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Hafnium (Hf^{72})

Properties

Hafnium is a lustrous, silvery-gray transition metal with an atomic mass of 178.49 u. Hafnium has a density of 13.31 g/cm^3, a melting point of 2233 ^{o}C and a resistivity of 33.1 μOhm cm. It is hard and has a Brinell hardness of 1450 – 2100 MPa.

Refractory metals are the group of elements in the Periodic Table that exhibit very high resistance to Heat, Corrosion and Wear while exhibiting the higher melting points than that of Nickel (1455 ^{o}C), Cobalt (1495 ^{o}C) and Iron (1538 ^{o}C). Refractory metals include Titanium (1668 ^{o}C), Zirconium (1855 ^{o}C), Chromium (1907 ^{o}C), Vanadium (1910 ^{o}C), Rhodium (1964 ^{o}C), Technetium (2157 ^{o}C), Hafnium (2233 ^{o}C), Ruthenium (2334 ^{o}C), Iridium (2466 ^{o}C), Niobium (2477 ^{o}C), Molybdenum (2623 ^{o}C), Tantalum (3017 ^{o}C), Osmium (3033 ^{o}C), Rhenium (3186 ^{o}C), Tungsten (3422 ^{o}C).

Hafnium is found predominantly in +4 oxidation state while it also exists in -2, +1, +2, and +3 oxidation states. Its standard electrode potential in respect to Hf^{+4} is -1.7V. Hafnium is corrosion-resistant and chemically similar to zirconium. Hafnium reacts in air to form a protective film that inhibits further corrosion. The metal is not readily attacked by acids but can be oxidized with halogens or it can be burnt in air. Like its sister metal zirconium, finely divided hafnium can ignite spontaneously in air. The metal is resistant to concentrated alkalis. Its abundance has been estimated to be about 5.8 parts per million (ppm) in Earth's crust.

Plating Solutions

Refractory metals, that can be plated from aqueous solutions, include Cr, Tc, Ru, Rh, Re, Os and Ir. Other refractory metals such as Hf and Zirconium can be electroplated from molten salts or ionic liquids.

Hafnium can be electrodeposited from molten salts of alkalis chlorides, for example, containing NaCl-KCl or CsCl with hafnium tetrachloride ($HfCl_4$) or potassium hexafluorohafnate (K_2HfF_6), respectively, at deposition temperature of 575–750 ^{o}C and current densities of 5-10 mA/cm^2 [1].

Refractory metals including hafnium can be also electroplated from ionic liquids, for example, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ([$Py_{1,4}$]TFSA at 200 ^{o}C, 1-ethyl-3- methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide, trihexyl-tetraadecyl phosphonium bis(trifluoromethylsulfonyl)amide et al [2, 3].

Applications

Most of the hafnium produced is used in the manufacture of control rods for nuclear reactors due to its large neutron capture cross-section. Hafnium is also used in filaments and electrodes. Semiconductor fabrication processes use its oxide for integrated circuits at 45 nm and smaller feature sizes. Some superalloys used for special applications contain hafnium in combination with niobium, titanium, or tungsten.

References:

1. S.A. Kuznetsov. *Chemical Papers* **66**(5), 511-518, 2012.
2. J.A. Maurer. *ECS Abstract MA2018-02 1826*, Oct. 2018.
3. C. H. Riwe. US Patent Application, US 2012/0189778, published Jul. 26, 2012.