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HAFNIUM ALLOY

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This invention relates to a novel hafnium alloy having improved strength, corrosion resistance, weldability, and fabrication properties.

Hafnium is produced as a by-product of zirconium production inasmuch as it is present in the proportions of about 2% hafnium to zirconium in zirconium ores. Though zirconium and hafnium always have been found to occur together in nature and have unusually similar chemical properties, they differ greatly in their respective abilities to absorb neutrons, for which reason both metals use useful in nuclear reactors.

Hafnium has a high neutron absorption cross section (105 barns) which is not diminished materially even over long periods of irradiation. For that reason one of its principal uses has been as a control rod material in a reactor. Other desirable properties include its corrosion resistance in hot water and its physical properties. The physical properties of hafnium at elevated temperatures have made it useful as a component of electric light filaments either as unalloyed hafnium or as an alloy with tungsten to increase the strength of the filament.

Notwithstanding the foregoing, hafnium has been subjected to extensive metallurgical investigation to improve its properties. A disadvantage of early hafnium alloys was that they cracked during welding due to impurities. It has been found that improved strength, corrosion resistance, weldability, and fabricability may be imparted to hafnium by the addition of certain elements.

Briefly, addition of oxygen and iron in critical limited amounts, respectively improves the strength and corrosion resistance of hafnium. Moreover, additions of titanium and nickel in specific proportions improve the weldability and fabricability of hafnium as, for instance, for use as a control rod for nuclear reactors. Hafnium alloys with oxygen and iron in the critical range and incorporating both titanium and nickel in specific ranges exhibit greatly improved properties.

Accordingly, it is an object of this invention to provide useful hafnium alloys having unusually high oxidation resistance and strength at elevated temperatures.

It is another object to provide hafnium alloys having improved welding and fabricating properties.

These and other objects and desiderata may be accomplished in a simple and effective manner.

The present invention satisfies those objects by providing a hafnium base alloy comprising as its essential components from 100 to 600 p.p.m. oxygen, 200 to 500 p.p.m. iron, 20 to 200 p.p.m. titanium, 20 to 250 p.p.m. nickel, up to about 4.5% by weight of zirconium, and the balance being hafnium with incidental impurities. The alloys may have substantial amounts of zirconium present without detrimental effects on the physical properties. Zirconium is normally present in small amounts in hafnium by reason of the difficulty of effecting complete separation of the two elements. Zirconium has a far lower neutron absorption constant and this should be taken into account for control rod applications. Ordinarily not over 10% zirconium is desirably present.

Small amounts of aluminum and copper, up to 100 p.p.m., may be present without adverse effects. Also hydrogen may be present up to about 25 p.p.m., while up to 70 p.p.m. of nitrogen may be in the alloy. Also tungsten

up to 300 p.p.m. may be present. Molybdenum preferably does not exceed 20 p.p.m. for control rod applications of the alloy.

For some purposes, small amounts of uranium may be present not in excess of 20 p.p.m. with U–235 not in excess of about 0.14 p.p.m. if control rods are made of the alloy.

More particularly the overall preferred chemical composition of the hafnium base alloys of this invention is shown in Table I.

TABLE I.—COMPOSITIONS IN P.P.M.

Oxygen	100–600
Iron	200–500
Titanium	20–200
Nickel	20–250
Zirconium (max.) (percent)	4.5
Aluminum (max.)	100
Copper (max.)	100
Tugsten (max.)	300
Total Uranium (max.)	20
Uranium-235 (max.)	0.14
Nitrogen (max.)	70
Hydrogen	About 25
Molybdenum	20
Hafnium (balance) percent (by difference)	About 95.3

The alloy may be prepared by mixing hafnium sponge and/or crystal bar with wire or pieces of nickel, titanium and iron into a compacted mass which is tack welded in an inert atmosphere to form an electrode. Hafnium sponge may contain the desired amount of oxygen. Oxygen also may be incorporated by adding iron oxide to hafnium crystal bar or sponge. The procedure for producing a homogeneous hafnium alloy ingot preferably involves the double consumable electrode vacuum arc melting process which is set forth in U.S. 3,072,282 known in the art for producing other alloys such as titanium base alloys. Electron beam melting also can be employed to produce ingots of the alloy. The electrode is arc melted in vacuum to form an ingot and the ingot is then remelted in vacuum by arc melting or electron beam melting to obtain better alloy homogeneity. The resulting alloy ingot is then rolled down to form flat rod, bar wire, or strip of the desired dimensions. The wrought strip or bar can be either hot rolled or cold rolled and annealed to produce the final product.

In accordance with the invention oxygen and iron are the controlling elements in improving the strength, corrosion resistance, weldability, and fabricability of the hafnium base alloy. By increasing the oxygen to the level of 100 to 600 p.p.m., the mechanical properties are improved as is indicated in Table II.

TABLE II

Hafnium composition	Mechanical properties		
	0.2% yield strength	Ultimate strength	% elongation in 2″
Without oxygen	19,800	30,950	58.2
With oxygen, 250 p.p.m.	25,180	34,750	52.7

With oxygen added, the yield strength is increased by over 35% and the ultimate strength by over 10%. A relatively insignificant decrease in ductility results from the addition of the oxygen. The effective reduction in ductility due to oxygen addition is negligible because normal ductility requirements are only 30%. Thus, oxygen primarily adds strength to the alloy. Although the amount of oxygen listed in Table I is 100 to 600 p.p.m., the preferred range is from about 200 to 300 p.p.m.; the optimum being about 250 p.p.m. If oxygen materially exceeds 600 p.p.m., the alloy becomes progressively more brittle.

Iron is added in the amount of from 200 to 500 p.p.m. to improve corrosion resistance and stabilize the grain structure. Although oxygen additions above a minimum percentage do not affect corrosion resistance, further additions do reduce such resistance. However, the iron additions more than compensate for oxygen with the result that corrosion resistance is equal to or better than normal for hafnium alone. The preferred range of iron additions are about 200 to 300 p.p.m., and the optimum is about 250 p.p.m. If iron exceeds 500 p.p.m., it precipitates out of solid solution in hafnium.

Titanium and nickel are added to improve the fabricability and weldability of the alloy. Titanium is added in the amount of 20 to 200 p.p.m. with an optimum of 150 p.p.m. Nickel is added in the amount of 20 to 250 p.p.m. with the optimum being about 175 p.p.m.

The hardness of an alloy having the foregoing analyses with the optimum proportions of iron, oxygen, titanium and nickel is about 200 BHN (3000 kg.) maximum.

EXAMPLE

Hafnium alloy has been prepared, fabricated into a control rod and successfully tested in accordance with this invention. The alloy was prepared from hafnium sponge mixed with pieces of nickel, titanium, and iron by use of the double consumable electrode vacuum arc melting process mentioned above. The resulting ingot was rolled down to the bar of desired dimensions, it was annealed to produce the final product. This bar was welded to other bars and members of the alloy to produce a control rod. A chemical analysis of the alloy indicated the following composition: 250 p.p.m. oxygen, 350 p.p.m. iron, 150 p.p.m. titanium, 175 p.p.m. nickel, 4.5% zirconium, 100 p.p.m. aluminum, 100 p.p.m. copper, 300 p.p.m. tungsten, about 20 p.p.m. uranium with 0.14 p.p.m. in uranium-235, 70 p.p.m. nitrogen, 25 p.p.m. hydrogen, 20 p.p.m. molybdenum, and the balance (about 95.3%) hafnium. The alloy displayed improved fabricability and weldability during the manufacture of the control rods. The control rod of the alloy was tested in a nuclear reactor and improved physical properties and corrosion resistance were satisfactorily established.

Accordingly, the hafnium base alloy of the present invention has improved properties of strength, corrosion resistance, weldability, and fabricability. Where a hafnium base alloy having elements falling within the chemistry limits listed in Table I is provided, the alloy is more suitable for use as control rods in a nuclear reactor.

It is intended that the disclosure be construed as illustrative of the invention and not in limitation thereof.

What is claimed is:

1. A hafnium base alloy consisting essentially of up to 4.5% by weight zirconium, from 100 to 600 p.p.m. of oxygen, from 200 to 500 p.p.m. of iron, from 20 to 200 p.p.m. titanium, from 20 to 250 p.p.m. of nickel, and the balance being hafnium and incidental impurities.

2. The alloy of claim **1** in which there are 200 to 300 p.p.m. of oxygen.

3. The alloy of claim **1** in which there are about 250 p.p.m. of oxygen.

4. The alloy of claim **1** in which there are 200 to 300 p.p.m. of iron.

5. The alloy of claim **1** in which there are about 250 p.p.m. of iron.

6. The alloy of claim **1** in which there are about 150 p.p.m. of titanium.

7. The alloy of claim **1** in which there are about 175 p.p.m. of nickel.

8. The alloy of claim **1** in which there are from 200 to 300 part per million of oxygen, from 200 to 300 parts per million of iron, about 150 parts per million of titanium, and about 175 parts per million of nickel.

9. The alloy of claim **1** in which there are about 250 parts per million of oxygen, about 250 parts per million of iron, about 150 parts per million of titanium, and about 175 parts per million of nickel.

10. A hafnium base alloy consisting essentially of from 0.002 to 4.5% by weight zirconium, about 250 parts per million of oxygen, about 250 parts per million of iron, about 150 parts per million of titanium, about 175 parts per million of nickel, about 100 parts per million of aluminum, about 100 parts per million of copper, about 70 parts per million of nitrogen, about 300 parts per million of tungsten, and the balance being hafnium with incidental impurities.

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