium was first prepared by van Arkel and deBoer by passing the vapor of the tetraiodide over a heated tungsten filament. Almost all hafnium metal now produced is made by reducing the tetrachloride with magnesium or with sodium via the Kroll Process.

The production processes used at primary zirconium and hafnium manufacturing plants depend largely on the raw material used. Six basic operations may be performed: (1) sand chlorination, (2) separation, (3) calcining, (4) pure chlorination, (5) reduction, and (6) purification. Plants that produce zirconium and hafnium from zircon sand use all six of these process steps. Plants that produce zirconium from zirconium dioxide only practice reduction and purification.

World resources of hafnium are associated with those of zircon and baddeleyite and exceed 1 million tons.

Global hafnium metal production is estimated to be around 90 tons.

Main uses & applications

Hafnium and its compounds have relatively few commercial uses.

Alloying

The leading end use for hafnium metal is as an alloy addition in polycrystalline nickel based superalloys, e.g. 1.5% Hf in MAR-M 247 alloy, primarily designed for directionally solidified (DS) turbine blade and vane applications to withstand high-stress situations, such as very high temperatures and pressures. 75% of the 150,000 metric tonnes of superalloys produced in 2006 were consumed by the aerospace industry,

Nuclear

Hafnium and zirconium are both used in nuclear reactors, including those that power nuclear submarines. In this application, each must be pure and free from the other. The manufacture of nuclear-grade zirconium therefore produces hafnium as a by-product and, conversely, the manufacture of nuclear-grade hafnium produces zirconium as a by-product. Nuclear power plant applications account for a large proportion of hafnium metal. Hafnium has three properties that make it useful in control rods used in nuclear reactors: a high-thermal neutron absorption cross section (almost 600 times that of zirconium), strength and corrosion resistance. The United States, France and Japan host half the world’s active nuclear reactors. China, India and Russia are the emerging centres for new nuclear reactor development.

Between 1995 and 2006, the world production of Hafnium has been flat, increasing at an average rate of 1% per annum.

Refractory

Hafnium is also used to make binary compounds with interesting properties. Binary compounds consist of two elements and are among the best refractory materials known. A refractory material is one that can withstand very high temperatures by reflecting heat away from itself. Refractory ceramic materials are used to line the inside of high-temperature ovens used in the production of high temperature alloys. Examples of hafnium compounds used to line these furnaces are hafnium boride (HfB_2), hafnium nitride (HfN), and hafnium oxide (HfO_2). Hafnium carbide is the most refractory binary composition known, and the nitride is the most refractory of all known metal nitrides (m.p. 3310C).

Scavenger Metal

Finely powdered hafnium can spontaneously ignite in air; because of this reactivity hafnium is used in incandescent light bulb filaments as a scavenger or "getter" to absorb contaminant oxygen and nitrogen in the bulb vacuum. A scavenger metal is one which aids in the collection of gases without reacting with them to form other compounds.

Microchips

As a replacement for Silicon in semiconductors; chip makers have used silicon as the element of choice for such transistors for more than forty years. Now, because of atomic-level constraints, they have had to a pick a new element – hafnium.

In early 2007, the world’s largest computer chip manufacturer, Intel, announced that by using a new material combination of high-k gate dielectrics and metal gates in their next generation 45nm transistors, performance would be significantly improved to deliver faster multi-core processors that consume less power. The high-k dielectric is created using atomic layer deposition (ALD) whereby a single layer of the high-k material molecule is deposited at a time. At the same time, IBM announced plans to incorporate high-κ materials, also for some products in 2008.

For nearly half a century, the number of components on integrated circuits, such as silicon computer processors, has roughly doubled every couple of years, while the cost per component has declined at a commensurate rate. This phenomenon was named “Moore's Law”, after Intel co-founder Gordon Moore, who first identified it more than 40 years ago. But in recent years, many semiconductor researchers have worried that silicon-based chips could not sustain Moore's Law for much longer.

A computer chip transistor features a gate, the on-off switch that regulates the flow of power, and has a thin silicon dioxide insulator underneath. But the thinner the insulator, the more current leaks. The leaked energy generates heat and causes battery drain. The use of High-k materials means that the hafnium oxide layer can be made thicker than the existing silicon-base, making it harder for electrons to leak through. Thus, less power is required to switch the flow of electrons through the transistor on and off.

Intel said the new chip materials would reduce leakage tenfold and make the transistors 20% faster. Intel also claimed the metal gate and high-k combo would yield around a 30 per cent reduction in the power needed to switch the transistor.

While not identified, it is most likely the high-k dielectrics used by these chip makers are some form of HfSiON. HfO2 and HfSiO are susceptible to crystallization during dopant activation annealing. NEC Electronics has also announced the use of a HfSiON dielectric in their 55nm UltimateLowPower technology.

Other uses

Other uses of hafnium include; nozzles for plasma arc cutting because of its ability to shed electrons into air, radio & television tubes, cathode in X-ray tubes, as a coating on tantalum in rocket engine parts.

Substitutes

Silver-cadmium-indium control rods are used in lieu of hafnium at many nuclear power plants. Zirconium can be used interchangeably with hafnium in certain superalloys; in others, only hafnium produces the desired or required grain boundary refinement.

Leading producers

There are very few global players in primary Hafnium production.

Cezus, a subsidiary of nuclear power plant construction company Framatome-ANP in Jarrie, France, produces approximately 45 tonnes per annum of Hf metal and since 1961 has also been the world’s largest producer of Zirconium sponge.

Wah Chang (an Allegheny Technologies, Inc. company), Albany, Oregon, USA and Western Zirconium (a subsidiary of Westinghouse Electric Co.), Ogden, Utah, USA collectively produce another 45 metric tonnes.

Other world producers of hafnium-bearing minerals include Germany, the United Kingdom, Brazil, China, India, Russia, South Africa, Ukraine, and the United States.

Additional nuclear-related material is no doubt produced surreptitiously.

Markets, trade & price movements

Hafnium’s commercial availability coincided with the expiration of U.S. Department of Defense contracts for nuclear reactors in 1962. The price remained stable at about $165 per kilogram ($75 per pound) for 15 years, and the continued availability of the metal resulted from the growth and development of the commercial nuclear industry.

Demand for hafnium declined in the 1990’s as no new orders for nuclear reactors were placed. Demand is primarily for replacement parts and control rods in existing nuclear reactors and as an alloying agent in certain superalloys.

Hafnium prices averaged $187 per kg in 2005 and $235 per kg in 2006. 2007 has seen prices soar above $250 per kg in 2007.

Global production of zirconium concentrates increased to 920,000 tons in 2006, which was a moderate increase compared with that of 2005. Global demand for zircon by the ceramics and chemicals industries helped to increase the demand by 3% compared with that of 2005. Meanwhile, prices for zircon concentrate increased to record-high levels.

Cost-cutting measures were expected to idle mining operations in Green Cove Springs, FL, and Lulaton, GA, by year end. The Green Cove Springs operation has been in production since 1972, and the Lulaton operation was started in 2004. The closures will leave the United States with mining operations in Stony Creek, VA, and Starke, FL. Mine production at the Moma mineral sands project in Mozambique was expected to begin in January 2007. By 2008, Moma’s production capacity was expected to reach 800,000 tons per year of ilmenite, 56,000 tons per year of zircon and 21,000 tons per year of rutile. New production from Australia (Douglas, Mindari, Pooncarie, Tiwi Islands), The Gambia (Sanyang), Madagascar (Fort Dauphin), and Malawi (Lake Malawi) are expected to bring the supply of and demand for zirconium concentrates into balance.

Future outlook

There are currently 440 nuclear reactors in operation today and it is estimated that 168 new reactors will be built over the next 15 years, marking a 38% increase. Increased demand for Hafnium will be an inherent part of this expansion.

Intel has promoted the successful use of hafnium and other so-called high-k materials as the industry's biggest advancement since silicon-based transistors in the 1960s. The California based company has working versions of the chip and plans to start mass-producing versions for PCs and computer servers in the second half of 2007. Potential future uses for the chip include cellphones that perform advanced computing tasks but maintain their battery charge, dramatic reduction in overall power consumption by computers, allowing for longer battery life for notebooks and ultra mobile PCs (UMPC) or ultra slim and fan-less desktop designs to co-ordinate with living room décor.

The competing breakthroughs from Intel Corp. and IBM Corp. should silence doubts, at least for several years, that the industry can prolong the decades-long trend of pushing semiconductor performance, whilst simultaneously cutting size and cost. It would be premature to speculate on the impact of the supply/demand repercussions of the new demand for microchip applications, suffice to say that extra hafnium requirements would require major investment to be met.

The advent of this new technology and the potential replacement of silicon has lead to the media coining the phrase “Hafnium Valley”!

Supply & Demand Tables

World Hafnium Supply (Primary Production)

Wah Chang	USA	30 MT
Cezus	France	25 MT
Western Zirconium	USA	10 MT
?	Ukraine	5 MT
?	China	1 MT
	Total	**71 MT**

World Hafnium Demand by Sector

Superalloys (Aerospace)	30 MT
Nuclear Finished Products	12 MT
Superalloys (Non-Aerospace)	10 MT
Hafnium Oxide	10 MT
Plasma Cutting	7 MT
Hafnium Chloride	5 MT
Thin Film (CVP/PVD)	3 MT
Total	**77 MT**

Author profile

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