MOLYBDENUM AND MOLYBDENUM ALLOYS

1. Introduction

Molybdenum [7439-98-7], identified as a discrete element in 1778 by Scheele, remained a laboratory curiosity until the late 1880s when French metallurgists produced a molybdenum-containing armor-plate steel. Molybdenum was also found to be useful as an additive to tool steels and in chemical dyes (see STEEL; TOOL MATERIALS). The first significant industrial applications of molybdenum were developed during World War I when it was employed in armor-plate steels, tool steels, and high strength steels for aircraft engines.

After World War I, the demand for molybdenum dropped to very low levels. In the 1920s, the Society of Automotive Engineers adopted the 4100 series of chromium–molybdenum steels. From that beginning, the importance of molybdenum both as an alloying element and as a refractory metal grew steadily (see REFRACTORIES). Along with the many metallurgical uses of the metal, molybdenum compounds (qv) are used in such chemical applications as catalysis (qv), corrosion protection (see CORROSION AND CORROSION CONTROL), and lubrication (see LUBRICATION AND LUBRICANTS). A series of conferences (1) on the chemistry and uses of molybdenum provides excellent background information, including discussion of the role of molybdenum in life processes.

2. Sources and Supply

Most of the world's supply of molybdenum comes as a by-product or co-product from copper (qv) mining. Only about one quarter of the supply comes from primary mines. A small but significant supply of molybdenum is also obtained from the processing of spent petroleum catalysts (see CATALYSTS, REGENERATION; RECYCLING, NONFERROUS METALS). The most abundant mineral, and the only one

Table 1. **World Mine Production, Reserves, and Reserve Base, t**

	Mine production		Reserves	Reserve base
	1998	1999[a]	(thousand metric tons)	
United States	53,300	44,100	2,700	5,400
Armenia	2,500	2,500	20	30
Canada	7,991	8,000	450	910
Chile	25,298	25,000	1,100	2,500
China	30,000	33,000	500	1,000
Iran	600	700	50	140
Kazakhstan	100	200	130	200
Mexico	5,949	6,000	90	230
Mongolia	2,000	2,000	30	50
Peru	4,344	4,000	140	230
Russia	2,000	3,000	240	360
Uzbekistan	500	500	60	150
Other countries				590
World total (may be rounded)	135,000	129,000	5,500	12,000

[a] Estimated.

of commercial significance, is molybdenite [1309-56-4], MoS_2. The minerals powellite [14020-57-0], $Ca(MoW)O_4$, and wulfenite [14913-82-7], $PbMoO_4$, also are known but are not sources of the metal. Primary ore bodies in the Western Hemisphere contain ca 0.2–0.4% molybdenum and give a recovery of 2–4 kg/t of ore. Copper ores typically contain less than 0.1% Mo.

Distribution of molybdenum reserves and production capacity are concentrated in a few countries of the world. The United States, Chile, Canada and Mexico provided 91% of molybdenum contained in concentrate in 1998. These countries possess about 90% of the estimated 12×10^6 t in world reserve (2). World reserve and production data for 1998 and 1999 are shown in Table 1 (3).

2.1. Market Demand. U.S. exports of molybdenum ore and concentrates for 1997 and 1998 are shown in Table 2 (2). U.S. Imports for consumption of molybdenum for 1997, 1998, and November 1999 are shown in Table 3 (2). U.S. production of concentrate was 53,300 t in 1998. This represented 39% of world production (135,000 t). U.S. net production of molybdenum products increased by 9200 t in 1998 (see Table 4) (2).

There is no United States government stockpile of molybdenum.

3. Physical Properties

Molybdenum has many unique properties, leading to its importance as a refractory metal (see REFRACTORIES). Molybdenum, atomic no. 42, is in Group 6 (VIB) of the Periodic Table between chromium and tungsten vertically and niobium and technetium horizontally. It has a silvery gray appearance. The most stable valence states are +6, +4, and 0; lower, less stable valence states are +5, +3, and +2.

Table 2. **U.S. Exports of Molybdenum Ore and Concentrates (Including Roasted and Other Concentrates), by Country**[a,b]

	1997		1998	
Country	Quantity (contained molybdenum)	Value (thousands)	Quantity (contained molybdenum)	Value (thousands)
Australia	219	$1,070	82	$539
Belgium	14,300	67,300	4,470	23,000
Brazil	53	321	60	475
Canada	556	3,790	731	4,120
Chile	6,450	23,500	6,840	20,400
China	313	1,040	423	829
Germany	845	3,560	461	1,640
India			9	200
Italy	322	2,090	449	2,280
Japan	5,840	44,600	4,410	31,300
Korea, Republic of	2	24	9	115
Mexico	6,060	25,400	4,220	19,900
Netherlands	15,600	84,500	12,800	68,700
Sweden	916[c]	6,460[b]	894	4,870
United Kingdom	5,610	28,300	5,480	31,000
Other	150	1,280	362	1,640
Total	57,200	293,000	41,700	211,000

[a] Data are rounded to three significant digits; may not add to totals shown.

[b] Source: Bureau of the Census.

[c] Revised.

Molybdenum, a typical transition element, has the maximum number, five, of unpaired 4*d* electrons, which account for its high melting point, strength, and high modulus of elasticity. There are many similarities between molybdenum and its horizontal and vertical neighbors in the periodic system.

The melting point of molybdenum is about 2626°C, 1100°C above that of iron. Only two other commercially significant elements, tungsten and tantalum, have higher melting points than molybdenum. As a result of its high melting temperature, molybdenum metal has strength characteristics at temperatures where most metals are in the molten state, and some applications, such as for furnace parts, rocket nozzles, welding tips, thermocouples, glass melting electrodes, dies, and molds, are based on this property. Atomic properties are given in Table 5, thermal properties in Table 6, and electrical, magnetic, and optical properties are given in Table 7.

4. Chemical Properties

Molybdenum has good resistance to chemical attack by mineral acids, provided that oxidizing agents are not present. The metal also offers excellent resistance to attack by several liquid metals. The approximate temperature limits for

Table 3. **U.S. Imports for Consumption of Molybdenum**[a,b]

		1997			1998				Nov. 1999	
Item	HTS No.	Gross weight, t	Contained molybdenum	Value (thousands)	Gross weight, t	Contained molybdenum	Value (thousands)	Gross weight	Contained molybdenum	Value (c.i.f.) (thousands)
molybdenum ore and concentrates, roasted	2613.10.0000	8,100	5,040	$48,600	8,020	5,090	$39,700	842,000	529,000	$3,110
molybdenum ore and concentrates, other	2613.90.0000	2,420	1,290	8,810	2,710	1,480	7,810	—	—	—
molybdenum oxides and hydroxides	2825.70.0000	1,420	NA	11,200	1,180	NA	9,610	41,400	NA	256
molydates of ammonium	2841.70.0000	848	456[d]	6,580	1,240	684	8,980	160,000	90,400	820
molybdates all others	2841.70.5000	240	156	1,320	192	113	982	17,000	5,970	59
molybdenum orange	3206.20.0000	1,620	NA	5,880	2,050	NA	7,950	109,000	NA	439
mixtures of inorganic compounds	3823.90.3400	[c]	[d]	[c]		[d]				
ferromolybdenum	7202.70.0000	5,840	3,640	36,700	7,690	4,830	44,000	1,070,000	676,000	4,670
molybdenum powders	8102.10.0000	77	68	2,570	110	103	3,210	11,200	10,900	233
molybdenum unwrought	8102.91.0000	326	301	4,890	145	137	2,110	1,280	1,260	55
molybdenum waste and scrap	8102.91.5000	536	527	8,670	296	292	4,080	10,000	9,990	126
molybdenum wire	8102.93.0000	4	NA[d]	475	6	NA[d]	500	474	NA	34
molybdenum other	8102.99.0000	7	NA[d]	1,170	8	NA[d]	1,650	1,430	NA	85
Total		21,400 [c]	11,500	137,000	23,700	12,700	131,000	2,270,000	1,320,000	9,880

[a] Data are rounded to three significant digits; may not add to totals shown.

[b] Revised.

[c] NA = Not available.

[d] Source: Bureau of the Census.

Table 4. **Salient Molybdenum Statistics**[a,b]

	1994	1995	1996	1997	1998
United States:					
concentrate:					
production	46,800	60,900	54,900	60,900	53,300
shipments	46,000	61,700	57,900	59,100	50,500
value, $\times 10^3$	$284,000	$651,000	$456,000	$406,000	$200,000
reported consumption	17,200	25,500	24,500	24,300	35,900
imports for consumption	2,280	5,570	5,480	6,330	6,570
stocks, December 31:					
concentrate, mine and plant	5,510	5,390	2,470	3,660	6,270
product produces[c]	3,940	4,820	5,780	6,500	7,780
2,130[d]	2,130[d]	2,220[d]	1,650	1,220	2,170
Total	*11,600*[d]	*12,400*	*9,900*	*11,400*	*16,200*
primary products:					
production	31,100	46,000	46,300	48,000	57,200
shipments	21,400	24,000	24,100	25,900	38,000
reported consumption, by end use	19,100	19,900	20,900	20,000[d]	19,000
World: mine production	*108,000*[d]	*136,000*[d]	*126,000*[d]	*139,000*[d]	*135,000*[e]

[a] Data are rounded to three significant digits; may not add to totals shown.

[b] Metric tons, of contained molybdenum, unless otherwise specified.

[c] Includes technical and purified molybdic oxide, briquets, ferromolybdenum, phosphomolybdic acid, molybdenum disulfide, molybdic acid, ammonium molybdate, sodium molybdate, calcium molybdate, molybdenum metal, pellets, molybdenum pentachloride, and molybdenum hexacarbonyl.

[d] Revised.

[e] Estimated.

molybdenum to be considered for long-time service while in contact with various metals in the liquid state are as follows:

Metal	Limit, °C	Metal	Limit, °C
bismuth	1425	mercury	600
gallium	400	potassium	1100
lead	1200	sodium (liquid and vapor)	1500
lithium	925		
magnesium	700		

In addition, molybdenum has high resistance to a number of alloys of these metals and also to copper, gold, and silver. Among the molten metals that severely attack molybdenum are tin (at 1000°C), aluminum, nickel, iron, and cobalt. Molybdenum has moderately good resistance to molten zinc, but a molybdenum–30% tungsten alloy is practically completely resistant to molten zinc at temperatures up to 800°C. Molybdenum metal is substantially resistant to many types of molten glass and to most nonferrous slags. It is also resistant to liquid sulfur up to 440°C.

Above ca 600°C, unprotected molybdenum oxidizes so rapidly in air or oxidizing atmospheres with formation of volatile MoO_3, that extended use under

Table 5. **Physical Properties of Molybdenum**[a]

Property	Value
isotopes	
natural	92,94,95,96,97,98,100
artificial	90,91,93,99,101,102,105
atomic weight	95.94
atomic radius, coordination number 8, pm	136
ionic radius, pm	
Mo^{3+}	92
Mo^{6+}	62
atomic volume, cm^3/mol	9.41
lattice	
type	body-centered cubic
constant at 25°C, pm	314.05
fast-neutron absorption cross section, 10/250 keV, m^2[b]	9×10^{-28}
ionization potential, eV	7.2
work function, eV	
apparent positive-ion	8.6
apparent electron	4.2
density at 20°C, g/cm^3	10.22
coefficient of friction vs steel at HRC[c] 44	
dry	
static	0.271
dynamic	0.370
humid	
static	0.405
dynamic	0.465
compressibility at 293°C, cm^2/kg	3.6×10^{-7}
velocity of sound at 2.25 MHz, cm/s	
longitudinal wave, V_L	$6.37 \pm 0.02 \times 10^5$
shear wave, V_S	$3.41 \pm 0.06 \times 10^5$
thin rod, V_O	5.50×10^5
surface tension at melting point, mN/m(=dyn/cm)	2240

[a] Refs. (4–8).
[b] To convert m^2 to barn, divide by 10^{-28}.
[c] HRC = Rockwell C hardness.

these conditions is impractical. Because no molybdenum-base alloy that combines high oxidation resistance and good high temperature properties has been discovered, protective coatings are required where oxidation is a problem. Various coatings, differing in maximum time–temperature capabilities and in physical and mechanical characteristics, are available. The most widely used coatings depend on the formation of a thin surface layer of $MoSi_2$ on the molybdenum metal part. This compound has outstanding oxidation resistance at temperatures up to about 1650°C (see REFRACTORY COATINGS).

In a vacuum, uncoated molybdenum metal has an unlimited life at high temperatures. This is also true under the vacuum like conditions of outer space. Pure hydrogen, argon, and helium atmospheres are completely inert to molybdenum at all temperatures, whereas water vapor, sulfur dioxide, and nitrous and nitric oxides have an oxidizing action at elevated temperatures. Molybdenum is relatively inert to carbon dioxide, ammonia, and nitrogen

Table 6. **Thermal Properties of Molybdenum**[a]

Property	Value
melting point, °C	2626 ± 9
heat of fusion,[b] kJ/mol[c]	28
boiling point, °C	5560
heat of vaporization, kJ/mol[c]	491
entropy of crystals, $S°_{298.16}$, J/(mol·K)[c]	28.6
vapor pressure, Pa[d]	
at 1725°C	3.95×10^{-9}
2225°C	4.35×10^{-6}
2610°C	1.72×10^{-4}
2725°C	4.05×10^{-4}
3225°C	8.71×10^{-3}
3725°C	8.41×10^{-2}
4225°C	4.76×10^{-1}
4725°C	1.82
5225°C	5.57
rate of evaporation, r_{ev}, g/(cm^2·s)	$\log r_{ev} = 17.11 - 38,600\,T^e - 1.76 \log T^e$
diffusivity, cm^2/s	
at 200°C	0.43
540°C	0.40
870°C	0.38
specific heat at 100°C, kJ/(kg·K)[c]	0.27
coefficient of linear expansion, %	
at 0–400°C	0.23
0–800°C	0.46
0–1200°C	0.72
thermal conductivity, W/(m·K)	
at 500°C	122
1000°C	101
1500°C	82

[a] Refs. (4–8).

[b] Value is estimated.

[c] To convert J to cal, divide by 4.186.

[d] To convert Pa to mm Hg, multiply by 0.0075.

[e] T in Kelvin.

atmospheres up to about 1100°C; a superficial nitride film may be formed at higher temperatures in the latter two gases. Hydrocarbons and carbon monoxide may carburize molybdenum at temperatures above 1100°C.

In a reducing atmosphere, molybdenum is resistant at elevated temperatures to hydrogen sulfide, which forms a thin adherent sulfide coating. In an oxidizing atmosphere, however, molybdenum is rapidly corroded by sulfur-containing gases. Molybdenum has excellent resistance to iodine vapor up to about 800°C. It is also resistant to bromine up to about 450°C and to chlorine up to about 200°C. Fluorine, the most reactive of the halogens, attacks molybdenum at room temperature.

Table 7. **Electrical, Magnetic, and Optical Properties**[a]

Property	Value
electrical resistivity, nΩ·m	
at 0°C	50
1000°C	320
2000°C	610
Franz-Wiedemann or Lorenz constant	2.72
hydrogen overpotential, 1×10^{-2} A/cm^2, V	0.44
electrochemical equivalent, Mo^{6+}, mg/C	0.1658
minimum arcing amperage, A	
at 24 V	10
110 V	1.5
220 V	1.0
magnetic susceptibility,[b] κ_p, m^3/kg	
at 25°C	0.93×10^{-6}
1825°C	1.11×10^{-6}
optical reflectivity, %	
at 500 nm	46
10,000 nm	93
total hemispherical emissivity	
at 1200 K	0.104
1600 K	0.163
2000 K	0.209
2400 K	0.236
thermionic emission of high vacuum, mA/cm^2	
at 1600°C	ca 0.7
2000°C	85
spectral emissivity	
at 390 nm	ca 0.43
6700 nm	0.40
radiation for 550 nm at 20°C, % of black-body radiation	54
total radiation, W/cm^2	
at 527°C	ca 0.2
1127°C	3.0
1727°C	19
2327°C	68

[a] Refs. (4–8).

[b] Mo is paramagnetic.

5. Processing Ores

Molybdenite is concentrated by first crushing and grinding the ore, and passing the finely ground material through a series of flotation (qv) cells (see MINERALS RECOVERY AND PROCESSING). Operations which recover molybdenum as a by-product of copper mining produce a concentrate containing both metals. Molybdenite is separated from the copper minerals by differential flotation.

Molybdenite concentrate contains about 90% MoS_2. The remainder is primarily silica, with lesser amounts of Fe, Al, and Cu. The concentrate is roasted to convert the sulfide to technical molybdic oxide. Molybdenum is added to steel in the form of this oxide. In modern molybdenum conversion plants, the oxidized sulfur formed by roasting MoS_2 is converted to sulfuric acid.

Technical molybdic oxide can be reduced by reaction of ferrosilicon in a thermite-type reaction. The resulting product contains about 60% molybdenum and 40% iron. Foundries generally use ferromolybdenum for adding molybdenum to cast iron and steel, and steel mills may prefer ferromolybdenum to technical molybdic oxide for some types of steels.

A small portion of molybdenite concentrate production is purified to yield lubricant-grade molybdenum disulfide, a widely used solid-state lubricant.

Chemical products are produced from technical-grade oxide in two very different ways. Molybdenum trioxide can be purified by a sublimation process because molybdenum trioxide has an appreciable vapor pressure above 650°C, a temperature at which most impurities have very low volatility. The alternative process uses wet chemical methods in which the molybdenum oxide is dissolved in ammonium hydroxide, leaving the gangue impurities behind. An ammonium molybdate is crystallized from the resulting solution. The ammonium molybdate can be used either directly or thermally decomposed to produce the pure oxide, MoO_3.

6. Manufacturing Processes

Ammonium molybdate or molybdenum trioxide is reduced to molybdenum metal powder by hydrogen in a two-stage process. In the first stage, MoO_3 or ammonium molybdate is reduced to molybdenum dioxide, MoO_2, at temperatures around 600°C; in the second stage, the dioxide is reduced to metallic powder at temperatures near 1100°C. Both rotary and boat-and-tube types of furnaces are used for first-stage reduction. Boat-and-tube furnaces are used for the second stage.

6.1. Wire. Molybdenum wire is produced by a long-established powder metallurgy process (see METALLURGY, POWDER). Molybdenum powder is compacted in dies in a hydraulic press at pressures in the 210–280 MPa (30,000–40,000 psi) range to produce bars approximately 30 mm square. These bars are sintered by electrical resistance heating in hydrogen atmosphere chambers or bells. Currents are adjusted to about 90% of that required to cause melting; the bars attain temperatures in the range 2200–2300°C. The sintered bars are hot-rolled or swaged to small-diameter rods which are subsequently drawn to fine wire. Tungsten carbide dies are used for drawing heavy-gauge wire and diamond dies for fine-gauge wire. Drawing of the coarse sizes is accomplished at elevated temperatures; final drawing of fine wire is performed at ambient temperatures. Lubrication is provided by suspensions of graphite or molybdenum disulfide. At various stages in the reduction process, the wire may be annealed at 800–850°C to facilitate further working.

6.2. Mill Products. Two consolidation processes are used to produce molybdenum mill products such as forging billets, bars, rods, plate, sheet, and foil: powder metallurgy and arc-casting or vacuum-arc melting. In the powder metallurgy process, molybdenum powder is compacted isostatically in hydraulic pressure chambers to cylindrical bars or billets and to rectangular sheet bars. The green compacts are subsequently sintered in hydrogen atmosphere muffle furnaces for several hours at 1600–1700°C. The longer time at lower temperature results in about the same 95% density produced by bell sintering. Sintered bars up to 75 mm in diameter are rolled directly to smaller bars; larger consolidations of 155–300 mm diameter are extruded to bars for further processing. Pressed and sintered sheet bars are rolled directly to plate, sheet, and foil. As mechanical work proceeds, the density of powder metallurgy molybdenum improves to the full theoretical density.

In the arc-casting process developed in the 1940s, a consumable electrode of compacted molybdenum powder is melted by an alternating current arc inside a water-cooled copper tube, or mold, to form an ingot. A blend of molybdenum powder, carbon for deoxidation, recycled machine chips of pure molybdenum, and any required alloying elements is charged into a hopper. The hopper feeds a device that continuously compacts the loose bulk charge into a column of hexagonal wafers about 67 mm across flats and 15–20 mm thick. Following compaction the column is sintered by resistance heating to temperatures near 1200°C to strengthen the compacted metal and to weld adjacent wafers together. The pressed and sintered electrode extends downward along the axis of the water-cooled copper mold to the position of the arc between it and the molten pool of metal at the top of the ingot. Compacting, sintering, and melting are performed continuously and consecutively in connected chambers evacuated to pressures of 1.3–6.5 Pa (10–50 μm Hg). Ingots weighing 820 kg have been produced consistently in the pressing, sintering, and melting (PSM) machine. The cast ingots have full theoretical density. The distribution of alloying elements is microscopically uniform throughout the entire ingot.

6.3. Metalworking. Molybdenum metal can be mechanically worked by almost any process: forging, extrusion, rolling, bending, punching, stamping, deep drawing, spinning, conventional forming, and power roll forming. Except for fine wire and thin sheet, it is recommended that mill products be heated moderately for most shaping operations. Infrared lamps or hot plates often provide adequate heating for thinner gauges of molybdenum sheet; for heavier gauges, it is advantageous to heat the metal in a furnace or to use an oxyacetylene torch.

Using proper tool angles, molybdenum can be machined without difficulty. Although high speed steel tools are recommended for heavy, intermittent cuts on lathes, sintered carbide tools are preferred for most turning operations, shaping, or milling. Speeds up to 182 surface m/min can be used on lathes having carbide tools.

For many applications requiring joints of molybdenum, mechanical methods and brazing are satisfactory. Mechanical joints can be produced without deterioration of the properties developed by cold-working the metal. Brazed joints suffer from loss of strength at high temperatures and lowering of the melting range at the juncture. Nickel foil has been used successfully as the brazing metal to join flat surfaces of molybdenum.

Molybdenum can be welded to itself by a number of fusion welding (qv) processes, including electric arc (gas–tungsten arc and gas–metal arc), electric resistance (spot welding and flash welding), and electron beam. In these welding processes, all the physical properties of molybdenum are retained but the tensile properties developed by cold-working are reduced. In fusion welding there is always the cast weld metal and a heat-affected zone (haz) comprising recrystallized, coarse grains. Each of these structures has lower strength and lower ductility than the parent metal. The high melting point of molybdenum and its high thermal conductivity necessitate high energy input and rapid travel to minimize the heat-affected zone for optimally welded joints. To improve the strength and ductility of a fusion weld, it is beneficial to warm-work the joint whenever feasible.

Because the ductility of molybdenum is adversely affected by even minute amounts of oxygen, stringent precautions must be taken to prevent it from being present during fusion welding. Inert gas atmospheres must be as free of oxygen as possible. Commercial argon, helium, and hydrogen may contain oxygen levels which can cause cracking and porosity unless specific purification measures are provided. Thorough cleaning of the faying surfaces is essential for optimum ductility. Such surfaces have usually become contaminated during prior processing and handling. Wrought arc-cast molybdenum can be welded with less difficulty than powder metallurgy products because the arc-cast metal has been out-gassed and deoxidized during melting.

Excellent high strength welds have been produced by inertia-welding, or friction-welding, which develops essentially no heat-affected zone. The actual interface is wrought molybdenum because the molten metal and the adjacent solid metal that has been raised to very high temperatures have been expelled from the joint.

7. Economic Aspects

In 1998, iron and steel production accounted for about 75% of molybdenum consumed. Major applications were as follows: machinery, 35%; electrical, 15%; transportation, 15%; chemicals, 10% oil and gas industry, 10%; and others, 15% (3).

Annual average prices of molybdenum concentrate are shown in Table 8 (9). From 1971 to 1974 price controls were imposed by the U.S. government. Between 1970 and 1980, a shortage was expected, but did not materialize. New mines came on stream three years after the peak prices in 1980. Between 1992 and 1994, after the Persian Gulf War, dissolution of the USSR, and a recession prices decreased. In 1995, a shortage was presumed and the price increased. This shortage did not come to pass. Prices remained about the same between 1996 to 1998 as the market stabilized.

8. Analytical Methods

Molybdenum contents in ore concentrates and technical oxide are most accurately determined gravimetrically by precipitating lead molybdate. Molybdenum content is usually not determined on pure compounds or metal. Instead, spectrographic methods are used to measure impurity elements that must be controlled. Carbon and oxygen in metal products are measured by standard gas analysis methods.

Table 8. **Annual Average Molybdenum Concentrate Price**[a,b]

Year	Price	Year	Price	Year	Price	Year	Price
1912	0.45	1934	1.57	1956	2.51	1978	10.40
1913	0.67	1935	1.57	1957	2.64	1979	13.60
1914	2.24	1936	1.48	1958	2.67	1980	20.10
1915	2.24	1937	1.52	1959	2.80	1981	17.80
1916	2.24	1938	1.57	1960	2.80	1982	14.80
1917	3.16	1939	1.52	1961	2.90	1983	7.60
1918	3.27	1940	1.55	1962	3.00	1984	7.10
1919	2.58	1941	1.52	1963	3.00	1985	6.90
1920	1.12	1942	1.59	1964	3.30	1986	5.60
1921	1.57	1943	1.59	1965	3.50	1987	5.70
1922	0.49	1944	1.59	1966	3.50	1988	6.00
1923	1.70	1945	1.59	1967	3.60	1989	7.10
1924	2.02	1946	1.52	1968	3.60	1990	5.70
1925	0.90	1947	1.52	1969	3.70	1991	4.60
1926	1.57	1948	1.55	1970	3.80	1992	4.90
1927	1.70	1949	1.86	1971	3.70	1993	3.80
1928	2.24	1950	1.90	1972	3.70	1994	2.50
1929	1.12	1951	2.13	1973	3.60	1995	8.30
1930	1.23	1952	2.15	1974	4.40	1996	5.00
1931	0.94	1953	2.17	1975	5.50	1997	5.00
1932	1.12	1954	2.24	1976	6.50	1998	5.80
1933	1.68	1955	2.31	1977	8.00	1999	3.75[c]

[a] Dollars per kilogram molybdenum content.

[b] Sources: Prices for the period from 1912 to 1955 were published by the U.S. Bureau of Mines, but origin is undetermined. E&MJ Metal and Mineral Markets (1956–66). Metals Week (1967–92). Platt's Metals Week (1993–98).

[c] From Ref. .

9. Environmental and Health and Aspects

Because of its position in the Periodic Table, molybdenum has sometimes been linked to chromium (see CHROMIUM AND CHROMIUM ALLOYS) or to other heavy metals. However, unlike those elements, molybdenum and its compounds have relatively low toxicity, as shown in Table 9. On the other hand, molybdenum has been identified as a micronutrient essential to plant life (18,19) (see FERTILIZERS), and plays a principal biochemical role in animal health as a constituent of several important enzyme systems (see MINERAL NUTRIENTS).

Information on the toxic effects of molybdenum in humans is scarce. A high incidence of gout was reported in a locale in Armenia where the soil contained exceptionally high levels of both molybdenum and copper (20). However, the significance of the suggested correlation is questionable because of the lack of information on the study population and the absence of a control group.

Industrial exposure of humans to molybdenum has been reported in both the former Soviet Union and the United States. In the former, workers having the highest exposure had the highest blood level of uric acid (21). In the latter, urinary and plasma molybdenum levels were higher for the worker group than for a control group (22). However, the urea level of the exposed group was still within the range of the control group, and no goutlike symptoms were reported.

Table 9. **Toxicity of Molybdenum Compounds**

Compound	Species	Time, h	LC_{50}, mg/L	Reference
		Freshwater fish		
ammonium dimolybdate	bluegill	48	157	10
	rainbow trout	48	135	10
molybdenum trioxide	bluegill	48	$>87<120$	10
	rainbow trout	48	$>65<87$	
		Daphnia		
sodium molybdate dihydrate	all species	96	3940	11
		Saltwater species		
sodium molybdate dihydrate	mysid shrimp	96	3997	12
	sheepshead minnow	96	6590	
	pink shrimp	96	3997	
	American oyster		3526	
ammonium molybdate	marine shore crab	48	1018[a]	13
		Mammals		
molybdenum trioxide	rat[b]		2.73[c]	14
molybdenum trioxide (technical grade)	rat[b]		6.66[c]	15
sodium molybdate	[d]		344[e]	16
molybdenum disulfide	rat[b]		[f]	17

[a] Value is mg of Mo.
[b] Compound given orally.
[c] Units are g/kg.
[d] Compound given intraperitoneally or intramuscularly.
[e] Units are mg/kg.
[f] No effect level >15 g/kg given orally.

10. Recycling

Secondary molybdenum in the form of molybdenum metal or superalloys are recovered in small amounts in 1998 (3). About 1000 t of molybdenum was reclaimed from spent catalysts. Molybdenum is not recovered from scrap steel, but recycling of steel alloys is significant and molybdenum content is reutilized (3).

The OSHA and ACGIH standards for soluble compounds of Mo are both 5 mg Mo/m^3. The TLV for the insoluble compounds is 10 mg Mo/m^3 whereas OSHA PEL for the respirable fraction is 5 mg Mo/m^3 for and 15 mg Mo/m^3 total dust (23).

11. Uses

Molybdenum metal is the most widely used electrical resistance element in furnaces where temperatures beyond the limits of ordinary resistance alloys are required. Such furnaces are generally used for temperatures up to about

1650°C, but some are in successful operation at 2200°C. The elements, which may be wire, rod, ribbon, or expanded sheet, must be protected from oxidation by a reducing or inert atmosphere, or a vacuum. Hydrogen is commonly employed. Under these conditions, molybdenum has a long life and seldom is the limiting factor in the durability of the furnace. The furnace industry also consumes sizable amounts of molybdenum sheet for susceptors in high frequency units, as well as radiation shields, baffles, structural supports, muffle liners, skids, hearths, boats, and firing trays in all types of high temperature vacuum and controlled atmosphere furnaces.

The same properties that make molybdenum metal effective in high temperature furnace applications make it useful as support wires for tungsten filaments in incandescent light bulbs and as targets in x-ray tubes.

The glass (qv) industry has become an important user of large molybdenum parts. The advantages of molybdenum include its high melting point, high strength at elevated temperature, good electrical conductivity, resistance to attack by most molten glasses, as well as the fact that any oxide formed is colorless under normal operation conditions. The main application is in electrically heated glass furnaces, where it serves as electrodes which may be either of the plate or rod type. Stirrers, pumps, bowl liners, wear parts, and molds are also made from molybdenum metal.

Because of its high modulus of elasticity, molybdenum is used in machine-tool accessories such as boring bars and grinding quills. Molybdenum metal also has good thermal-shock resistance because of its low coefficient of thermal expansion combined with high thermal conductivity. This combination accounts for its use in casting dies and in some electrical and electronic applications.

12. Molybdenum Base Alloys

The strength of molybdenum depends on work-hardening. The greater the amount of cold-working, ie, percent reduction of area below the recrystallization temperature, the higher the yield and tensile strengths at all temperatures and the lower the creep rates at elevated temperatures. Exposure of the work-hardened structure to temperatures high enough to cause recrystallization produces a drastic reduction in tensile properties, and a loss of ductility as measured by bending tests or notched-bar impact tests. Unalloyed molybdenum cold-worked by 90% reduction of area fully recrystallizes at 1175°C in 1 h.

Additions of selected alloying elements raise the recrystallization temperature, extending to higher temperature regimes the tensile properties of the cold-worked molybdenum metal. The simultaneous additions of 0.5% titanium and 0.1% zirconium produce the TZM alloy, which has a corresponding recrystallization temperature of 1500°C and which cold-works to higher hardness and strength than unalloyed molybdenum. The alloy is recognized as a standard by the American Society for Testing and Materials for critical, high temperature structural applications (ASTM B386, B387); its superior properties justify the higher cost of processing. Tensile strength data for molybdenum and TZM are given in Table 10.

Table 10. **Tensile Strength of Rolled Bars**[a]

	Tensile strength, MPa[b]	
Temperature, °C	Unalloyed molybdenum	TZM alloy
ambient	790	830
200	750	790
400	660	730
600	570	670
800	480	600
1000	370	530
1200	180	450

[a] Ref. 24.

[b] To convert MPa to psi, multiply by 145.

An alloy of molybdenum containing 1.2% hafnium with carbon at the level of 0.08–0.10% has a slight advantage over TZM. This alloy has been produced in small quantities for special extrusion dies and ejector pins in the isothermal forging of superalloys.

Tungsten has little effect on recrystallization temperature or the high temperature properties of molybdenum. However, the Mo–30% W alloy is recognized as a standard commercial alloy for stirrers, pipes, and other equipment that is required to be in contact with molten zinc during processing of the metal and in galvanizing and die casting operations.

Molybdenum–rhenium alloys received increased attention during the 1980s for special low volume applications. The addition of 40–50% rhenium increases the tolerance for oxygen, improves ductility at ambient temperatures, and enhances weldability. The alloy containing 41% Re is used for critical high temperature structures in aerospace applications, especially where welding is required (see HIGH TEMPERATURE ALLOYS). The Mo–47.5% Re alloy is produced for high temperature thermocouple wire, for radar equipment, and for microwave communication applications. These alloys are produced by powder metallurgy operations. The high and unstable price of rhenium powder has limited the market for Mo–Re alloys.

13. Molybdenum as an Alloying Element

Molybdenum, an unusually versatile alloying element, imparts numerous beneficial properties to irons and steels and to some alloy systems based on cobalt, nickel, or titanium. Comprehensive summaries of uses through 1948 (25) and 1980 (26) are available.

Steels develop excellent combinations of strength and toughness if heat-treated by quenching to martensite, followed by tempering (see STEEL). Steels having adequate hardenability develop martensitic structures in practical section sizes. Molybdenum is a potent contributor to hardenability, and has been shown to be even more effective in the presence of carefully selected amounts of other alloying elements (27). The end-quench test has become the accepted method for measuring hardenability, and the data can be correlated with section size. Technical societies worldwide have standardized hardenability limits (bands) for a large number of carbon and alloy steels; standards of the Society of Automotive Engineers are examples (28).

Many steels used for gears and bearings are surface-hardened by carburizing, quenching, and tempering. Molybdenum is frequently used in carburized steels, and carburized Ni–Mo steels have been shown to provide optimum resistance to fatigue and impact effects (29).

The microstructures which can be developed using a wide range of heat treating conditions can be predicted from data presented in continuous-cooling transformation (CCT) diagrams and from isothermal transformation (IT or TTT) diagrams. These diagrams represent an extension of the hardenability concept. Many such diagrams exist (30). Reviews of specific applications show the ability of molybdenum, in combination with other alloying elements, to develop the desired microstructure (31,32).

The concentration of molybdenum in constructional alloy steels is usually in the range of 0.15–0.30%. A few specialty steels contain 0.30–0.80% Mo. The best-known steels are the Cr–Mo and Ni–Cr–Mo grades. Molybdenum is particularly effective in reducing the susceptibility of Cr–Ni steels to embrittlement following tempering at >600°C or exposure to temperatures ca 500°C for extended times. Embrittlement is attributed to the presence of undesirable trace elements in the grain boundaries. Molybdenum tends to concentrate at the grain boundaries, rendering the trace elements less harmful.

Molybdenum-alloyed steels have been found to perform better than other steels in service in the oil industry (see PETROLEUM). Drill pipe and casing for deep wells are exposed to high concentrations of hydrogen sulfide, which causes sulfide stress cracking (SSC). Steels containing molybdenum in amounts as high as 0.80% can be heat-treated to high strength levels and still resist SSC (33).

An early application of molybdenum was its substitution for tungsten in the high speed steels popular before World War I. The red hardness of a steel containing 9% molybdenum is as high as that of a steel containing 18% tungsten. Subsequently, a series of high speed steels containing 3.75–9.5% molybdenum was developed. Substantially all hacksaws and twist drills made in the United States are manufactured from molybdenum-containing high speed steels.

High strength, low alloy (HSLA) steels often contain 0.10–0.30% molybdenum. These steels exhibit toughness at low temperatures and good weldability. They are used extensively for undersea pipelines (qv) transporting gas and oil from offshore wells to pumping stations on shore, and are also used extensively in remote Arctic environments.

Molybdenum improves the corrosion resistance of stainless steels that are alloyed with 17–29% chromium. The addition of 1–4% molybdenum results in high resistance to pitting in corrosive environments, such as those found in pulp (qv) and paper (qv) processing (34), as well as in food preparation, petrochemical, and pollution control systems.

A simple, low cost steel for high temperature service in electric power generation (qv) is the C–0.5% Mo steel known as carbon–half moly, which was widely used for many years. The power industry and oil refineries have turned to 1.25% Cr–0.5% Mo and 2.25% Cr–1% Mo steels for high stress and high temperature service, because these steels have improved resistance to graphitization and oxidation, as well as higher creep and rupture strength.

In cast irons, alloying with molybdenum increases hardness and strength. Such irons have been used for crankshafts in large diesel engines for power generation, in ship propulsion and linepipe pumps (qv), and in some special railroad castings. There is increasing interest in specially heat-treated nodular graphite (ductile) irons as alternatives to steel in automotive parts such as gears, crankshafts, and pistons (35,36). Additions of molybdenum are important to the development of the unique acicular microstructure which characterizes these irons.

Abrasion-resistant white cast irons are used in ore processing (see MINERALS RECOVERY AND PROCESSING), in the crushing and pulverizing of coal (qv), and in the grinding of cement (qv) clinker. These white irons are alloyed with 15–28% chromium and 2–3% molybdenum to provide effective wear resistance. Although the highly alloyed irons are sometimes heat-treated to develop the desired martensite–austenite structure, castings often develop a suitable matrix structure in the mold and can be put into service without heat treatment, providing substantial savings in fuel and handling costs. The relevant effect of molybdenum in these castings is its ability to stabilize the structure so effectively that undesirable pearlite does not form during relatively slow cooling to room temperature.

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