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Traditional and Emerging Applications of Molybdenum Metal and Its Alloys

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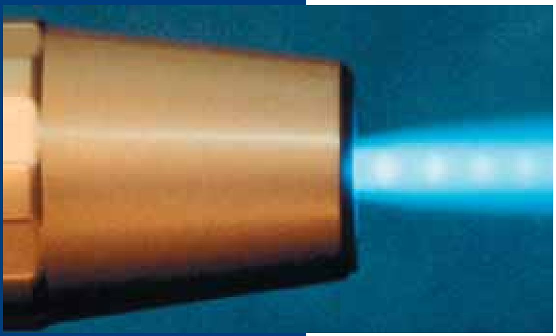

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Introduction

Carl Wilhelm Scheele identified molybdenum as an element in 1778, and Peter Jacob Hjelm produced metal powder by reduction in 1782. However, molybdenum did not find application in metallic form until 1910, as a filament support for incandescent lamps.[1]

Its strength at high temperatures, and its greater ease of working and lower cost compared to tungsten made it a clear choice for the application. The advent of vacuum-tube electronics created a great need for materials with high temperature strength and stability, increasing the demand for molybdenum. Molybdenum metal and its alloys found more and more applications, always based upon some unique property or suite of properties that no other material could provide. Most of these applications relied in one way or another on molybdenum's elevated temperature strength. The process of property-driven application development continues today. Because of molybdenum's high cost compared to more common engineering materials, designers do not select it unless it is required. Today designers use molybdenum to meet specific needs with respect to elevated temperature strength, chemical compatibility, tribological properties, or physical properties like thermal expansion, thermal conductivity, and electrical conductivity. This article discusses molybdenum's unique property suite, identifies commercially available alloys and materials systems based upon molybdenum, and presents some of the processing technologies used for these materials; it then discusses molybdenum's place in the market using examples of traditional and emerging applications.

[1] *Wadsworth & Wittenauer, "The History of Development of Molybdenum Alloys for Structural Applications,"* ***Evolution of Refractory Metals and Alloys,*** *Edward N. C. Dalder, Toni Grobstein, and Charles S. Olsen, Eds, TMS-AIME, Warrendale, PA pp 85-108 (1993).*

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Molybdenum, Its Alloys, and Its Processing

Table 1 summarizes some of the properties of molybdenum and identifies competitive materials and materials systems. While it is tempting to believe that applications are controlled by a single property, in truth many molybdenum applications exist because of a useful combination of several properties. For instance, hot strength is a critical property for high-temperature tooling like casting die inserts, but molybdenum's high resistance to failure by thermal shock and thermal fatigue are equally important. These qualities relate to molybdenum's unique combination of low heat capacity and high thermal conductivity, which minimizes thermal stresses. Molybdenum's long-standing use as a power semiconductor heat sink is due in part to its excellent thermal expansion match with silicon, but its good electrical and thermal conductivity provide additional advantages compared to competitive materials.

Table II summarizes classes of molybdenum-based alloys and materials systems that have evolved in order to optimize specific properties and improve performance. Each of the systems evolved in response to performance needs in certain applications. The carbide-stabilized alloy TZM is one of the oldest commercial alloys; MHC, stabilized with hafnium carbide precipitates, is a more recent member of the same family. These alloys improve molybdenum's hot strength, creep resistance, and recrystallization resistance. Alloying with tungsten also improves hot strength, but molybdenum-tungsten alloys find widest use in handling molten zinc, where they resist zinc corrosion. The Mo-30 wt. % W alloy is nearly as corrosion resistant as pure tungsten at a greatly reduced density and cost. Oxide-dispersed alloys impart extraordinary creep resistance at temperatures as high as 2000° C. Molybdenum sheet clad with copper provides enhanced thermal and electrical conductivity and increased thermal expansion coefficient (CTE), allowing a good match with ceramic substrates used in integrated circuits. Copper-molybdenum powder composite materials have the added advantage of isotropic properties; if enhanced properties are required, they can also be clad with copper. Molybdenum-nickel laminates provide an easily soldered or brazed nickel surface, eliminating environmentally challenging nickel plating processes.

Molybdenum is produced by both powder metallurgical (PM) and vacuum casting techniques. ***Figures 1 and 2*** illustrate the two processing routes schematically. In the PM route, pure metal powder is made from high-purity starting material (ammonium dimolybdate or molybdenum trioxide) in a two-step hydrogen reduction process. This powder is blended with constituents appropriate to the alloys being manufactured. Blended powder is isostatically pressed to produce a preform, which is sintered at high temperatures in hydrogen or vacuum to produce a billet that is 94%-97% of molybdenum's pore-free density. Hot and cold processing operations are combined with appropriate intermediate and final annealing practices to manufacture mill products (plate, sheet, foil, bar, rod, wire, and forgings).
PM processing has the advantage of being a lower-cost route to produce material, and can produce shapes with relatively low scrap losses.

Table I. Properties of Molybdenum

Property Class	Property	Applications	Competing Materials
Mechanical	Hot strength	Lighting, furnaces, hot tooling	Tungsten
	Creep resistance	Lighting, furnaces	Tungsten, graphite
	Wear resistance	Hot tooling, anti-friction coatings	Tungsten
	Machinability	Fabricated parts for a variety of applications	Many, most are more machinable
Chemical	Corrosion resistance	Metal handling and casting	Noble metals, graphite
	Compatibility with molten glass	Glass melting electrodes, furnace components	Platinum, tin oxide, nickel alloys
	Adherence to glass substrates	Lighting components, integrated circuits	Titanium, chromium
	Etchability	Lighting components, integrated circuits	Titanium, chromium
Physical	Low vapor pressure	High temperature vacuum components	Tungsten, tantalum
	Electron emission	Lamp components	Nickel, others
	Thermal expansion	Silicon power devices, integrated circuits, hot work tooling	W, W-Cu, AlSiC, AlN, AlGr Traditional tooling materials
	Thermal conductivity	Silicon power devices, integrated circuits, hot work tooling	Copper, aluminum, W, W-Cu, AlSiC, AlN, AlGr
	Electrical conductivity	Silicon power devices, integrated circuits	Copper, aluminum, W, W-Cu, AlSiC, AlN, AlGr
	Low diffusivity into other materials	Integrated circuits, flat panel displays	Ti, Cu-Al
	Low friction	Anti-friction coatings	Carbon, brass

Table II. Molybdenum Alloys and Materials Systems

System	Example	Properties of Interest
Pure Mo	99.95 wt % Mo	Elevated temperature strength, thermal conductivity, thermal expansion
Substitutional alloys	Mo-W	Improved hot strength; Zn corrosion resistance
	Mo-Re	Improved low temperature ductility
Carbide-stabilized alloys	TZM	Improved hot strength and creep resistance
	MHC	Higher hot strength and creep resistance than TZM
Oxide-dispersed systems	La_2O_3(ML,ODS-Mo)	Outstanding hot strength and creep resistance
	Y_2O_3(MY)	Outstanding hot strength, creep resistance
Other systems	Cu-Mo-Cu laminate	Engineered thermal properties
	Mo-Ni laminate	Solderability
	Mo-Cu powder composite	Isotropic engineered thermal properties

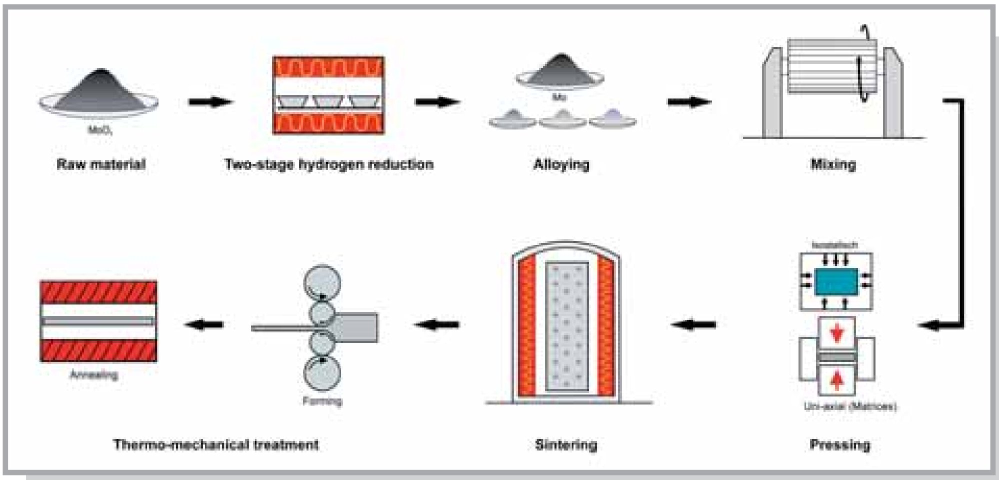

Figure 1.
Powder metallurgical processing of molybdenum metal products. *Courtesy of PLANSEE Metall.*

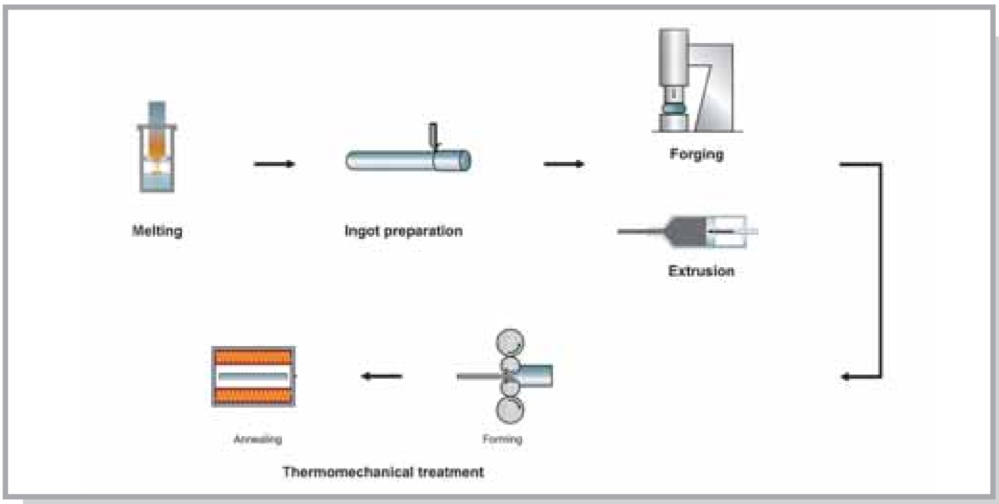

Figure 2.
Processing molybdenum via EB melting or arc-casting technology. *Courtesy of PLANSEE Metall.*

The oxide-doped alloys cannot be produced by melting techniques at all. Powder processes are required to obtain the fine dispersion of oxide particles in the molybdenum matrix that are responsible for these alloys' extraordinary high-temperature mechanical properties. PM processing must be controlled carefully to avoid the detrimental effects of adsorbed oxygen and oxide films on powder particles. Alloys containing reactive metals like Ti, Zr, and Hf form very stable oxides that affect microstructure and can affect performance as well. Manufacturers, over the years, made great progress on these problems, and PM processing now accounts for the vast majority of all molybdenum metal and alloy produced in the world.

Both vacuum arc-casting (VAC) and electron beam (EB) melting are used to cast molybdenum and its alloys. In the arc-casting process, molybdenum ingot is melted using a semi-continuous press-sinter-melt (PSM) process. The process consolidates powder blends into electrodes and melts the electrodes in a water-cooled copper crucible under vacuum. Arc-cast ingots are usually extruded in their first processing step to prevent hot cracking at grain boundaries and break down the large as-cast grains. EB melting also uses a water-cooled copper crucible to contain the melt. It is usually performed under lower pressures than VAC melting. EB melting does not require virgin powder; this means that the process can be used to recycle process scrap. Because the heat used to melt the material is applied independently of the heat to maintain the molten solidification pool, EB-melted ingots typically have smaller grain size than VAC ingots. Because of this, EB-melted material is often forged in the as-cast condition.

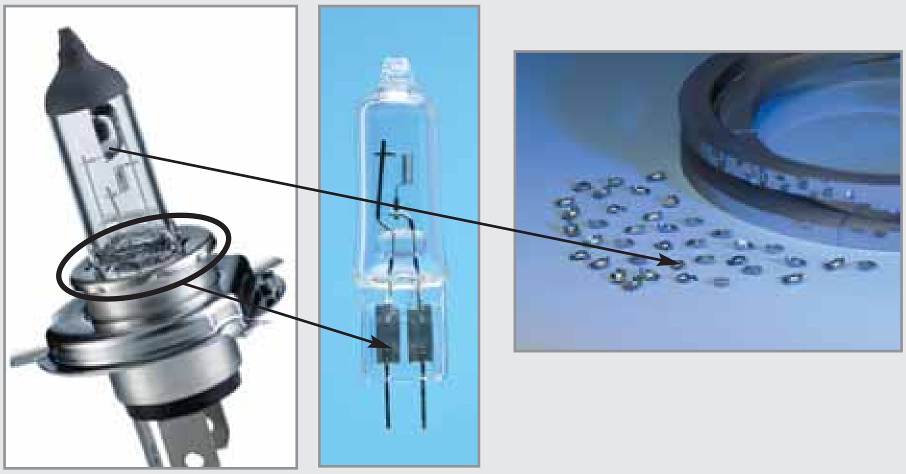

Figure 3.
Automotive halogen lamp, showing molybdenum sealing ribbons and reflector caps.
Courtesy of PLANSEE Metall.

All ingot-casting techniques require a surface preparation step prior to forging or extrusion, in order to remove surface porosity and possible contaminants from the ingot mold. Cast alloys, while typically more expensive to produce than PM alloys, provide benefits for that additional cost. They are lower in impurities, especially volatile species that evaporate in the casting process. Alloying is accomplished in the melt, where it is more likely to be homogenized than in solid-state sintering. Since the technologies use a deoxidizer, excess oxygen is not a problem. Oxygen contents of 10 ppm or less are normal in cast material.

In all of these processing techniques, thermomechanical processing serves two roles: to create a useful final product form, and to impart the required mechanical properties. Manufacturers employ various hot, warm, and cold deformation processes in combination with annealing steps to produce the desired microstructures and properties in finished products. Round, flat, and shape rolling, rod and wire drawing, rotary forging, swaging, forming and deep drawing are all used to process molybdenum.

Applications

Molybdenum touches our lives every day, but in ways that are usually invisible to the end user. Traditional applications consume significant volumes of material, but new applications are emerging that promise to supplant and surpass many traditional applications.

Lighting

Lighting is the oldest application for molybdenum metal. In fact, some applications in this market are nearly unchanged from the earliest applications. ***Figure 3*** illustrates the most highly evolved example of the traditional tungsten filament incandescent lamp: the automotive halogen headlamp. The high temperatures in halogen lamps require a pure silica (quartz) glass envelope. Molybdenum sealing ribbons provide a transition from the external lamp wiring to the internal refractory metal components. Molybdenum's low thermal expansion coefficient and good bonding with silica glass make it ideal for this application. The profile of the strip used in the sealing ribbons is engineered to minimize stresses in the glass arising from expansion mismatches during manufacturing and operation. Molybdenum reflector caps control the shape of the lamp beam, so that it does not impair the vision of oncoming drivers. Strip used for reflectors must meet stringent surface finish and ductility requirements because it is drawn into the cup shape at high speeds. Strip failure during drawing creates significant productivity losses, and may result in damage to expensive multi-cavity tooling. Molybdenum also finds application in other traditional lighting applications such as discharge lamps.

A example of an emerging lighting application is shown in ***Figure 4***. The cold cathode fluorescent lamp (CCFL) illuminates liquid crystal flat panel displays (FPDs). The dramatic increase in sales of FPDs drives demand for molybdenum in these lamps. Molybdenum hollow cathode cups replaced the formerly used nickel cups due to its better sputter resistance and emissivity, while doped molybdenum lead pins replaced Kovar, offering a much higher thermal conductivity and allowing lower lamp temperatures. The rapidly evolving high brightness light emitting diode (HBLED) technology may also be an area where copper-clad molybdenum or Mo-Cu composites are needed. Even though HBLEDs are extremely efficient in

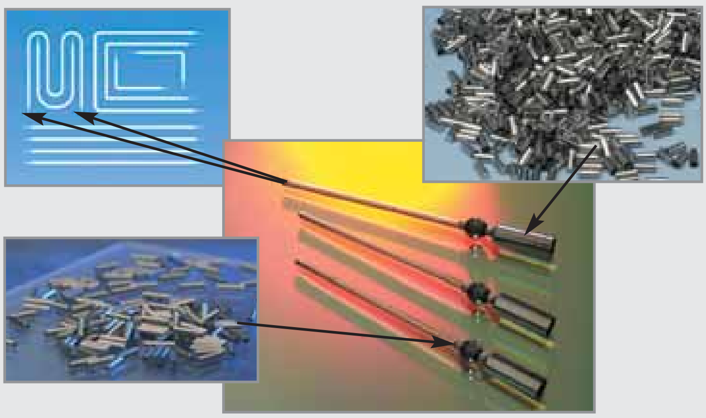

Figure 4.
Cold cathode fluorescence lamp (CCFL) and molybdenum components. Clockwise from upper left: examples of lamp geometries, molybdenum cups, Mo/Mo/Dumet electode assembly, HT pins.
Courtesy of PLANSEE Metall.

Table III. Characteristics and Status of Lighting Industry Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ Halogen lamps ■ Discharge lamps	■ Sealing and support wire ■ Reflector caps ■ Sealing foil	■ Strength for sealing process ■ Creep resistance	■ Corrosion resistance against lamp gases ■ Good bond strength with glass	■ High melting point ■ CTE ■ Thermal and electrical conductivity	None
	Mo powder demand: ~1300 mt/yr Market status: shrinking				
Emerging applications					
■ CCFL lamps ■ HBLED lamps	CCFL: ■ Mo cup and pin for electrode HBLED: ■ MoCu or Cu-Mo-Cu heat sink	CCFL: ■ Strength for sealing process ■ Creep resistance	CCFL: ■ Compatible with mercury	CCFL: ■ Electron emission, thermal and electrical conductivity ■ Sputter resistance HBLED: ■ Thermal and electrical conductivity ■ CTE	CCFL: ■ Ni & Ni alloy ■ Nb ■ Kovar HBLED: ■ Cu ■ Al ■ AlSiC ■ AlN ■ Etc.
	Mo powder demand: ~100 mt/y Market status: rapidly growing				

comparison to traditional incandescent lamps, they still generate high power densities that require efficient heat removal.

Table III summarizes the status of lighting applications. Traditional applications depend primarily on molybdenum's elevated temperature strength and creep resistance, and its chemical compatibility with the glass systems and halogen gases present in lamps. Molybdenum's attractive thermal properties (conductivity and expansion) and electrical conductivity are also factors in these applications. Because of molybdenum's unique property suite, no suitable replacement materials have yet been found. Emerging applications like CCFLs rely on the same suite of properties, combined with sputter resistance and emissivity, while HBLEDs exploit the thermal and electrical properties of molybdenum. In these applications, there are numerous alternatives to molybdenum. Time and the evolution of device design will determine the ultimate optimal material choices. The material competition is particularly robust in the area of HBLEDs, where many of the well-developed thermal management materials also compete, and where design improvements may still significantly reduce thermal loads on the devices. Emerging applications, while not yet consuming as much powder as traditional applications, have high growth rates. The quantity of molybdenum powder required to serve traditional markets is

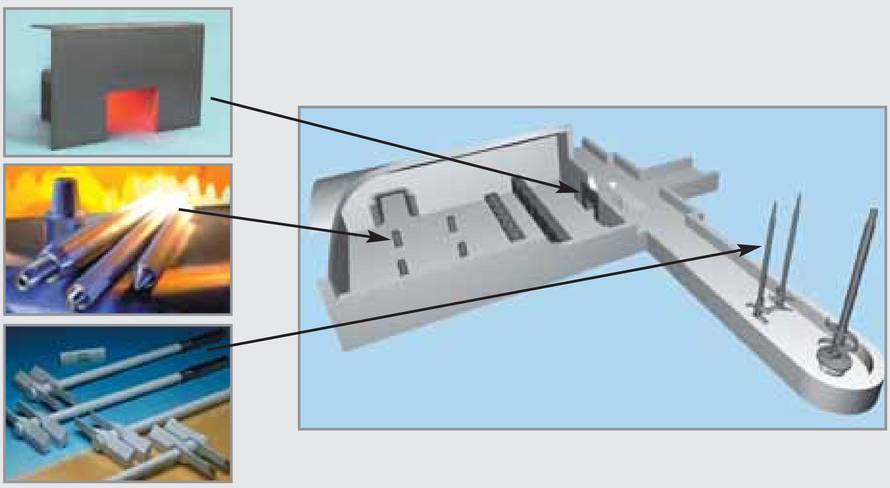

Figure 5.
Glass melting furnace components. Top left to bottom left: furnace protection shields, glass-melting electrodes, molbdenum glass stirrers. Right: schematic of glass-melting furnace showing molybdenum applications.
Courtesy of PLANSEE Metall.

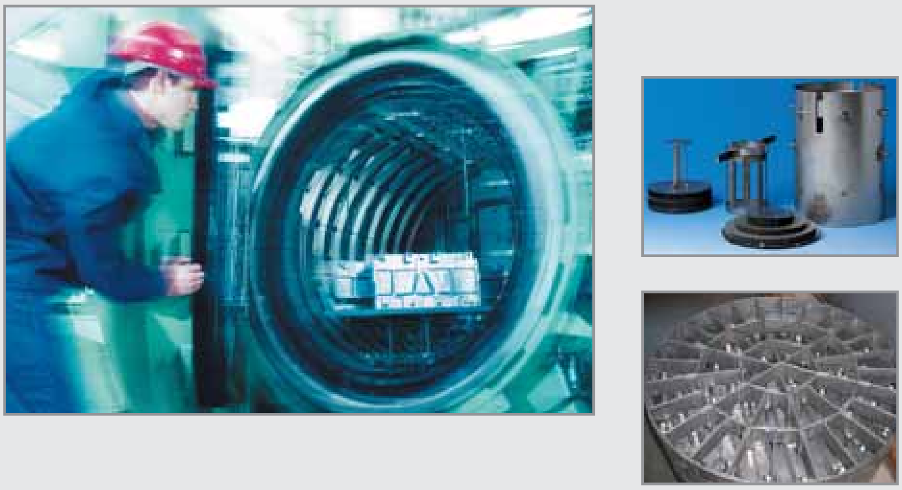

Figure 6.
Typical molybdenum vacuum furnace and components.
Bottom right: load support structure. Top right: Heating elements and heat shields.
Courtesy of PLANSEE Metall.

significant now, but is decreasing. The extent to which emerging markets will replace traditional markets will depend critically upon the evolution of the applications within the markets, and upon molybdenum's ability to succeed against competing materials. Cost is a significant factor in all these applications.

The traditional lighting applications are commodity-like businesses, and require low costs. The emerging applications, aimed at the high-volume consumer markets, are also highly cost-sensitive. Material cost stability and tight control of manufacturing costs are important factors for success in this market.

Glassmaking and High-temperature Furnaces

Glass manufacturing and furnace construction have long been important applications for molybdenum. Molybdenum's high-temperature strength, fabricability, and compatibility with most glass compositions make it an ideal choice in glassmaking. ***Figure 5*** illustrates a typical glass-melting furnace installation with molybdenum components. Molybdenum's strength, creep resistance, and erosion resistance in glass melts make it ideal for stirrers, glass melting electrodes (GMEs), and furnace shields, all of which must resist stresses and erosion imposed by the molten glass. Molybdenum also resists glass corrosion, and the small amounts that dissolve in the melt do not discolor the glass. Molybdenum can be made with very low carbon content ($<$ 20 wt. ppm), preventing the formation of CO_2 bubbles

Table IV. Characteristics and Status of Glass and Furnace Industry Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ Glass tank components	■ GMEs ■ Stirrers ■ Shields ■ Dies for glass fiber manufacture	■ Strength ■ Creep resistance	■ Corrosion resistance in molten glass ■ No discoloration of glass ■ No formation of CO_2 bubbles	■ Melting point ■ Thermal and electrical conductivity	■ Noble metals ■ Nickel base alloys ■ SnO ■ Refractories
	Mo powder demand: ~400 mt/y Market status: shrinking				
Emerging applications					
■ Vacuum furnaces ■ Hydrogen atmosphere furnaces	■ Heat shields ■ Heating elements ■ Support structures ■ Boats ■ Setter tiles	■ Strength ■ Creep resistance	■ Compatibility with hydrogen	■ Melting point ■ Thermal and electrical conductivity ■ Low vapor pressure	■ Graphite ■ Tungsten ■ Tantalum ■ Ceramics
	Mo powder demand: ~300 mt/y Market status: slowly growing				

Figure 7.
Traditional molybdenum applications in hot metal forming. Upper right: TZM and MHC isothermal forging die components used to manufacture aircraft gas turbine (upper left) components. Lower right: TZM piercing plugs for the manufacture of pierced stainless steel tubing (lower left). *Courtesy of PLANSEE Metall.*

in the molten glass due to reaction between glass and carbon in solution.

Figure 6 illustrates typical applications in the vacuum furnace industry. Pure molybdenum, oxide-dispersion strengthened alloys such as ML or ODS Mo, and TZM are used because of their high temperature strength and creep resistance. Molybdenum's low vapor pressure at high temperature means that it does not contaminate workloads, an important factor when heat treating reactive metals like titanium. Molybdenum is used for support structures, heat shields, heating elements, and all manner of vacuum furnace hardware. Molybdenum's poor oxidation resistance prevents its use in oxygen-containing atmospheres, but it is used extensively for furnace boats, setter tiles, heating elements, and load-bearing components in hydrogen atmosphere furnaces. Unlike the refractory metals tantalum and niobium, molybdenum forms no deleterious hydrides. Hydrogen gas protects molybdenum against oxidation, providing an ideal environment.

Table IV summarizes the status of glass melting and furnace applications. Molybdenum has held a significant position in the glass melting industry since the advent of electrically boosted furnaces to increase productivity. Several materials theoretically can compete with molybdenum in certain areas, but none has a combination of properties like molybdenum's. For example tin oxide and platinum are used in niche applications requiring specific chemical characteristics or other properties, but they cannot compete with molybdenum's overall cost-effectiveness. Improvements in efficiency gained by furnace design and operating practice have resulted in a slowly declining demand for molybdenum in these applications.

Competing materials have had an effect on molybdenum consumption in the furnace industry, especially in vacuum furnace technology. Graphite is a strong competitor for vacuum furnaces in general duty applications. Molybdenum's place in the vacuum furnace industry is in applications that require the ultimate in cleanliness and contamination-free operation. Superalloys and high-tech materials systems are processed in all-molybdenum furnaces. This segment has seen a slight growth with time. With the increasing interest in nuclear technology, there may be an increase in demand for fuel sintering furnaces, which typically use molybdenum components.

Material Forming

Molybdenum and its alloys have made important contributions to hot metal forming. Molybdenum's high strength at elevated temperatures, creep resistance, and resistance to thermal shock and fatigue make it the material of choice for demanding applications. Hot work tooling is manufactured from TZM or MHC, because of their improved strength and creep resistance over pure molybdenum. ***Figure 7*** illustrates two well known applications for these alloys: isothermal forging dies and components, and piercing plugs for stainless steel tube forming. Molybdenum's unique high-temperature mechanical properties and wear resistance allow it

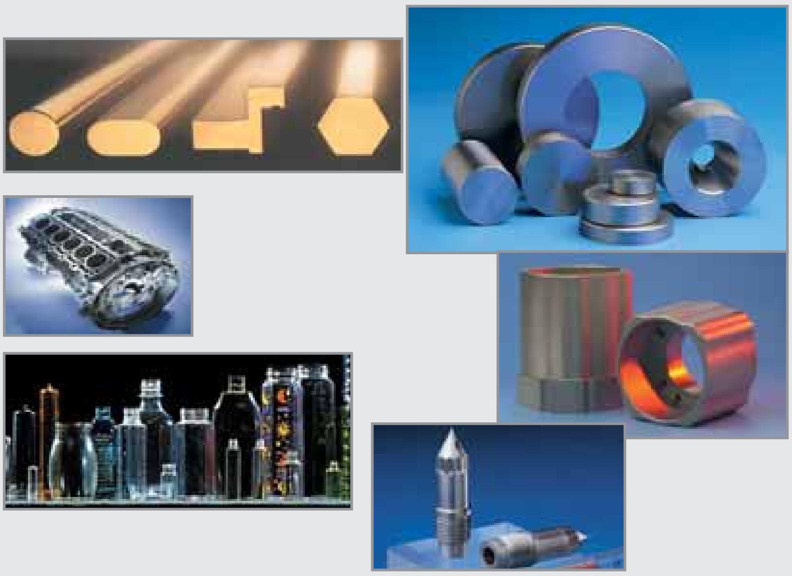

Figure 8.
Emerging applications of molybdenum alloys (right) and products made using them (left). Top to bottom: MHC dies for brass extrusion, TZM inserts for Al and Mg die-casting, TZM hot runner die inserts for plastic injection molding. *Courtesy of PLANSEE Metall.*

Table V. Characteristics and Status of Material Forming Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ Isothermal forging ■ Tube forming ■ Molten Zn handling	■ TZM and MHC forging dies and accessories ■ TZM piercing plugs ■ Mo-W molten Zn tooling	■ High temperature strength ■ Creep resistance	■ TZM, MHC: None identified MoW alloys: ■ Corrosion resistance in molten Zn ■ Good hot strength	■ Thermal conductivity and heat capacity (thermal shock resistance) ■ Wear resistance	None
	Mo powder demand: ~100mt/y Market status: stable				
Emerging applications					
■ Metal extrusion ■ Plastic injection molding ■ Al and Mg casting	■ MHC dies ■ TZM hot runner nozzles ■ TZM tool inserts	Extrusion and casting: ■ High temperature strength ■ Creep resistance	Plastic injection molding: ■ Good corrosion resistance against plastics at medium temperatures Casting: ■ Stable to Al, Mg, Zn attack	■ Thermal conductivity and heat capacity (thermal shock resistance) ■ Wear resistance	■ Stellite ■ CuBe ■ Steel
	Mo powder demand: ~10 mt/y Market status: growing				

to forge nickel base superalloys in the superplastic deformation regime. The machining savings that accrue by producing a near net shape part easily justify the expense of using massive molybdenum die sets, in forging presses operating in controlled environments to prevent oxidation of the tooling. Piercing plugs operate in ambient atmospheres, and the same strength and wear resistance enable significant increases in productivity in tube-making mills.

The molybdenum trioxide that forms during use can also provide some lubricity, reducing friction and improving internal surfaces of the finished product.

Figure 8 illustrates several emerging applications for molybdenum tools. Some of these were identified in the past, but earlier alloys could not provide the required performance. Improvements in molybdenum alloy properties and increased demands for productivity and quality have made them feasible, and they now consume substantial amounts of material. TZM alloy has been used for many years as a die insert material for brass extrusion dies, but was relegated to leaded brass alloys and small sizes because of strength limitations. The higher strength MHC alloy can extrude a wider range of stronger, more abrasive alloys, and can produce larger sizes. Molybdenum has also been used for inserts in aluminum and magnesium die casting dies where

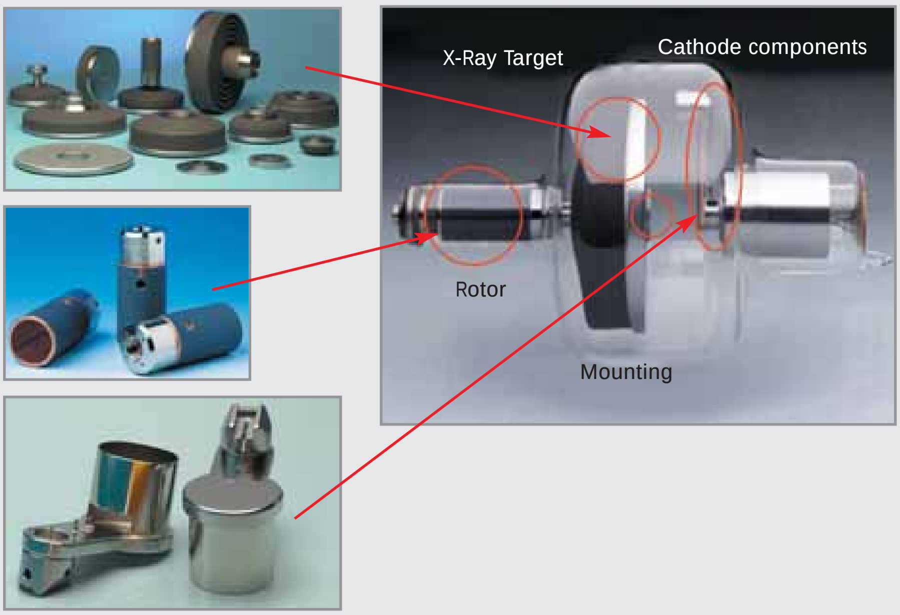

Figure 9.
Medical X-ray tube (right) and molybdenum components. Left, top to bottom: rotating anodes, rotors, and cathodes. *Courtesy of PLANSEE Metall.*

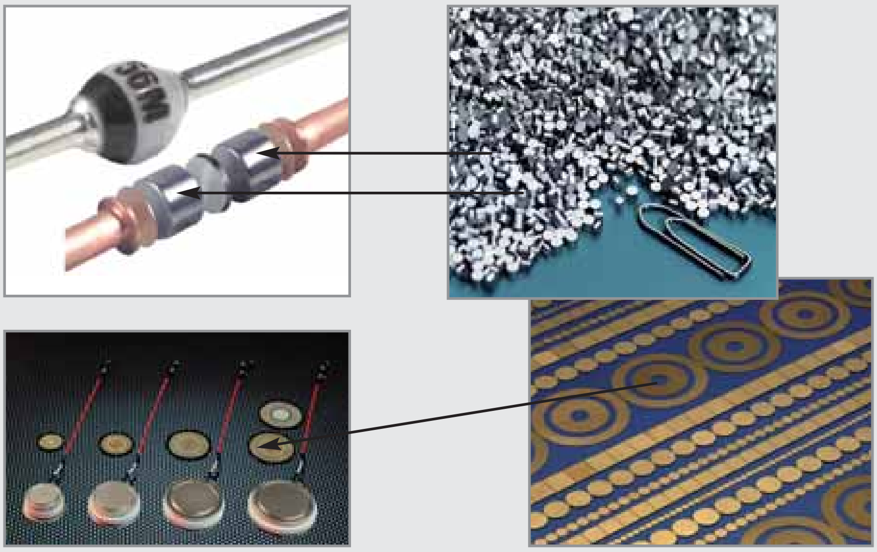

Figure 10.
Traditional molybdenum electronic applications. Clockwise from upper left: Diodes used for low power rectification, molybdenum heat sinks used in that application, molybdenum base plates for high-power semiconductors, assembled power semiconductor packages. *Courtesy of PLANSEE Metall.*

hot cracking is a problem. Molybdenum's combination of low heat capacity and low thermal expansion make it significantly more resistant to surface cracks from thermal shock. Increasing demands for quality in automotive castings, and casting design that has pushed traditional die materials to their limits, spurred an increased use of TZM in critical regions of casting tools. Manufacturers of plastic injection-molded components are finding advantages for TZM tooling, despite the fact that their operating temperatures are much lower than traditional metalworking or metal casting processes. TZM's excellent strength, corrosion and erosion resistance, and thermal stability all contribute to its selection in this application.

Table V provides an overview of the material forming industry and molybdenum's place in it. Here the emerging applications are evolutionary in nature, representing extensions of applications long known for molybdenum and its alloys. The traditional applications provide a stable market, while the emerging applications are growing.

Medical

Medical applications of molybdenum are almost exclusively components of high-energy rotating anode tubes used in computerized axial tomography (CAT) scanners. Some molybdenum is also used in the detector arrays of CAT scanners, but here it competes against tungsten, which absorbs the scattered radiation even more effectively than molybdenum. ***Figure 9*** illustrates molybdenum applications in a typical rotating anode X-ray tube. The rotating anode, the tube's "business end," uses pressed, sintered, and forged TZM. The anode contains a focal track of W-Re alloy manufactured integrally with the rest of the target in this process. Electrons emitted by the cathode assembly bombard the W-Re track as the anode rotates, causing the track to emit X-rays. The electron beam heats the W-Re track nearly to its melting point immediately underneath the beam, generating enormous amounts of heat. The tube stores this heat in a graphite heat sink brazed to the TZM target, and then re-radiates it from the heat sink to the surrounding environment, which in the case of the tube assembly is an oil bath. The rotor used to spin the target also reaches high temperatures, so it is made from TZM alloy. The rotor is designed to limit the amount of heat transferred down the shaft to the bearings.

Table VI. Characteristics and Status of Medical Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ X-ray tubes ■ X-ray detectors	■ Rotating anodes ■ Bearings and rotors ■ Cathode parts ■ Collimator components	■ High temperature strength ■ Creep resistance	■ None identified	Tubes: ■ Thermal conductivity ■ CTE Collimators: ■ Radiation absorption ■ Dimensional control of sheet ■ Surface finish	Tubes: ■ Tungsten Collimators: ■ Tungsten ■ Tungsten heavy alloy
	Mo powder demand: ~350mt/y Market status: slowly growing				

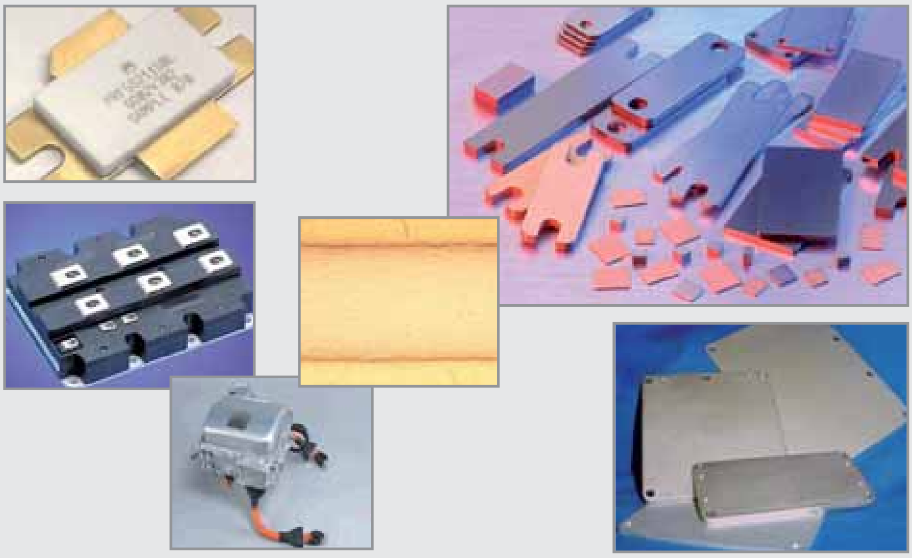

Figure 11.
Emerging molybdenum electronic applications. Clockwise from upper left: Radio frequency integrated circuit for telecommunications, PVD-coated Cu-Mo-Cu heat sinks for radio frequency packages, nickel plated baseplates for power electronics, two IGBT power modules for hybrid vehicles. Center: Cu-CuMo-Cu clad sheet microstructure.

Courtesy of PLANSEE Metall.

X-ray tube components are a traditional application. The designs are highly evolved, and the higher power densities they require push the materials to their limits. Larger and larger targets spinning at faster and faster speeds are needed to handle the energy deposited by the electron beam. Weight restrictions driven by stress and balance considerations continue to force reduction in molybdenum weight in the targets. As a result, the amount of powder required to serve the medical industry grows only slowly. ***Table VI*** summarizes these considerations. Given the unique engineering requirements of X-ray tube design, molybdenum is one of only a few alternatives now available.

Electronics

Electronic applications have required molybdenum from the earliest days. Molybdenum's elevated temperature strength and creep resistance, compatibility with tube glass formulations, low vapor pressure, and compatibility with standard metalworking technologies made it an optim choice in vacuum tubes. These applications consumed a significant amount of material for many years. With the advent of solid-state electronics, it appeared that molybdenum's place in the industry might disappear. However, molybdenum's unique combination of physical properties (excellent thermal expansion match with silicon, good electrical and thermal conductivity), good mechanical properties at ambient temperatures, ease of plating, and compatibility with existing brazing and soldering technologies made it the material of choice for construction of these devices as well. Molybdenum is used extensively in the industry as a heat sink material for rectifier diodes in consumer goods, and for high-power semiconductors used in motor control and power generation. ***Figure 10*** illustrates some of these components. The small heat sinks are manufactured by the millions daily in highly automated pressing and sintering operations, while the heat sinks for large power devices are typically made from sheet that is stamped, machined, and plated to exacting specifications. These traditional applications consume molybdenum at growth rates that mirror the overall economic development of the world, and are tied to rail transportation, power generation, and capital investment in manufacturing plant equipment.

Molybdenum is also found in tooling and other equipment used to manufacture electronic devices and multilayer circuit board assemblies. Molybdenum sheet is used in masks to apply circuit inks in multilayer ceramic circuit board assemblies. In the same technology, molybdenum powders formulated to specific particle size distributions are contained in inks that create the circuits on these boards.

Arc chambers of ion implanter equipments used to dope semiconductors are often entirely made of molybdenum or TZM enabling a long service life in the highly corrosive environment created by the chemicals used in this process.

Applications for molybdenum are also emerging in the integrated circuit and power semiconductor areas. ***Figure 11*** illustrates a few. Integrated circuits are built on ceramic substrates having higher thermal expansion coefficients than silicon. Molybdenum's thermal expansion coefficient (CTE) must be modified to provide an acceptable expansion match. This can be done by cladding molybdenum sheet with copper, by creating a MoCu powder composite material, or even by cladding this composite material with copper. This approach can produce tailored thermal properties and improved device performance. Telecommunications growth is a major driving force in this market. The expansion of mobile telephone technology around the globe created a large demand for integrated circuits, which generate high power densities and require advanced thermal management materials. The same materials used in telecommunication have recently found application in heat sinks for integrated gate bipolar transistor (IGBT) power modules used in hybrid vehicles.

Table VII. Characteristics and Status of Electronic Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ Power semiconductors ■ Multilayer ceramic board manufacturing ■ Device manufacturing	Semiconductors: ■ Mo semiconductor base plates ■ Mo glass diode pins Multilayer boards: ■ Fine powders ■ Sheet masks for circuit application Device manufacturing: ■ Ion implanter parts	None identified	Multilater boards ■ Controlled etchability Device manufacturing: ■ Corrosion resistance against dopant chemicals	Semiconductors: ■ CTE ■ Thermal and electrical conductivity Multilayer boards: ■ Powder sintering properties matching alumina substrates ■ Resistance to erosion from metal powder-filled inks ■ Strength and stiffness ■ Flatness control of sheet	Power semi-conductors: ■ AlSiC Multilayer boards: ■ Glass ceramic boards employing alternate ink formulations
	Mo powder demand: ~400 mt/yr Market status: stable				
Emerging applications					
■ Radio frequency, server, and processor chips ■ IGBTs for hybrid cars	■ Cu-Mo-Cu ■ MoCu ■ Cu-MoCu-Cu	None identified	None identified	■ CTE ■ Thermal and electrical conductivity	■ Cu ■ Al ■ AlSiC ■ AlN ■ Others
	Mo powder demand: ~350 mt/y Market status: rapidly growing				

Table VII summarizes molybdenum usage in electronic applications. The traditional applications use more or less material in concert with the general world economy, and particularly in relation to capital-intensive investments. The emerging applications show rapid growth in material consumption, and are likely to surpass the traditional applications.

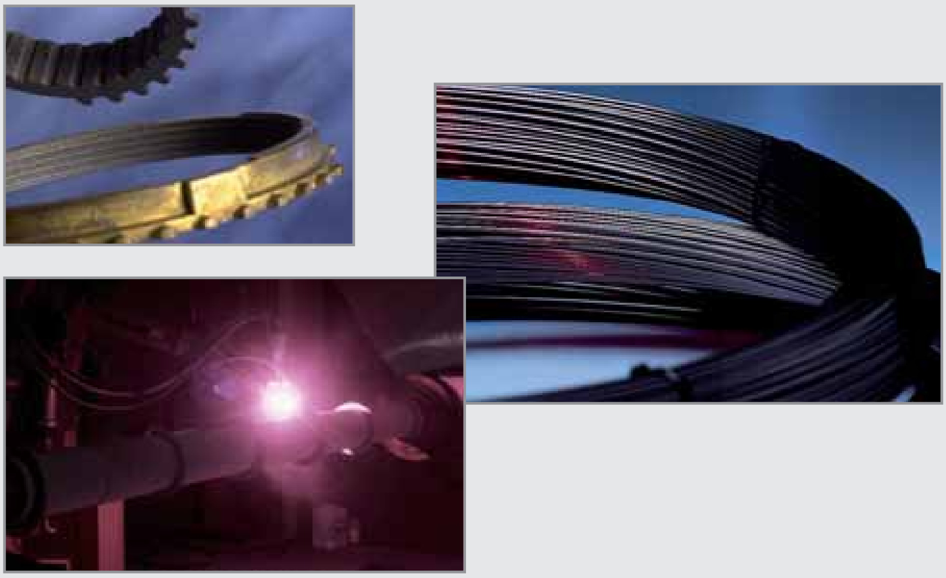

Figure 12.
Traditional molybdenum coating applications. Clockwise from lower left: coating a shaft for wear resistance, molybdenum-coated synchronizer rings, molybdenum wire for flame spray coating. *Courtesy of PLANSEE Metall.*

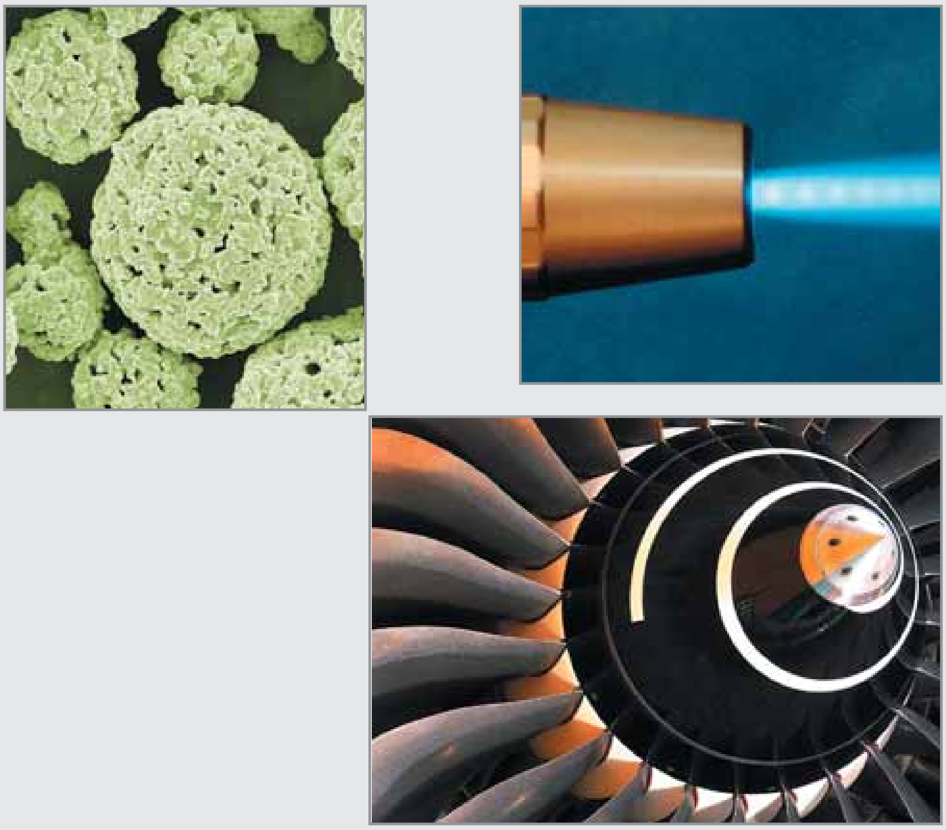

Figure 13.
Thermal spray coating with powders. Clockwise from upper left: engineered powder for plasma spray applications, plasma spray torch, aircraft engine employing plasma spray coatings.
Courtesy of H.C. Starck, Inc.

Coatings

Figures 12 and ***13*** illustrate traditional coating applications. Flame spraying has been used for years to improve the wear and friction properties of automotive components like gears, synchronizers, and piston rings. Recently, engineered molybdenum powders have taken a more prominent role in these applications, using plasma spray technology. The powders are often alloyed with nickel and chromium to produce highly corrosion resistant coatings. The compositional flexibility and improved performance has allowed molybdenum thermal spray powders to gain the lion's share of the traditional coating market. Even so, this traditional market is not growing, but stable.

Figures 14 and ***15*** illustrate coating applications that are growing steadily, after several years of very rapid growth. They are in the

Table VIII. Characteristics and Status of Coating Applications

Application	Mo Product	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
Traditional applications					
■ Flame spraying of wear parts ■ Plasma spraying of wear parts	■ Mo spray wire ■ Mo and Mo alloy powder blends	■ High yield strength contributes to good wear properties	■ Corrosion resistance against oils	■ Low friction ■ Good wear resistance	■ Carbon ■ Brass ■ CrN (piston rings)
	Mo powder demand: ~500mt/y Market status: stable				
Emerging applications					
■ PVD coating of TFT-LCD and solar panels	■ Mo and Mo alloy sputtering targets	None identified	■ Good adhesion to glass ■ Good etching behavior ■ Compatibility with processing environments	■ Good electrical conductivity ■ No diffusion of Mo into Al, Cu and glass	■ Cu and Al alloys ■ Ti ■ Cr ■ Organic materials with spin coating
	Mo powder demand: ~2000 mt/y Market status: steadily growing				

solid-state electronics area, where sputtered molybdenum coatings are used in the production of solar cells and thin film transister flat panel displays (TFT-FPDs). Molybdenum bonds well to glass, matches the thermal expansion of the glass or silicon substrate well, forms a stable diffusion barrier, and is compatible with processing environments used during device manufacturing. ***Figure 14*** shows the growth in glass substrate sizes for flat panel display manufacturing over the past several years. The nested blue squares illustrate the glass panel sizes that are coated using various generations of the technology (each glass panel yields multiple FPD glasses). Early in development of FPD manufacturing processes, molybdenum targets were sized to equal the glass substrate being coated. This required manufacturers to find ways to roll larger and larger plates. The largest molybdenum targets made were the Generation 5 targets. At this point in the process evolution, equipment designers realized they would soon exceed the ability of mills to roll individual molybdenum targets. Succeeding generations continued to coat larger and larger glass panels, but sputtering is now accomplished with an array of narrow and long molybdenum targets, each with its own magnetron. An example of such a target array is also shown in ***Figure 14***. Molybdenum tubular targets are also available. ***Figure 15*** shows examples of both flat targets and cylindrical targets.

Table VIII summarizes traditional and emerging coating applications. While wire and powder demand for traditional thermal spray applications is stable, the amount of molybdenum required for emerging applications in the sputtering target market continues to increase at a steady rate, after several years of rapid growth. Here success depends upon molybdenum's physical and chemical properties, not on its high-temperature strength and creep resistance, properties that have been responsible for molybdenum's success in its traditional applications.

Figure 14.
Emerging coating applications in flat panel display (FPD) technology. Clockwise from top left: Modern wall-mounted FPD, Gen 6/7 target array, schematic of relative production glass sizes as a function of process generation (dimensions in mm), mounted Gen 5 target. Courtesy of PLANSEE Metall.

Figure 15.
Targets can be manufactured as flat panels bonded to copper substrates (right top, bottom), or as tubular targets (left). Courtesy of PLANSEE Metall.

Summary

Table IX. **Application Characteristics and Estimated 2005 Powder Demand**

Application	Elevated-temperature Mechanical Properties	Chemical Properties	Physical Properties	Alternative Materials
	Very important	Less important	Important	Limited
Traditional: Stable or slowly growing markets	**Molybdenum powder demand, mt:**			
	Lighting	1300		
	Glass/Furnace	700		
	Material forming	100		
	Medical	350		
	Electronics	400		
	Coating	500		
	Other	3000		
	Total	**6350**		
	Elevated-temperature Mechanical Properties	**Chemical Properties**	**Physical Properties**	**Alternative Materials**
	Unimportant	Very important	Very Important	Many
Emerging: Steadily growing markets	**Molybdenum powder demand, mt:**			
	Lighting	100		
	Material forming	100		
	Electronics	350		
	Coating	2000		
	Total	**2550**		

Table IX summarizes characteristics of traditional and emerging applications, and presents estimates of the molybdenum powder required to serve each application type in 2005. There is a shift in the properties that drive molybdenum's use in emerging markets. Elevated temperature strength and creep resistance have been key in traditional applications, but emerging applications take advantage of molybdenum's unique combination of physical properties (coefficient of thermal expansion, thermal conductivity, electrical conductivity) and chemical properties (compatibility with the application environment). This change brings with it more competition. Elevated temperature mechanical properties are directly correlated with melting temperature, limiting the number of potential competitive materials. Physical properties do not necessarily correlate with melting temperature, and this allows a wider spectrum of competitve materials. In fact, creative materials system design with composite materials can readily create new materials systems capable of competing with molybdenum and in some cases exceeding molybdenum's performance in emerging applications.

Emerging applications are also concentrated in markets like consumer electronics that are extremely price sensitive. Cheaper alternative solutions are constantly being evaluated in these applications, and materials substitution is commonplace. Molybdenum has always been a target for substitution because of its cost. It is not used unless it confers a clear performance advantage or an overall cost benefit. Molybdenum has not previously faced the breadth of potential competition that it now faces in emerging applications. There are reasons for optimism, as well as caution regarding the growth of molybdenum applications, as noted in the following points:

- Traditional applications are mainly based on molybdenum's unique mechanical properties at elevated temperatures, with very few material alternatives (optimism);
- Demand for traditional applications is stable or shrinking (caution);
- Material requirements for emerging applications are already one third of those for traditional applications and have potential for strong growth (optimism);
- Emerging applications are mainly based on molybdenum's chemical and physical properties with many competing materials whose prices are lower and less volatile (caution);
- Emerging applications are mainly in the price-sensitive electronics and automobile industry (caution); and
- Averaged over all products, raw material costs account for 60 % or more of total production costs, and are the main cost driver (caution).

The stable or declining nature of traditional applications means that new applications based on molybdenum's unique suite of mechanical, physical, and chemical properties are critical to the health of the molybdenum metal industry. Molybdenum technologists have established an enviable record of new product generation over the years, and there is every reason to expect them to continue to identify new opportunities for growth. However, to be successful in emerging markets where cost is constantly under pressure, reasonable and stable raw material prices are requirements.

Membership

Welcome to:

- **Commercial Metals Co**, *a US company involved in marketing, distribution and project investment on moly related products*

- **Dala Mining LLC**, *a private company incorporated in the Republic of Kazakhstan, working on the development of the Koktenkol molybdenum project*

- **Glencore International AG**, *a Swiss company trading Ferro Molybdenum and Molybdenum Oxide*

- **Haldor Topsoe A/S**, *a Danish consumer of molybdenum compounds used in manufacturing of catalysts, and a supplier of technology for sulphuric acid recovery from molybdenum sulphide and other metal sulphide roaster off-gasses*

- **Joe H Smith Co Ltd**, *a long-term distributor in Southern USA for a major US producer*

- **Oriental Minerals Inc**, *a Canadian-based exploration and mine development company, with a diverse portfolio of precious and base metals projects in South Korea. The Company's current projects include the Sangdong tungsten-molybdenum mine, historically one of the largest past producing tungsten mines in the world*

REACH .... Molybdenum Consortium formed by IMOA .... Member companies and non-members invited to join.

See IMOA website for details (in English and Chinese)

Stainless Steel World Conference

As an official "Supporter" of these conferences which are organised every two years by "Stainless Steel World", IMOA draws the attention of readers to the 2007 event which will be held from 6-8 November in Maastricht. For further information, visit their website - **www.stainless-steel-world.net**, or contact them by email **ssw2007.conf@kci-world.com** or **Fax No: +31 575 511099**

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