What are Refractory Metals?

Refractory metals are different. As a group they provide a number of unique characteristics – such as resistance to high heat, corrosion and wear – making them useful in a multitude of applications.

The next time you climb into your automobile take note that you are surrounded by components which are made of refractory metals or have been cut or formed by them. Your car’s electrical or electronic systems may also make use of the metals’ electric and heat-conducting qualities. On the other hand, refractory metals were used in the tools which helped to drill the well which produces the gasoline in your tank. Piping of refractory metal alloys helped process it. And your oil may contain a refractory metal compound to increase its lubricating ability.

The paradox of refractory metals is that, despite their wide and constantly growing list of applications, many people – sometimes even engineers, working with one of the metals – do not fully understand how and where each is mined, how it is processed, how it is formed, or even understand the full extent of the diversity of refractory metals’ applications.

Five Metals with Unique Characteristic

<table>
<thead>
<tr>
<th>Tungsten</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
</tr>
<tr>
<td>Niobium</td>
<td>Nb</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Ta</td>
</tr>
<tr>
<td>Rhenium</td>
<td>Re</td>
</tr>
</tbody>
</table>

Excellent strength at high temperatures. Even when heated to 1000°C (1832°F) tungsten rocket nose cones still have twice the tensile strength iron has at room temperature.

Very high melting point (2468°C/4474°F to 3410°C/6170°F): High melting points of tungsten, tantalum and molybdenum make them useful in processing molten metals and minerals such as glass making.
Exceptional resistance to corrosion: Stainless steel piping in chemical plants contains refractory metals.

High resistance to thermal shock: The stresses of rapid expansion due to heat would destroy most metal filaments in just a few on-off cycles. A tungsten filament, because of its high melting point and good non-sag characteristic, will withstand thousands of on-off cycles and still remain intact.

Excellent wear and abrasion resistance: Refractory metals, often in alloy form extend the life of seals, bushings, nozzles, valve seats and many points of high wear. Alloys with gold and silver also make excellent long-life contact points or electronic equipment.

Good Electrical and heat conducting properties: Besides their use in many electrical and electronic applications, refractory metals are often used as heat sinks...this semiconductor chip is set in a molybdenum or tungsten sink.

Hardness: Cutting tools today are made of tungsten carbide. For cutting, forming steel and other metals...even for drilling oil wells and in mining.

Many other qualities: From excellent radiation shields to chemical catalysts, individual refractory metals offer a wide variety of useful capabilities.
High specific gravities or density:
Some of the refractory metals are among the highest in density; they are used as a weight for precision ballasts on gyroscopes of aircraft and as weights in golf club heads.

How Refractory Metals Compare with Other Familiar Metals

<table>
<thead>
<tr>
<th>METALS</th>
<th>ATOMIC WEIGHT</th>
<th>ATOMIC NUMBER</th>
<th>DENSITY</th>
<th>ELECTRICAL CONDUCTIVITY</th>
<th>ELECTRICAL RESISTIVITY</th>
<th>THERMAL CONDUCTIVITY</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>amu</td>
<td>g/cm³</td>
<td>lb/in³</td>
<td>°C</td>
<td>°F</td>
<td>K</td>
</tr>
<tr>
<td>Tungsten - W</td>
<td>163.95</td>
<td>74</td>
<td>19.3</td>
<td>6.097</td>
<td>3410</td>
<td>6170</td>
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<tr>
<td>Rhenium - Re</td>
<td>186.2</td>
<td>75</td>
<td>21.04</td>
<td>0.759</td>
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<td>5756</td>
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<td>Tantalum - Ta</td>
<td>190.95</td>
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<td>16.6</td>
<td>0.8</td>
<td>2996</td>
<td>5425</td>
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<td>Molybdenum - Mo</td>
<td>85.94</td>
<td>42</td>
<td>10.22</td>
<td>0.0309</td>
<td>2610</td>
<td>4730</td>
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<tr>
<td>Niobium - Nb</td>
<td>52.91</td>
<td>41</td>
<td>8.51</td>
<td>0.31</td>
<td>2460</td>
<td>4474</td>
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<tr>
<td>Titanium - Ti</td>
<td>47.9</td>
<td>22</td>
<td>4.5</td>
<td>0.163</td>
<td>1666</td>
<td>3030</td>
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<td>Iron - Fe</td>
<td>55.85</td>
<td>20</td>
<td>7.87</td>
<td>0.254</td>
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<td>2757</td>
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<tr>
<td>Nickel - Ni</td>
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<td>8.9</td>
<td>0.32</td>
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<td>2647</td>
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<td>Cobalt - Co</td>
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<td>8.85</td>
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<td>2723</td>
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<tr>
<td>Copper - Cu</td>
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<td>29</td>
<td>5.96</td>
<td>0.324</td>
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<td>1981</td>
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<td>Gold - Au</td>
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<td>19.3</td>
<td>0.697</td>
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<td>1945</td>
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<td>Aluminum - Al</td>
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<td>Lead - Pb</td>
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<table>
<thead>
<tr>
<th>METALS</th>
<th>Room Temp</th>
<th>800°C (1732K)</th>
<th>1600°C(2373K)</th>
<th>25°C</th>
<th>1000°C (1737K)</th>
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<tbody>
<tr>
<td></td>
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<td>MPa</td>
<td>Ksi</td>
<td>MPa</td>
<td>Ksi</td>
<td>MPa</td>
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<td>689.3445</td>
<td>100.00</td>
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<td>1828.2</td>
<td>134</td>
<td>923.6</td>
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<td>33.70</td>
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<td>172.510</td>
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<td>Molybdenum - Mo</td>
<td>120.20</td>
<td>828.5-1378</td>
<td>20.65</td>
<td>142.4479</td>
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<td>Niobium - Nb</td>
<td>30.60</td>
<td>206.4113</td>
<td>20.40</td>
<td>137.8-275.6</td>
<td>8.15</td>
<td>55.12-193.3</td>
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<tr>
<td>Titanium - Ti</td>
<td>36.10</td>
<td>261.9-699</td>
<td>20.47</td>
<td>137.8-323.8</td>
<td>15-15.5</td>
<td>1.034-1.067</td>
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<tr>
<td>Nickel - Ni</td>
<td>50.10</td>
<td>344.5-689</td>
<td>30.82</td>
<td>130.9-220.5</td>
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<td>34.13</td>
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<tr>
<td>Copper - Cu</td>
<td>32.55</td>
<td>220.48-278.85</td>
<td>17</td>
<td>1.171</td>
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<td>Gold - Au</td>
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<td>136.91-220.48</td>
<td>12</td>
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<td>Aluminum - Al</td>
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<td>68.9-166.03</td>
<td>10</td>
<td>0.669</td>
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<td>Zinc - Zn</td>
<td>41.47</td>
<td>262.49-323.63</td>
<td>10</td>
<td>0.669</td>
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<tr>
<td>Lead - Pb</td>
<td>2.26</td>
<td>13.78-17.914</td>
<td>2</td>
<td>0.138</td>
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</tbody>
</table>

What are refractory metals?
Refractory metals have one characteristic in common: an exceptionally high melting point. Tungsten, for example, melts at 3410°C (6170°F), which is more than double that of iron and ten times that of lead.

As a group, they are found in one section of the periodic table of elements. Although there are twelve refractory metals, only five are widely used: Tungsten, Molybdenum, Niobium, Tantalum and Rhenium.
All but Rhenium have a body-centered cubic structure. Despite the fact that refractory metals have many similar qualities—such as high density, resistance to wear and corrosion—each metal is different in its own way, providing each with its own individual combination of qualities. Many of these individual qualities are rather unique, such as an ability to combine with gases and then release them under heat. Or, remarkable lubricating qualities.

This selection of unusual characteristics provides engineers with a virtually uncountable number of potential applications ... each a key to solving a problem.

**If refractory metals have such a high metal melting point, how is anything ever fabricated from them?**

Refractory metals are extracted from ore concentrates, processed into chemicals and then into powders. The powders are consolidated into finished products or mill shapes and ingots for further processing. Because of their high melting points and ease of oxidation, refractory metals are usually worked in powder form.

The science of modern powder metallurgy (P/M) actually started in the early 1900's when incandescent lamp filaments were made from tungsten powders. Another early P/M product was cemented tungsten carbide used in the manufacture of cutting tools. From this early beginning with refractory metals has grown one of the most depended upon methods of metal part fabrication—important because of P/M technology's manufacturing productivity advantages, materials conservation, wide range of engineering properties, design flexibility and energy savings.

**What other important properties do these metals have?**

The mechanical and physical properties of refractory metals are compared to other common metals in Table 1.

The strength values of the metals in Table I are given in ranges because the strengths of these metals may vary considerably with form and processing.

Strength is not the only thing which can vary because of processing methods. Alloying or combining the metals in composites can often provide properties which are, in some respects, superior to those inherent in the base metal itself. So, although there are only five principal refractory metals, they serve as major constituents in dozens of important metal and alloy compositions.

Alloys containing varying amounts of refractory metals are vital to virtually every major industry, including automotive, mining, aerospace, chemical and petroleum processing, electrical and electronics, medical electronics and prosthetics, metal processing, nuclear technology and ordnance. The principal areas of uses for the five refractory metals are shown in Table II.

<table>
<thead>
<tr>
<th>Applications</th>
<th>W</th>
<th>Mo</th>
<th>Ta</th>
<th>Nb</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronics</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Alloying</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Nuclear Power</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
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<tr>
<td>Aerospace</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals/Catalysts</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Metal Cutting &amp; Forming</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical Parts</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mining/Oil Drilling</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Other examples are given throughout this book, particularly on the back cover.*
**Tungsten (W)**

Derived from the Swedish word "tung" for heavy and "sten" for stone, it is traced to the 1781 identification of calcium tungstate by Swedish chemist, Karl Wilhelm Scheele. "Scheelite" (as it is now called) and another mineral, "Wolframite", are the most important sources of tungsten.

Tungsten is the most plentiful of the refractory metals. However, about half of the world's reserves are found in China. Korea is another important source along with Bolivia, Portugal, Australia, Thailand, Canada and United States. Despite its resources, the United States still must import most of its consumption. Since the late 70's the use of W reclaimed from scrap has steadily increased. Estimates today are that about 30% of W consumption is from scrap.

Tungsten has the highest melting point of all metals. It also has one of the highest densities of all metals. When combined with carbon, it becomes one of the hardest man-made materials.

While most people are familiar with tungsten filaments for light bulbs, its most common and most invaluable use is in metal cutting, mining and oil drilling tools. Actually, there are three different tungsten materials and each has its own areas of application: (1) tungsten metal, (2) tungsten carbide, and (3) tungsten heavy metals. However, all start with the same powder form.

**What is the basic tungsten metal like, what are its primary properties?**

It has the highest melting point, 3410 °C (6170 °F), and one of the highest densities of any metal. It also has exceptional strength at ambient and elevated temperatures.

Although tungsten can be used at high temperatures, oxide films become volatile above temperatures of approximately 538 °C (1000 °F). So, for use at extremely high temperatures, tungsten parts must be coated, used in a vacuum; or be surrounded by a protective atmosphere. Typical uses involving protective atmospheres - or vacuum - include incandescent lamp filaments, electron tube electrodes and various types of heating elements.

Silicide coating and noble metal cladding are effective oxidation-resisting coatings; for example, cladding the tungsten with platinum-gold alloys.

**If you have to coat tungsten or use a special atmosphere at high temperatures, what do you mean when you say it's "corrosion resistant"?**

Tungsten has good resistance to water and atmospheric corrosion at ambient temperature, and is resistant to many severe environments which readily attack other metals. It resists nitric, sulfuric and hydrofluoric acids at room temperatures. It is inert to oxygen-free liquid ammonia at room temperature. It is only subject to slight attack by hot alkaline solutions such as potassium, sodium and ammonium hydroxides.

Tungsten also has good resistance to several liquid metals including sodium, mercury, gallium, and magnesium; to oxide ceramics such as alumina, magnesia, zirconia and thoria. It is often used for crucibles to melt these materials in an inert atmosphere. Although resistant to hydrogen, tungsten reacts at high temperatures with carbon dioxide, carbon monoxide, nitric oxide, nitrogen dioxide and sulfur.

**What are some of tungsten's other properties and uses?**

A cubic inch weighs over two-thirds of a pound; only platinum, iridium, osmium and rhenium would weigh more. Also, tungsten has a relatively high thermal neutron absorption cross-section; good electrical conductivity (31% IACS), which is better than iron, nickel and many other common metals. And, it can be improved substantially by alloying with copper or silver.

The first application of pure tungsten metal was the incandescent lamp filament. The way to this was found by Dr. William D. Coolidge of General Electric Company, who developed ductile tungsten through mechanical working and heat treatment of a powdered tungsten metal. Mechanical working produced a fibrous structure in the metal. One pound of tungsten (physically smaller than even the size of a ping pong ball) can be drawn into a wire 8.5 miles long enough filament for 23,000 60-watt light bulbs.
Tungsten's high melting point and low vapor pressure make it very useful for welding electrodes. Helium or argon prevent oxidation of the electrode in gas tungsten arc (TIG)* welding, as well as protecting the metal being welded. Exceptional heat resistance makes tungsten extremely useful for heating elements, trays and radiation shields in vacuum and controlled atmosphere furnaces. It also is used in evaporation boats to produce thin surface coatings by vacuum deposition in optical and electronic industries.

Good electrical conductivity, combined with resistance to wear and spark erosion, makes tungsten, tungsten-copper and tungsten-silver useful in electrical contacts.

*Tungsten Inert Gas welding.

For example, it is used in electrical contacts and heat sinks, choppers for broadcasting equipment, light switches, and voltage control thyratron devices. (The tables on the back cover show many other uses of tungsten.)

**Tungsten as an alloy**

Tungsten is used extensively as an alloying element in tool steels and high temperature alloys. High speed steels use from 1 to 18% tungsten depending upon the grade. It is also an important alloying element in hot work tool steels used in die casting, forging and extrusion dies. Tungsten is also used as an alloying element in molybdenum, tantalum and niobium alloys.
Are there any other interesting uses?
Tungsten chemicals have many surprising applications. For example, tungsten compounds, especially the oxides, sulfides, and heteropoly complexes, form stable catalysts for a variety of commercial chemical processes. Petroleum processing is a major field of application for tungsten compounds. Tungsten sulfide has the ability to form adherent, soft, continuous films on a variety of substrates and exhibits superior lubrication under extreme conditions of temperature, load, and vacuum. It can be an effective lubricant in wire drawing, metal forming, valves, gears, bearings and packing materials.

Heteropoly tungsten acids have the following uses: analytical chemistry and biochemistry; precipitants and ion-exchangers in atomic energy; fixing and oxidizing agents in photographic processes; plating additives; plastics curing or drying agents. Compounds are used in printing inks, paper coloring, nontoxic paints, and wax pigmentation.

The tungstates are good corrosion inhibitors and have been used for some time in antifreeze solutions. The tungstates are also widely used in blood chemistry analyses, and for x-ray intensifying screens. In addition, they are used as laser host materials, phosphors and in flame proofing of textiles.

Another interesting use is that tungsten alloy wire and filaments are being developed for use as reinforcements in metal-matrix composites and armor piercing projectiles.

Isn’t tungsten carbide also an alloy?
Not really. The most common form is the compound tungsten monocarbide (WC). Mixtures of WC and cobalt powders are used to produce a myriad of cemented tungsten carbide products for cutting, forming, and mining tools, and for wear parts. The eutectic form, often called cast carbide, is used extensively for hard facing, for mining and excavating, and for machine tools. Because of their hardness and wear resistance, cemented carbides are best known for their ability to cut, machine or grind difficult materials, including other metals. However, cemented carbides have diverse applications, usually under severe working conditions. For example, inserts and tips for tools used to cut and drill coal, rock and other minerals and the bits used to drill oil wells.

Tungsten carbide compositions have outstanding physical and mechanical properties, including: tensile strength to 200 ksi; compressive strength to 1000 ksi; hardness to 94 Rockwell A; good impact strength; outstanding dimensional stability; exceptional heat resistance and resistance to thermal shock; good cryogenic properties; good oxidation resistance to 538°C (1000°F) in oxidizing atmospheres. Because of the wide range of cemented carbide compositions, many of the outstanding properties can be combined in a single grade tailored to meet a specific set of conditions.

Structural applications demanding resistance to wear as well as high strength, rigidity and hardness include a variety of machine components and wear parts such as boring bar shanks, crusher rolls, ball mill liners, punches and dies for cold extrusion of steel. Corrosion-wear applications include seal rings, nozzles, orifice plates, bushings, valve components, mortar and pestle sets, and critical wear parts in magnetic tape recorders, including video tape machines.

Tungsten carbide in a nickel binder is the choice where electrolytic attack of the binder or etching might occur. Such attack can take place when a part is immersed in mineralized or boiler feed water. It also is more resistant to sodium hydroxide and hot sulfuric acid than the cobalt tungsten carbides.

Tungsten carbide compositions which provide excellent wear resistance with exceptional toughness and compressive strength are used for high pressure pistons, anvils, woodworking tools, nozzles, wear guides and slitter knives for nonmetallics. (The back cover lists the principal uses of tungsten carbides.)

Are tungsten heavy metals alloys?
Tungsten heavy metals are not true alloys, although they usually are designated as such. Essentially, tungsten heavy metals contain between 90 and 97% tungsten and the balance either copper and nickel or iron-nickel plus other appropriate elements.
Tungsten heavy metal compositions are easier to machine than pure tungsten. Tensile strength is several times higher than carbon steel and twice that of brass or cast iron. Tungsten heavy metals have low thermal expansion coefficients (about half that of iron). They retain dimensional stability over a wide temperature range. They also have excellent corrosion resistance; are fabricated economically by powder metallurgy methods; and, are readily machined to close tolerances.

**Where are heavy metals used?**

Tungsten heavy metals find extensive use in aircraft and helicopter counterweights used for static and dynamic balancing of ailerons, rudders and elevator controls and helicopter rotor blades. In some instances the weights are made in the form of screws which are adjusted to achieve balancing.

One of the most significant uses of tungsten heavy metals is in radiation shielding which utilizes the high density of these alloys to attenuate gamma- and x-rays. The efficiency permits use of smaller shielding devices with substantial overall weight savings. Applications include containers for radioactive cobalt 60, collimators, oil well exploration equipment and as x-ray targets in radiation therapy devices for cancer treatment.

Tungsten heavy alloys, along with other W components, used extensively in military and civilian ordnance. The main driver is the elimination of lead and depleted uranium, which result in greater risk to health and the environment than tungsten.

Tungsten heavy metal alloys recently have been finding uses in sporting goods. One use is in inserts for golf club heads. Locating of the heavy alloy redistributes the club's weight and increases its "sweet spot." An upsurge in dart throwing as a sport has resulted in the use of tungsten heavy metals being adopted as the material from which to make extremely well-balanced, accurate darts. The back cover shows the principal uses of tungsten heavy metals.

**How is tungsten processed and fabricated?**

Mineral and ore concentrates of tungsten are chemically decomposed to produce a high purity tungstate or oxide which can be hydrogen-reduced to a pure metal powder (Figure 1). In addition, tungsten is processed from concentrates by aluminothermic methods and by submerged arc electric furnaces to ferrotungsten, a common alloying additive, used in the production of steels and specialty alloys.

Powder metallurgy is used to produce most tungsten parts. Whether formed into ingots or bars for further processing, or into final shapes, powders are pressed and sintered in hydrogen atmospheres at temperatures of 1800°C (3270°F) or higher. Less common methods for producing tungsten products from powders include: vacuum arc melting; electron beam melting; zone melting and refining; slip casting and sintering; gas pressure bonding; and plasma spraying.

**Molybdenum (Mo)**

Tungsten pioneer, Scheele, was also a factor in discovering molybdenum in the 18th century. However, it wasn't until 1893 that German chemists prepared a 96% pure metal. The first commercial use was a year later when a French firm used it as an alloy in armor plate. Around 1919, Dr. Coolidge, another tungsten pioneer, prepared the first ductile molybdenum metal. Applications evolved very slowly for the next few decades and then accelerated rapidly after about 1925. More molybdenum is consumed annually than other refractory metals.

It is primarily used as an alloying element in steel for structural pipelines, tool steels and stainless steels. However, it also has many uses as a pure metal, in molybdenum-base alloys and in chemical forms.

Unlike tungsten, the largest reserves of molybdenum are found in the Western Hemisphere, with the principal reserves in the United States and Canada. About half comes from mines where its recovery is the principal goal. The rest comes as a byproduct from copper mining. Usually its content in ores is very low. It generally takes more than one ton of ore to recover four pounds of molybdenum.
**In what ways does molybdenum compare to tungsten?**
It has outstanding electrical and heat conducting capabilities, and relatively high tensile strength. Also molybdenum has good corrosion and wear characteristics which it imparts to the steel when used as an alloying element.

**What are the properties of unalloyed molybdenum?**
The expansion coefficient of molybdenum is almost a straight line over a wide temperature range. This quality in combination with its heat conducting is the reason it is used in bimetal thermocouples. Thermal conductivity is approximately 50% higher than that of steel, iron or nickel alloys. This property has led to its use in heat sinks. Its electrical conductivity is the highest of all refractory metals. It is about one-third that of copper, but is higher than that of nickel, platinum, or mercury.

In silicon semiconductors, molybdenum's electrical conductivity provides an efficient path for current. Its vapor pressure is low.

**What about its mechanical properties; is strength really affected that much by "working" the metal?**
Mechanical properties of unalloyed molybdenum are a function of the degree of work done below the recrystallization temperature. For superior ductility, parts should be given at least a 50% reduction in area.

The metal has unusual strength and hardness at elevated temperatures. However, when hot strength is necessary an alloy rather than pure molybdenum generally is chosen. Adding titanium and zirconium to molybdenum produces alloys having hot strength and recrystallization temperatures well above those of unalloyed molybdenum.

**Molybdenum is used in a number of corrosion resistant stainless steel alloys; how corrosion resistant is it?**
Molybdenum is used in many stainless steels. It is resistant to hydrofluoric acid and resists attack by iodine and chlorine at room temperature. It is attacked slowly by hydrochloric, sulfuric and phosphoric acids, rapidly by nitric acid. Molybdenum is not subject to hydrogen embrittlement and it does not form a hydride.

If oxidizing agents are not present, molybdenum is resistant to corrosion by mineral acids. It is resistant to some molten metals but at temperatures above 1000°C (1832°F), molten tin, aluminum, nickel, iron and cobalt will attack molybdenum rapidly.

Because molybdenum oxidizes rapidly at about 600°C (1112°F) in air, a protective coating is needed in hot air applications. Many coatings involve formation of a thin layer of MOSi2 on the surface of the molybdenum part. The compound has outstanding oxidation resistance up to about 1650°C (3002°F). In vacuum, uncoated molybdenum has a virtually unlimited life at high temperature. In outer space, for example, the oxidation rate of molybdenum is insignificant.

**What about high strength, high temperature molybdenum alloys?**
An important molybdenum alloy contains 0.5% titanium and 0.08% zirconium. At about 1100°C (2012°F) its strength is about twice that of unalloyed molybdenum. It can be considered for structural applications operating over 1000°C (1832°F) under conditions where unalloyed molybdenum normally is used. It has proved to be one of the best materials for hotwork applications because of its combination of high hot-hardness, high thermal conductivity, low thermal expansion and high resistance to heat checking when compared to hot-work steels. Major uses include die casting dies and cores, extrusion dies and special forging dies.

**What are the major applications of molybdenum alloys?**
Molybdenum’s most important use is as an alloying addition in steel. It provides tool steels and stainless steels with better wear resistance, strength and toughness. It also increases hot strength and corrosion resistance. Molybdenum is added in the form of molybdenic oxide or ferromolybdenum.

Molybdenum also is used in nickel- and cobalt-base high performance superalloys for turbine engine components. It improves high temperature strength and corrosion resistance.
Molybdenum exhibits valences of zero to six; as a result it or its compounds are used in catalysts in oxidation-reduction reactions, for organic synthesis and for a wide variety of petrochemical and pharmaceutical reactions.

Molybdenum disulfide powder is a natural lubricant and is used in lubricating oils and greases. It is an effective lubricant in vacuum and at high temperatures. It is very useful in preventing galling or seizing of metals under severe conditions. It has a low coefficient of friction, resists extreme pressures, shears readily and adheres to metals and plastics. Other major applications are listed on the back cover.

**How is molybdenum processed and fabricated?**

The chief source of molybdenum is molybdenite, molybdenum disulfide (MoS$_2$). It’s a soft mineral that looks like graphite.

Molybdenum is recovered by flotation beneficiation which yields a high grade concentrate containing about 90 to 95% MoS$_2$. The concentrate is roasted to drive off sulfur and a technical grade molybdic trioxide (MoO$_3$) is obtained. MoS$_3$ is sublimed to produce high purity molybdenum trioxide, or leached and processed to yield ammonium molybdate. These materials are reduced by hydrogen to molybdenum metal powder.

Figure 2 is a flow chart showing production steps from ore to finished product.

Molybdenum P/M ingots are rolled into sheet and rod, drawn into wire and tubing. The metal can then be stamped into simple shapes on conventional equipment. It is also machined with ordinary tools and GTA and EB welded or it can be brazed.
Columbium/Niobium (Cb/Nb)

When in 1801 Columbium was first identified from a piece of columbite found in Connecticut, it was named in honor of its land of origin. However, the true separation and identification of tantalum and columbium is difficult, since they are so frequently found together and have so many similar properties. The major difference being that columbium is less than one-half as heavy as tantalum. In fact, columbium's density falls into the range of nickel, copper and iron.

A European chemist in 1844 separated the two. Knowing that tantalum was named after the mythical Greek king, Tantalus, he named the other after the king's daughter, Niobe. He called it "niobium" In most countries around the world, this is the metal's accepted name.

The earliest use of niobium was as an alloying element for steel and this is still its major use. Although it has many other uses, its total applications are expected to increase dramatically in the next few decades.

Niobium has a wide variety of exciting potential uses. For example, superconducting columbium alloys are used in the construction of high-field strength magnets for research purposes. Although columbite is still the metal's major source, substantial quantities of niobium have been found in massive pyrochlore deposits, located in Africa, Brazil, and Canada.

Why is niobium used so frequently as an alloy?
Besides alloying well with nickel, cobalt and iron, and other popular alloying metals, niobium gives the alloy many of its refractory metal properties without adding unduly to the weight. Alloys containing niobium are widely used in aircraft gas turbines and aerospace rocket engines.

What are some of the basic properties of niobium?
The mechanical properties of niobium can vary greatly. A wide range of properties is obtainable by working and annealing, thereby making niobium a very versatile material. For example, a wide variety of strengths and elasticity can be obtained. It can also be strain-aged (or prestressed) within a temperature range of 300°C to 500°C (572°F to 932°F). The metal is also sensitive to interstitial elements.

Niobium has a high melting point and is immune to attack by most acids. It also offers lower density and low thermal neutron cross section compared to other refractory metals, which makes niobium useful in atomic reactors.

In use, columbium forms stable anodic oxide films which act as insulators. The element combines with all but the noble gases at elevated temperatures, but can release some species when heated in a vacuum to higher temperatures.

Isn't niobium used in gases because it is corrosion resistant?
Niobium resists attack by most gases below 200°C (392°F). However, at 350°C (662°F) it will begin to oxidize. It will react with nitrogen above 300°C (572°F). It is embrittled by hydrogen above 250°C (482°F). Fluorine and hydrofluoric acid gas also react at room temperature.

At ordinary temperatures niobium will resist attack by all mineral acids, with the exception of hydrofluoric acid, and it is not affected by mixed acids such as aqua regia. Above 175°C (347°F) concentrated sulfuric acid will dissolve the metal.

Niobium affinity for oxygen at elevated temperatures has led to its use as a getter in radio and electronic equipment. The stable, fully conductive oxide film formed on the surface when it is used as the anode in an electrolytic cell, has led to some use as a rectifier and for the manufacture of electrolytic capacitors.

Unalloyed niobium resists molten sodium, potassium, lithium, calcium, cerium, bismuth, lead and silver up to 1000°C (1832°F).
What are some of niobium’s major applications?
Niobium alloys fall into three major groups: moderately strengthened alloys for nuclear applications; high strength alloys for aerospace applications; and, superconducting alloys for electronic applications. Because of the poor oxidization resistance at high temperatures of niobium-base alloys, they must be coated before use in such environments. A niobium 1% zirconium alloy is used as a construction material in nuclear engineering, where its low neutron absorption coefficient and good resistance to liquid sodium or lithium is utilized. Niobium and some niobium-base alloys also have been used for heat shields in high temperature vacuum furnaces.

Niobium largest use is in the form of ferro-niobium containing from 63 to 68% Cb. This material is used in the production of austenitic stainless steels and high-strength low alloy steels (HSLA) and other alloys. Several such alloys are used in rocket and altitude control engines. The back cover lists the major uses of niobium and its alloys.

Why are niobium superconducting alloys so important?
At cryogenic temperatures electrical power can be transported without any loss due to resistance. This phenomenon can reduce energy consumption in many important high energy applications by as much as 80%. Niobium alloys have proven thus far to be the most practical superconductive material.

How is niobium processed?
Figure 3 shows how both tantalum and niobium are first dissolved from the ores, then separated from each other and prepared into pure compounds. They are then reduced and then refined, being consolidated into workable forms such as ingots, bars, or rods (from powder, pellets or sponge).

Niobium not only alloys with tantalum but also with iron, nickel, cobalt, chromium, tungsten, and many other elements. Niobium powder is fabricated by standard P/M methods. Powder is pressed into bars both mechanically and isostatically and presintered in a vacuum induction furnace until the bars have sufficient strength to be clamped into pairs between the electrodes of the sintering furnace.
Under high vacuum a heavy current is then passed through the bars until a temperature just below the melting point is reached. When cooled, the bars are rolled to consolidate the pores and then the bars are returned to the sintering furnace for resintering at 2300°C (4172°F). The metal then can be forged, rolled or swaged and reaches almost theoretical density.

However, niobium most frequently is consolidated by arc-melting under vacuum, in an inert gas, or by electron beam melting. Bars prepared from powders are used as consumable electrodes. The metal is available as ingot, sheet, rod, wire, and other standard mill shapes.

**Tantalum (Ta)**
As mentioned on the previous pages on niobium, these two metals are usually found together. It was identified in 1802 by the Swedish chemist, Ekeburg, who found the tantalum oxide ores so difficult to dissolve that he called the metal after the mythical Greek "Tantalus."

Tantalum is one of the most corrosion resistant materials available. The first ductile tantalum was developed in 1905 and until 1922, most applications were limited to certain instruments, particularly surgical.

Tantalum forms very stable anodic oxide films which make excellent electronic capacitors. For example, an oxide film provides both corrosion resistance and the dielectric properties that give the electrical flow "valve" action needed in a capacitor.

Tantalum comes principally from tin slags, and tantalite and columbite ores. Tantalite-rich ores are being mined in Canada.

**What are some of tantalum's applications?**
Mill products such as sheet are made into corrosion resistant chemical equipment such as bayonet heaters, vapor condensers, multi-tube heat exchangers, thermowells, rupture diaphragms and orifices.

Tantalum plugs are used to repair perforations in glass-lined steel equipment. Tantalum components are used in sulfuric acid concentrators, in temperature controllers for chromium plating and in distillation and condensation of acids and acidic chemicals.

Many surgical applications have been opened to tantalum because it is inert to body fluids and tissues. It is used for surgical implants, for suture wire, cranial repair plates and for wire gauze for abdominal muscle support in hernia repair surgery.

Tantalum carbide is added to some grades of cemented carbides to make hard carbide cutting tools which have a low coefficient of friction and a high resistance to mechanical shock. The back cover lists some of the major uses of tantalum and tantalum alloys.

**Isn't its corrosion resistance a factor in many applications?**
Tantalum's inertness to many chemicals has fostered its use as a corrosion resistant material in severe acid environments. It is resistant to sulfuric, hydrochloric, and nitric acids, organic chemicals and many liquid metals. Thus it is used in heat exchangers, spargers and reaction vessels in organic reactions, particularly when corrosive inorganics are involved.

Applications are determined by inertness to chemical attack at moderate temperatures, reactivity at high temperatures, good strength and ductility and by the dielectric properties of its electrolytic oxide film.

**Are tantalum capacitors widely used?**
The electronic industry is a major market for high purity tantalum, particularly for capacitors. Tantalum capacitors provide higher volumetric capacitance efficiency than other capacitor materials and perform better at both low and high temperatures.
Also, tantalum combines with certain gases at elevated temperatures and will release some of these gases when heated in a vacuum to a higher temperature. This property is extremely useful in electronic tubes. And, good high temperature strength, low vapor pressure and the gettering effect have made tantalum an important metal in special-purpose vacuum tubes where it removes residual gases. It can be formed and welded into anodes and grids, which are cleaned easily in strong acids. However, capacitors are the major electronic use of tantalum and the development of higher-capacitance powders has broadened the field of application. With these powders, less is needed to make a unit of a given capacitance rating; high capacitance permits miniaturization.

Tantalum capacitors operate in computers and military hardware, color television sets, radios and cell phones.

**What about tantalum alloys?**

Tantalum alloys that have good high temperature strength are used in many aerospace products. However, all tantalum alloys oxidize rapidly and surface coatings are required for elevated temperature service in oxidizing environments.

Tantalum and niobium alloy with each other and with nickel, cobalt, chromium, tungsten and many other elements. Tantalum alloys have good fabricating characteristics.

**With such a high melting point, how is it fabricated?**

The high melting point and reactivity of tantalum prevents its consolidation to near finished shape by casting. Thus, many fabricated shapes start from powders. However, the technology of powder metallurgy has advanced to such a high state that there is no loss of flexibility. In fact, even if tantalum did have a lower melting point, P/M processing would still be used because of other advantages.

Tantalum powder can be compacted mechanically or isostatically. Compacting presses are used for smaller shapes such as bars, which are resistance sintered. Isostatically pressed shapes can be either resistance or induction sintered.

Tantalum ingots up to 1600 Kilograms (3500 lbs.) are made by arc or electron beam melting of compacted and sintered bars. Electron beam melted ingots are noted for their high purity, excellent ductility and good weldability.

P/M bars or melted ingots are extremely ductile. They can be cold rolled into sheet and foil and can be formed and drawn into many shapes.

Tantalum can be lap or seam welded, TIG welded and electron beam welded. It is used in multi-tube heat exchangers in corrosive environments in the chemical industry. It is also used to clad steel and copper pipe and to line chemical reaction vessels.

**Rhenium (Re)**

Rhenium was discovered in 1925 by German scientists who detected the presence of the metal in platinum and columbium ores. Rhenium does not have its own specific ore. It is, however, widely distributed in many minerals such as molybdenites, tantalite, platinum ores, molybdenite bearing copper porphyry, and the oxides of manganese.

Molybdenites associated with the porphyry ores of copper are the most important commercial sources of rhenium. Rhenium is extracted from flue gases during the roasting of molybdenite concentrates. Recovered rhenium is then treated in ion exchange systems, precipitated as ammonium perrhenate and reduced by hydrogen to form a metal powder.

While it is similar in many respects to other refractory metals, rhenium's unusual combination of properties from both a chemical and metallurgical point of view makes it unique even among its close relatives.
How does it compare to other refractory metals?
Among the elements, rhenium has a melting point exceeded only by those of tungsten and carbon; density exceeded only by those of osmium, iridium and platinum; and a ductile to brittle transition temperature does not exist in the pure metal. It is unique among refractory metals in that it does not form carbides.

Is rhenium used in alloys?
It is highly desirable as an alloying addition with other refractory metals. The addition of rhenium greatly enhances the ductility and tensile strength of these metals and their alloys, even after heating above the recrystallization temperature. A prime example is the complete ductility exhibited by a Mo-Re fusion weld.

Rhenium alloys are gaining acceptance in nuclear reactors, semiconductors, electronic-tube components, thermocouples, gyroscopes, miniature rockets, electrical contacts, thermionic converters, and other commercial and aerospace applications.

Tungsten-rhenium alloys are used to surface molybdenum targets in x-ray tube manufacture. Other rhenium alloys (with tungsten or molybdenum) are used for filaments, grid heaters, cathode cups, and ignitor wires in photo-flash bulbs.

How is rhenium being used?
Surprisingly, the most important use of rhenium is as a chemical-rather than as a physical material.

Rhenium has found important applications in catalysts for reforming in conjunction with platinum, in selective hydrogenation, and in other chemical reactions. The most common processes in which it is used or has been tested and used as a catalyst include alkylation, dealkylation, dehydrochlorination, dehydrogenation, dehydroisomerization, enrichment of water, hydrocracking, hydrogenation, oxidation, and reforming. The outstanding property of rhenium catalysts is their high selectivity, particularly in hydrogenation reactions. It also displays unusually high resistance to such catalyst poisons as nitrogen, sulfur and phosphorus.

What are some of its properties?
Rhenium is unattacked in the presence of molten copper, silver, tin and zinc. It dissolves readily in molten iron and nickel. It is stable in contact with aluminum. The hardening effect of rhenium on platinum is also notable. At elevated temperature, rhenium stands up well in hydrogen and inert atmospheres. It is resistant to hydrochloric acid and shows good resistance to salt water corrosion and the mechanical effects of electrical erosion.

How is it fabricated?
The powders are compacted, vacuum presintered, and then hydrogen sintered at high temperatures. Rhenium and its alloys are processed by standard P/M technology. Fabrication is accomplished by cold working with frequent annealing steps.
Major Applications

Tungsten Metal

- Incandescent, fluorescent and automotive lamp filaments
- Anodes and targets for x-ray tubes
- Semiconductor supports
- Electrodes for inert gas arc welding
- High capacity cathodes
- Electrodes for xenon arc lamps
- Automotive ignition systems
- Rocket nozzles
- Electronic tube emitters
- Uranium processing crucibles
- Heating elements and radiation shields
- Alloying elements in steels and superalloys
- Reinforcement in metal-matrix composites
- Catalysts in chemical and petrochemical processes
- Lubricants

Cemented Tungsten Carbide

- Cutting tools for metal machining
- Mining and oil drilling tools
- Forming dies
- Metal forming rolls
- Thread guides
- Bushings
- Valve seats
- Blades for cutting hard and abrasive materials
- Ball point pen points
- Masonry saws and drills

Tungsten Heavy Metal

- Radiation shields
- Aircraft counterweights
- Self-winding watch counterweights
- Aerial camera balancing mechanisms
- Helicopter rotor blade balance weights
- Gold club weight inert
- Dart bodies
- Armament fuses
- Vibration damping
- Military Ordnance
- Shotgun pellets

Molybdenum

- Alloying additions in irons, steels, stainless steels, tool steels and nickel-base superalloys
- High-precision grinding wheel spindles
- Spray metallizing
- Die-casting dies
- Missile and rocket engine components
- Electrodes and stirring rods in glass manufacture
- Electric furnace heating elements, boats, heat shields and muffle liner
- Zinc refining pumps, launders, valves, stirrers and thermocouple wells
- Nuclear reactor control rod production
- Switch electrodes
- Supports and backing for transistors & rectifiers
- Filaments & support wires for automobile headlight
- Vacuum tube getters
- Rocket skirts, cones and heat shields
- Missile Components
- Superconductors
- Chemical process equipment
- Heat shields in high temperature vacuum furnaces
- Nuclear engineering equipment
- Alloying additives in ferrous alloys & superconductors

Tantalum

- Electrolytic capacitors
- Heat exchangers
- Bayonet heaters
- Thermometer wells
- Vacuum tube filaments
- Chemical process equipment
- High temperature furnaces components
- Crucibles for handling molten metal and alloys
- Cutting tools
- Aerospace engine components
- Surgical implants
- Alloy additive in superalloys

For further information on refractory metals and the names of firms in the industry contact the Refractory Metals Association at 105 College Road East, Princeton, N.J. 08540.
RMA is a division of the Metal Powder Industries Federation.
Tel: 609-452-7700 or visit our website www.mpif.org