



Hafnium Alloy Addition

(UNS R02001)

INTRODUCTION

Hafnium is a heavy, steel-gray metal in the reactive metals group that is very closely related to zirconium, and forms a continuous solid-solution at all concentrations of zirconium and hafnium. Hafnium occurs naturally with zirconium at a ratio of approximately 1:50, and is produced exclusively as a co-product of nuclear-grade zirconium. It is used in a variety of applications where few substitutes are available.

Hafnium and zirconium have nearly opposite nuclear properties; thus with its relatively high thermal neutron cross-section, hafnium's biggest application is as control rod material in nuclear reactors. In this application, the presence of a few percent of zirconium (< 4.5%) does not adversely affect its performance.

When used in relatively small amounts, hafnium strengthens the grain boundaries of nickel-based super-alloys and high temperature alloys, improving the creep ductility and rupture lifetime. It is extensively used in a number of alloys that find use in the hot end of jet engines. Hafnium has an extremely high affinity for oxygen, nitrogen, and carbon, and is one of the most effective solid-solution strengtheners via dispersion strengthening.

Like the other reactive metals, hafnium is HCP (Hexagonal Close-packed) at room temperature and anisotropic. Even more than zirconium or titanium, the mechanical properties of hafnium are affected by interstitial element contamination. In many applications, a very low interstitial content may be necessary to obtain the required ductility or other properties. For such critical applications, the iodide crystal bar process is used by ATI to produce hafnium with a typical oxygen concentration of 60 ppm or less.

Hafnium is also used extensively as a tip insert for plasma welding tips. With a low work function and a high melting point, hafnium has been found to extend the life of plasma welding tips, and to give better performance.

Its behavior in corrosive media is very similar to that of zirconium, and in the absence of data can be considered to be roughly equivalent. The general applications include: nuclear reactor control rods, neutron absorption, alloy additive in various superalloys, plasma torch welding tips. Hafnium is available in common mill forms including plate, sheet, foil, rod, and wire.

Hafnium metal is also available in a number of forms for alloying. For higher purity applications, where very low oxygen and nitrogen content are especially critical, crystal bar is produced with typical oxygen content of less than 60ppm. It is available in chunk form (chopped bars), whole bars, or milled chips. Where crystal bar chemistry is desired, but for less critical applications, tip material is available as unqualified crystal bar. Hafnium sponge is also available for standard alloying needs.

Hafnium powder is produced at ATI, and is also available in standard mesh sizes ranging from 80 – 325 mesh x down.



Figure 1. Hafnium Crystal Bar from the van Arkel / deBoer iodide process

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CHEMICAL PROPERTIES

Hafnium is available in a number of different grades. Mill products conform to ASTM B776. Hafnium that is used for alloy addition comes in four different grades that depend on zirconium content (See Table 1).

Table 1. Typical Composition				
	Mill Products Rod / Wire	Crystal Bar Nominal	Sponge Nominal	Powder Nominal
Aluminum	100	60	450	100
Carbon	150	30	50	150
Chlorine			200	
Chromium	100	20	50	
Copper	100	25		50
Hydrogen	25	5		20
Iron	250	100	750	250
Magnesium			600	
Molybdenum	20	10		
Nickel	50	25	30	
Niobium	100	5		
Nitrogen	100	10	50	120
Oxygen	400	60	1000	†
Silicon	100	25	25	
Tantalum	200	5		<100
Titanium	100	30	70	
Tungsten	150	1		<30
Uranium	10	2	2	
Vanadium	50	10		
Zirconium	<4.5%	**	**	<4.5%
Hafnium	Balance	Balance	Balance	Balance

** Alloy Addition zirconium contents		† Hf Powder Oxygen Contents	
Ultra Low Zr	≤ 0.2%	Nominal -80 x down	< 2500
Extra Low Zr	≤ 0.5%	Nominal -325 x down	< 3500
Medium Zr	≤ 1.5%		
Standard Zr	≤ 4.5%		



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PHYSICAL PROPERTIES

Table 2. Physical Properties of Hafnium	
Density	13.3 g/cm ³ (0.481 lbs / in ³)
Melting Point	2233°C (4051°F)
Phase Transition or Beta Transus	1760°C (3200°F) (aHCP bBCC)
Thermal Expansion	5.9 X 10 ⁻⁶ m/m • K ⁻¹
Thermal Conductivity	23.0 W/m • K @ 298K
Specific Heat	25.69 J/g • K
Boiling Point	4690°C (8474°F)
Electrical Resistivity	3.51 X 10 ⁻⁷ W • m @ 298K
Thermal Neutron Cross-section	104 Barns
Work Function	3.90 eV

MECHANICAL PROPERTIES

Table 3. Ultimate Tensile Strength (UTS) and Yield Strength (YS, 0.2% Offset)				
Form	Test Direction	Ultimate Tensile Strength, min ksi [Mpa]	Yield Strength 0.2% offset, min ksi [MPA]	Elongation, min % in 2 inch [50 mm]
Rod	Longitudinal	58 [400]	22 [150]	22
Plate	Longitudinal	58 [400]	22 [150]	20
Plate	Transverse	45 [310]	25 [172]	20
Strip	Longitudinal	58 [400]	22 [150]	20
Strip	Transverse	45 [310]	25 [172]	20

Table 4. High Temperature Strength Properties at 315°C (600°F)						
	Test Direction	Ultimate Tensile Strength, (MPa)	Yield Strength, 0.2% offset (MPa)	Ultimate Tensile Strength, psi	Yield Strength, 0.2% offset (psi)	Elongation %
Rod	Longitudinal	310	124	45000	18000	40
Plate	Longitudinal	276	124	40000	18000	45
	Transverse	234	165	34000	24000	48
Strip	Longitudinal	276	97	40000	14000	45
	Transverse	241	165	35000	24000	50

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Figure 2. Mechanical properties of hafnium as a function of test temperature. Long. Elongation = ■, long. Yield Strength = ●, long. UTS = ▲.

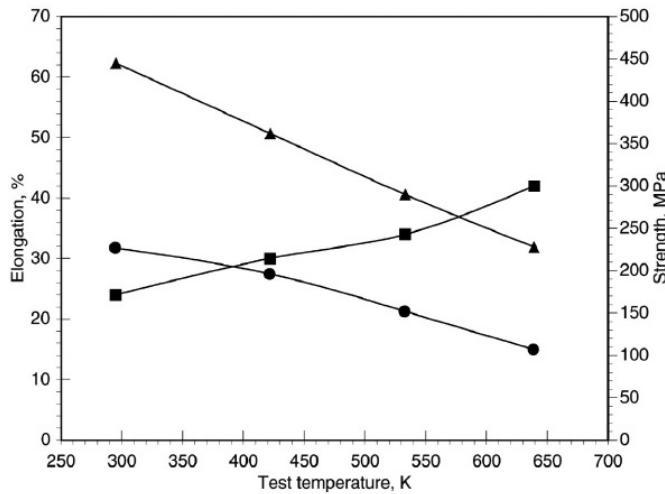


Table 5. Other Mechanical Properties

Hardness	BRINELL	1700 MPa
	VICKERS	1760 MPa
	Mohs	5.5
Elongation	25 – 30% at room temperature; dependent on purity	
Young's Modulus	137 GPa at room temperature	
Poisson's Ratio	0.29	
Shear Modulus	54.2 GPa at room temperature	

FABRICATION AND WELDING

Hafnium behaves similarly to zirconium in fabrication processes, but with higher strength and hardness, and greater sensitivity to contamination. Generally, equipment that is used to process zirconium is suitable for hafnium as well. With both metals, cleanliness is critical to successful fabrication.

SPECIAL PRECAUTIONS

Hafnium is nontoxic. It is pyrophoric however. Massive pieces of sheet, plate, bar, billet, tube, ingot, crystal bar, etc. can be heated and worked without burning. However, where the surface area to mass ratio is relatively high, such as sponge, fines, machine chips, foil, etc., hafnium can easily ignite and burn at extremely high temperatures. Large accumulations of chips and other finely divided materials should be avoided. When storing the chips and turnings, care should be taken to place the material in nonflammable containers and isolated areas. One effective storage method is to keep the material covered with water in the containers. However, the water must not be allowed to evaporate, or the material to dry out. Hafnium powder may require additional measures to handle safely.



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Fires, when they do occur, can be extinguished when they are small using salt, sand, metal, or type D fire extinguisher. For larger fires, isolate the burning material from combustibles and allow it to burn out. Fires should never be fought with water or CO₂, as they will provide an additional source of oxygen.

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